Modern Methods in Heterogeneous Catalysis
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Microkinetic Modeling

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Microkinetic analysis is a different approach!
Outline

• Why kinetic analysis ?
• What are main aspects of kinetic studies ?
• What are key problems in kinetic studies ?
• What is microkinetic analysis ?
• Which parameters ?
• Which theory is behind the parameters ?
• Which experiments ?
• How to build a microkinetic model ?
• How to describe methane partial oxidation ?
Why Kinetic Studies?

• Industrial catalysis
  – Major aspect: effective catalytic processes
  ⇢ Need for efficient approaches to enhance development

• Development and optimization of catalytic processes
  – Chemical intuition and experience
  – Supplement with quantitative analysis
Aspects of kinetics studies

1. Kinetics studies for design purposes
2. Kinetics studies of mechanistic details
3. Kinetics as consequence of a reaction mechanism
1. Kinetics studies for design purposes

• Results of experimental studies are summarized in the form of an empirical kinetic expression
  – Design of chemical reactors
  – Quality control in catalyst production
  – Comparison of different brands of catalysts
  – Studies of deactivation
  – Studies of poisoning of catalysts
2. Kinetics studies of mechanistic details

- Experimental kinetic study used to determine details in the mechanism
  - Problem:
    Different models may fit data equally well

- Mechanistic considerations as guidance for kinetic studies
3. Kinetics studies as a consequence of a reaction mechanism

- Deduction of kinetics from a proposed reaction mechanism
- Historically macroscopic descriptions of the reaction kinetics were used
- Today, detailed scientific information available
  - Guidance for catalytic reaction synthesis at various levels of detail
  - Hierarchical studies
Levels of Catalytic Reaction Synthesis

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<td>What other reactions are important?</td>
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<td>How are the kinetic parameters controlled by the catalyst?</td>
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<td>How might new and improved catalysts be formulated?</td>
<td>Chemical intuition, guided by microkinetic analysis</td>
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Study of reaction mechanisms

Experiments on well-defined systems
- Spectroscopic studies on single crystal surfaces
- Structure and reactivity of well-defined catalyst models

Detailed calculations for individual molecules and intermediates
- Electron structure calculations including calculations for transition states
- Monte Carlo (Kinetic MC)
Key Problems of Kinetic Studies
Key problems for kinetic studies

- Deduction of kinetics from net reaction is not possible

\[ r = k \cdot p_A^a \cdot p_B^b - \frac{k}{K_{eq}} \cdot p_C^c \cdot p_D^d \]

However: equilibrium is defined

\[ K_{eq} = \frac{p_A^a \cdot p_B^b}{p_C^c \cdot p_D^d} \]

\[ K_{eq} = \text{equilibrium constant} \]
Key problems for kinetic studies

• Analogy may be misleading

**Example:** \( \text{H}_2 + \text{I}_2 \leftrightarrow 2 \text{HI} \)

Simple mechanism and reaction rate of form:

\[
r = k \cdot p_{\text{H}_2} \cdot p_{\text{I}_2} - \frac{k}{K_{eq}} \cdot p_{\text{HI}}^2
\]

while

**Example:** \( \text{H}_2 + \text{Br}_2 \leftrightarrow 2 \text{HBr} \)

\[
r = \frac{d c_{\text{HBr}}}{d t} = \frac{2 k_3 \cdot k_2 \cdot \left( \frac{k_1}{k_5} \right)^{\frac{1}{3}} \cdot c_{\text{H}_2} \cdot c_{\text{Br}_2}^{\frac{1}{3}}}{1 + \left( \frac{k_4 \cdot c_{\text{HBr}}}{k_3 \cdot c_{\text{Br}_2}} \right)}
\]
Key problems for kinetic studies

- Simple kinetics \(\neq\) simple mechanism

\[
\begin{align*}
\text{decomposition of } \text{N}_2\text{O}_5 \text{ proposed by Ogg (1947)} \\
\text{N}_2\text{O}_5 &\xrightleftharpoons[k_2]{k_1} \text{NO}_3^* + \text{NO}_2 \\
\uparrow \text{radical} \\
\text{NO}_3^* &\xrightarrow[k_s]{k_3} \text{NO}^* + \text{O}_2 \\
\text{NO}^* + \text{NO}_3^* &\xrightarrow[k_s]{k_4} 2 \text{NO}_2 \\
\rightarrow r &= k_1 \cdot p_{\text{N}_2\text{O}_5} \quad \text{observed first order decomposition of } \text{N}_2\text{O}_5
\end{align*}
\]
Key problems for kinetic studies

• Different reaction mechanisms may predict the same overall reaction rate; unable to distinguish between the two mechanisms
Microkinetic Analysis
Microkinetics

- *Reaction kinetic analysis* that attempt to incorporate into the kinetic model the basic surface chemistry involved in the catalytic reaction.

- The kinetic model is based on a description of the catalytic process in terms of information and/or assumptions about the *active sites* and the *nature of elementary steps* that comprise the reaction scheme.
Microkinetics

• Convenient tool for the consolidation of fundamental information about a catalytic process and for extrapolation of this information to other conditions or catalysts involving related reactants, intermediates and products.

• Use of kinetic model for description of
  – Reaction kinetic data
  – Spectroscopic observations
  – Microcalorimetry and TPD
Microkinetic Analysis

• Combination of available experimental data, theoretical principles and appropriate correlations relevant to the catalytic process in a quantitative fashion

• Starting point is the formulation of the elementary chemical reaction steps that capture the essential surface chemistry

• Working tool that must be adapted continually to new results from experiments
MA – what is different?

- **No initial assumptions!**
  - Which steps of the mechanism are kinetically significant?
  - Which surface species are most abundant?
- Estimations of the *rates* of elementary reactions and surface *coverages* are a *consequence of the analysis* not a basis!
- *Beyond* the fit of *steady-state* reaction kinetic data
What delivers MA?

• Expected to describe experimental data from
  – Steady-state reaction kinetic data +
  – Data from related experimental studies
    • TPD
    • Isotope-tracer studies
    • Spectroscopic studies
• Feature: usage of physical and chemical parameters that can be measured independently or estimated by theory
Reaction Mechanism

• Net reaction \[ A_2 + 2B \rightleftharpoons 2AB \] consists of a number of steps:
  \[ A_2 + B \rightleftharpoons A_2B \]
  \[ A_2B + B \rightleftharpoons 2AB \]

• Concept of *elementary steps*: further subdivision and introduction of hypothetical intermediates:
  \[ A_2 + B \rightleftharpoons A_2B \]
  \[ A_2B + B \rightleftharpoons A_2B_2 \]
  \[ A_2B_2 \rightleftharpoons 2AB \]
Elementary Reactions

- A step in a reaction mechanism is *elementary* if it is the *most detailed*, sensible description of the step.
- A step which consists of a *sequence* of two or more *elementary steps* is a *composite step*.
- What makes a step in a reaction mechanism elementary?
  - depends on available information

The *key feature* of a mechanistic kinetic model is that it is *reasonable, consistent with known data* and *amenable to analysis.*
Parameters and Theory
Parameters for MA

- Sticking coefficients
- Surface bond energies
- Preexponential factors for surface reactions
- Activation energies for surface reactions
- Surface bonding geometries
- Active site densities and ensemble sizes
Theory behind the parameters

- Collision and transition-state theory
- Activation-energy-bond-strength correlations
  - Evans-Polanyi-correlation
- Molecular orbital correlations
  - Bond-order-conservation
  - Electronegativity scales
  - Drago-Wayland correlations
  - Proton affinity and ionization potential correlations
Concepts

- A *fundamental principle* in microkinetic analysis is the use of kinetic parameters in the rate expressions that have *physical meaning* and, as much as possible, that can be *estimated theoretically* or *experimentally*.

- *Framework* for quantitative *interpretation*, *generalization*, and *extrapolation* of experimental data and theoretical concepts for catalytic processes
Collision Theory (CT)

- Rate for a gas-phase bimolecular reaction

\[ r_{AB} = P_s \pi \sigma_{AB}^2 \sqrt{\frac{8k_bT}{\pi \mu_{AB}}} \exp \left(-\frac{E_a}{k_bT}\right) n_A n_B \]

\[ \sigma_{AB} \quad \text{...collision factor} \]
\[ \sqrt{\frac{8k_bT}{\pi \mu_{AB}}} \quad \text{...average relative velocity from Maxwell – Boltzmann velocity distribution} \]
\[ \mu_{AB} \quad \text{...reduced mass} \]
\[ P_s \quad \text{...steric factor} \]
\[ E_a \quad \text{...activation energy} \]
Collision Theory

- Bimolecular rate constant

\[
k_{AB} = P_s \pi \sigma_{AB}^2 \sqrt{\frac{8 k_b T}{\pi \mu_{AB}}} \exp \left( - \frac{E_a}{k_b T} \right)
\]

- Preexponential factor

\[
A_{AB} = P_s \pi \sigma_{AB}^2 \sqrt{\frac{8 k_b T}{\pi \mu_{AB}}}
\]

- Example: with \( P_s \approx 1 \) and estimate of \( \sigma_{AB} \)
  → upper limit for preexponential factor
CT- Bimolecular surface reaction

- Modification to represent bimolecular reactions between mobile species on surfaces

\[ r_{AB} = 2 P_s \sigma_{AB} \sqrt{\pi k_b T \over 2 \mu_{AB}} \exp \left( -{E_a \over k_b T} \right) \rho_A \rho_B \]

- \( \sqrt{\pi k_b T \over 2 \mu_{AB}} \) ...two dimensional average relative velocity
- \( \sigma_{A,B} \) ...surface concentrations
CT- Adsorption processes

- Use for definition of rate constants for adsorption processes in terms of the number of gas-phase molecules colliding with a unit surface area $F_i$

$$r_A = F_i \sigma(T) f(\theta) = \frac{P_i \sigma(T) f(\theta)}{\sqrt{2 \pi m_i k_B T}}$$

- Example: with $\sigma$ (sticking coefficient) $\approx 1$
  $\rightarrow$ upper limit for preexponential factor and rate constant for adsorption
Transition-State Theory (TS)

- Incorporation of details of molecular structure
- Critical assumption: equilibrium between reactants and activated complex and products
- Bimolecular gas-phase reaction
  \[ A + B \rightleftharpoons AB^\# \rightleftharpoons C + D \]
- Potential energy diagram as multidimensional surface
- Definition of a reaction coordinate
Transition-State Theory

- Ideal gas equilibrium constant for the activated complex $AB^#$

$$K^# = \frac{n_{AB^#}}{n_A n_B}$$

- Rate of chemical reaction

$$r_{AB} = \frac{k_b T}{h} K^# n_A n_B$$

$n_i$ ...concentrations

$\frac{k_b T}{h}$ ...frequency factor

$h$ ...Planck's constant
TS Theory

- **Macroscopic formulation** of TS is obtained by writing $K^\#$ in terms of standard entropy, $\Delta S^0\#$, and enthalpy, $\Delta H^0\#$, changes

$$r_{AB} = \frac{k_b T}{h} \exp\left(\frac{\Delta S^0\#}{k_b}\right) \exp\left(-\frac{\Delta H^0\#}{k_b T}\right) n_A n_B$$

- **Microscopic formulation** of TS is obtained by writing $K^\#$ in terms of molecular partition functions $Q_i$

$$r_{AB} = \frac{k_b T}{h} \frac{Q_{AB}^\#}{Q_A Q_B} \exp\left(-\frac{\Delta E^0\#}{k_b T}\right) n_A n_B$$
TS Theory

- Molecular *partition function* for a gas-phase species is a product of contributions from *translational*, *rotational* and *vibrational* degrees of freedom.

\[
q_{i,\text{trans}} = \frac{(2\pi m_i k_b T)^{3/2}}{h^3}
\]

\[
q_{i,\text{rot}} = \frac{8\pi^2 I_i k_b T}{\sigma_r h^2} \quad \text{(linear molecule)}
\]

\[
q_{i,\text{vib}} = \prod_j \frac{1}{1 - \exp\left(-\frac{h\nu_{ij}}{k_b T}\right)}
\]

- \(I_i\) ... moment of inertia
- \(\sigma_r\) ... rotational symmetry number
- \(\nu_{ij}\) ... frequencies of normal modes of vibration
**TS Theory**

\[ r_{AB} = \frac{k_b T Q_{AB}^#}{h \frac{Q_A Q_B}{Q_{A}Q_{B}}} \exp \left( -\frac{\Delta E_{0}^0}{k_b T} \right) n_A n_B \]

- Order-of-magnitude estimates

\[
k_B T/h = 10^{13} \text{ s}^{-1}
\]
\[
q_{i,\text{trans}} = 5 \times 10^8 \text{ cm}^{-1} \text{ (per degree of translational freedom)}
\]
\[
q_{i,\text{rot}} = 10 \text{ (per degree of rotational freedom)}
\]
\[
q_{i,\text{vib}} = 1 \text{ (per degree of vibrational freedom)}
\]
TS – Adsorption processes

1) $A_{(g)} \overset{\leftrightarrow}{\longrightarrow} A^\# \overset{\longrightarrow}{\longrightarrow} A^*$

- Rate of reaction for an activated complex of complete surface mobility

$$r_A = \frac{k_b T}{h} \frac{Q_A^\#}{Q_{Ag}} \exp\left(-\frac{\Delta E^{0\#}}{k_b T}\right)n_A$$
TS – Adsorption processes

2) \( A_{(g)} + * \rightarrow A^# \rightarrow A^* \)

- Rate of reaction for an immobile activated complex

\[
r_A = \frac{k_b T}{h} \frac{Q_{A^#}}{Q_{Ag}} \exp \left( - \frac{\Delta E^{0#}}{k_b T} \right) n_A \theta^*
\]

\[
Q_{A^#} = \rho^{sat} \; q_{A^#r} \; q_{A^#v}
\]
TS – Desorption processes

A* ←→ A# ←→ A_(g)

• Rate of desorption

\[ r_d = \frac{k_b T}{h} \frac{Q_{A^#}}{Q_{A^*}} \exp \left( -\frac{\Delta E^{0#}}{k_b T} \right) \rho_A \]

\[ r_d = \frac{k_b T}{h} \exp \left( -\frac{\Delta E^{0#}}{k_b T} \right) \rho_A \]

\[ \rho_A \ldots \text{concentration of species A on the surface} \]

\[ \frac{Q_{A^#}}{Q_{A^*}} \approx 1 \]

\[ \frac{k_b T}{h} \approx 10^{13} / s \]
### TS – Preexponential Factors Estimates

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<td></td>
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<tr>
<td>( A + \cdot \rightarrow A^* )</td>
<td>( r = A \left[ \exp^{-\left(E_a/k_B T\right)} \right] P_A \theta^* )</td>
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<tr>
<td>Mobile transition state</td>
<td>( A = 10^5/\text{Pa s} )</td>
</tr>
<tr>
<td>Immobile transition state</td>
<td>( A = 10^1/\text{Pa s} )</td>
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<tr>
<td><strong>Dissociative Adsorption</strong></td>
<td></td>
</tr>
<tr>
<td>( A_2 + 2\cdot \rightarrow 2A^* )</td>
<td>( r = A \left[ \exp^{-\left(E_a/k_B T\right)} \right] P_{A2}(\theta^*) )</td>
</tr>
<tr>
<td>Mobile transition state</td>
<td>( A = 10^5/\text{Pa s} )</td>
</tr>
<tr>
<td>Immobile transition state</td>
<td>( A = 10^1/\text{Pa s} )</td>
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<tr>
<td><strong>Langmuir–Hinshelwood Reaction</strong></td>
<td></td>
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<tr>
<td>( A^* + B^* \rightarrow C^* + D^* )</td>
<td>( r = A \left[ \exp^{-\left(E_a/k_B T\right)} \right] \theta^*_r \theta_0 )</td>
</tr>
<tr>
<td>Mobile surface species with rotation</td>
<td>( A = 10^8/\text{s} )</td>
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<tr>
<td>Mobile surface species without rotation</td>
<td>( A = 10^{11}/\text{s} )</td>
</tr>
<tr>
<td>Immobile surface species without rotation</td>
<td>( A = 10^{13}/\text{s} )</td>
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<tr>
<td><strong>Eley–Rideal Reaction</strong></td>
<td></td>
</tr>
<tr>
<td>( A + B^* \rightarrow AB^* )</td>
<td>( r = A \left[ \exp^{-\left(E_a/k_B T\right)} \right] P_A \theta^*_r )</td>
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<td>Immobile transition state</td>
<td>( A = 10^1/\text{Pa s} )</td>
</tr>
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TS – Preexponential Factors Estimates

Molecular Desorption

\[ A^* \rightarrow A + * \]

Similar freedom for adsorbed and transition states

More rotational and translational freedom for transition state

\[ r = A \left[ \exp \left(-\frac{E_a}{k_B T}\right) \right] \theta_A. \]

\[ A = 10^{13}/s \]

\[ A = 10^{16}/s \]

Associative Desorption

\[ 2A^* \rightarrow A_2 + 2^* \]

Mobile adsorbed and transition states with full rotational freedom

Mobile adsorbed and transition states without rotation

Immobile adsorbed and transition states

Immobile species with more rotational and translational freedom for transition state

\[ r = A \left[ \exp \left(-\frac{E_a}{k_B T}\right) \right] (\theta_A')^2 \]

\[ A = 10^{8}/s \]

\[ A = 10^{11}/s \]

\[ A = 10^{13}/s \]

\[ A = 10^{16}/s \]
Estimates for Activation Energies

- Rate constant = f (A ; E_A)
- E_A estimation difficult
  1) Empirical correlations for E_A from heats of reaction
     - Bond-order conservation (BOC) by Shustorovich

\[ A_2 \rightleftharpoons A^* + A^* \]

\[ E_A = D_{A_2} - \frac{3}{2} E_{A_{n\text{Metal}}} \]

- \( E_A \): act. energy for diss. adsorption
- \( D_{A_2} \): strength of \( A - A \) bond
- \( E_{A_{n\text{Metal}}} \): adsorption strength of \( A^* \) on site with \( n \) metal atoms
Estimates for Activation Energies

2) Conversion of elementary steps into families of reactions
   - especially for large mechanisms where limited experimental data are available
   - example: reaction of a paraffin over a metal surface including hydrogenation and dehydrogenation steps

Evans-Polanyi correlation

\[ E_{A_i} = E_0 + \alpha \Delta H_i \quad \text{exoth} \]
\[ E_{A_i} = E_0 - (1 - \alpha) \Delta H_i \quad \text{endoth} \]

\( E_0, \alpha \) ... Evans – Polanyi constants for the family
\( \Delta H_i \) ... heat of formation
\( \alpha \) ... elementary step
Consistency of the Model

1) Stoichiometric consistency
   reactants $\rightarrow$ $\rightarrow$ products :
   reactants, intermediates have to be formed and consumed to form products

2) Thermodynamic consistency
   If two or more different sequences lead from reactants to products, these sequences must describe the same gas-phase thermodynamics.
Thermodynamic consistency

\[ E_{i,rev} = E_{i,for} - \Delta H_i^0 \]
\[ A_{i,rev} = A_{i,for} \exp\left( \frac{\Delta G_i^0 - \Delta H_i^0}{RT} \right) \]

\[ E_i \quad \text{...forward, reverse activation energies} \]
\[ A_i \quad \text{...forward, reverse preexp. factors} \]
\[ \Delta G_i^0 \quad \text{...standard Gibbs free–energy changes of reaction i} \]
\[ \Delta H_i^0 \quad \text{...standard enthalpy changes of reaction i} \]

\[ \sum_i \sigma_i (E_{i,for}) - \sum_i \sigma_i (E_{i,rev}) = \Delta H_{net}^0 \]

\[ \prod_i \left( \frac{A_{i,rev}}{A_{i,for}} \right)^{\sigma_i} = \exp\left( \frac{\Delta G_{net}^0 - \Delta H_{net}^0}{RT} \right) \]

\[ \sigma_i \quad \text{...stoichiometric number of elementary step} \]
Informative Experiments
Experimental Techniques

How can information from these techniques be used in microkinetic analysis?

- Physical techniques → bulk structure, surface area, pore structure
- Spectroscopic studies → probe of composition and morphology of the surface
- Kinetic & therm. studies → probe catalytic properties of the surface; quantification of kinetic parameters
Techniques that probe catalyst properties:

- X-ray diffraction
- X-ray absorption spectroscopy
- extended X-ray absorption fine structure
- transmission and scanning electron microscopies
- magnetic susceptibility
- Mössbauer spectroscopy
- solid-state nuclear magnetic resonance spectroscopy
- electron paramagnetic resonance spectroscopy
- X-ray photoelectron spectroscopy
- ultraviolet photoelectron spectroscopy
- Auger electron spectroscopy
- scanning tunneling and atomic force microscopies
- low-energy electron diffraction
- infrared and Raman spectrosopies
- electron energy loss spectroscopy
- physical adsorption measurements

Techniques that probe adsorbed species:

- X-ray photoelectron spectroscopy
- ultraviolet photoelectron spectroscopy
- electron energy loss spectroscopy
- magnetic susceptibility
- low-energy electron diffraction
- infrared and Raman spectrosopies
- nuclear magnetic resonance spectroscopy
- electron paramagnetic resonance spectroscopy

Techniques that probe kinetic and thermodynamic properties:

- temperature programmed desorption
- isotope tracing
- microcalorimetry
- chemisorption measurements
- reaction kinetic measurements
X-ray Diffraction

- Crystal structure determines the coordination of the various catalyst components and bond distances between elements → surface structure and nature of active sites

- Measurement of average particle sizes with help of Scherrer equation → structure-sensitive behaviour

- Analysis of peak shapes can be used to probe the size of crystallites → particle size distribution
Photoelectron Spectroscopy - XPS

- Quantitative analysis of surface composition
  ! Surface and bulk composition may be different

- Information about surface oxidation state

- Use of treatment chamber – quantification of surface coverage by a particular species

- UPS: probe of valence levels of the catalyst surface
Infrared Spectroscopy

- Probe for vibrational properties of the catalyst surface groups

- Example: O-H stretching vibration
  - Intensity of O-H band in the IR spectrum provides a measure of the surface hydroxyl concentration depending on the catalyst treatment
  - Position of O-H band gives information about the nature of the hydroxyl group
Building a Microkinetic Model
Building a Microkinetic Model

- Build a set of elementary reactions which reflect all experimental and theoretical information
- Calculate for each reaction the thermodynamics (for all gaseous species and all adsorbed species)

\[
K_{i,eq} = \frac{k_{i, for}}{k_{i, rev}} = \exp\left( \frac{\Delta S_i^0}{k_B} \right) \exp\left( - \frac{\Delta H_i^0}{k_B T} \right)
\]

- Choose material balance of an appropriate reactor and characterize in and out flows
Reactor Models

• General types of ideal reactors
  – Batch reactor
  – Continuous-flow stirred tank reactor (CSTR)
  – Plug flow reactor (PFR)

• Typical characteristics of reactors
  – Batch: reactor volume $V_R$ and holding time $t$
  – Flow: reactor volume $V_R$ and space time $\tau$
Reactor Models in MA

- For catalytic reactions the space time may be replaced by $\tau_p$, defined as number of catalytic sites in the reactor, $S_R$, divided by the molecular flow rate of feed to the reactor, $F$

- Material balance for species $i$ in a general flow reactor is given by

$$F_i^0 + R_i = F_i + \left\{ \frac{dN_i}{dt} \right\}$$

- $F_i^0$ ... flow in reactor
- $F_i$ ... flow out of reactor
- $R_i$ ... rate of production of species $i$
- $N_i$ ... number of species $i$ in reactor
Reactor Models in MA

- Batch reactor
  \[ \frac{dN_i}{dt} = V_R r_i = S_R \Omega_i \]
  with \( \Omega_i \) as turnover frequency (number of reaction events per active site per second)

- CSTR
  \[ F_i - F_i^0 = V_R r_i = S_R \Omega_i \]

- PFR
  \[ F_i - F_i^0 = \int r_i dV_R = \int \Omega_i dS_R \]
Example
Methane Oxidation by Mo/V-Oxides


Development of a microkinetic model of the partial oxidation of methane over MoO$_3$-SiO$_2$ and V$_2$O$_5$-SiO$_2$ catalysts

Problem: limited data available
Start : seek of experimental data and theoretical concepts from related or analogous catalytic systems
Aim is to reproduce the kinetic data for methane partial oxidation

\[
\text{CH}_4 \rightarrow \text{CH}_3\text{OH, HCHO, CO, CO}_2, \text{H}_2\text{O}
\]

which includes also independent kinetic data for these subsequent partial oxidations

\[
\begin{align*}
\text{CH}_3\text{OH} & \rightarrow \text{HCHO, CO, CO}_2, \text{H}_2\text{O} \\
\text{HCHO} & \rightarrow \text{CO, CO}_2, \text{H}_2\text{O} \\
\text{CO} & \rightarrow \text{CO}_2
\end{align*}
\]
Macrokinetic analysis of the problem

- Kinetic investigations showed quantitative differences in the performances of MoO$_3$-SiO$_2$ and V$_2$O$_5$-SiO$_2$ catalysts
  - Selectivity to CO$_2$ at low CH$_4$ conversion was zero for the V-catalyst; for the Mo-catalyst it was between 10-20 %
  - CO$_2$ is a direct product of methane oxidation over Mo-catalyst and a secondary over V-catalyst
  - Need of two pathways to CO$_2$ to describe both catalysts
Macrokinetic analysis of the problem

- Addition of sodium leads to decrease in conversion level and drop in the selectivity to HCHO for both catalysts
  - Effect to be analyzed by semiempirical MO calculations

  d-band characteristics:
  - empty, to reduce CO$_2$ formation
  - located at sufficient low energy to accept electrons during methane activation to form methoxy and hydroxyl surface species
  - tetrahedral coordination for high conversion
Development of the model

Oxidation of CO

- Kinetic investigations on V-catalyst
- @ 733 K reaction is first order in CO and zero order in oxygen
- Activation energy in $\Delta T$: 673-773 K is 25.2 kcal/mol

\[
\begin{align*}
2M + O_2 & \rightleftharpoons 2MO \\
CO + MO & \rightleftharpoons MOCO \\
MOCO & \rightleftharpoons CO_2 + M
\end{align*}
\]
Development of the model

Oxidation of HCHO

Kinetic investigations on Mo-catalyst @ 600-925 K
- CO is principal product with small amounts of CO₂ at higher T
- Kinetic investigations on V-catalyst @ 500-900 K
- CO production passes through a maximum near 800 K and CO₂ production increases monotonically with T
- IR data

\[
\begin{align*}
H_2CO + M & \rightleftharpoons MOCH_2 \\
H_2CO + MO & \rightleftharpoons MOCH_2O \\
MOCH_2OM + 2MO & \rightleftharpoons CO_2 + 2MOH + 2M \\
MOCH_2O + MO & \rightleftharpoons CO + 2MOH \\
2MOH & \rightleftharpoons H_2O + MO + M
\end{align*}
\]
Development of the model

Oxidation of CH₃OH

- Catalytic activity of Mo-catalyst starts at 500 K with complete conversion at 700 K
- Methoxy species (IR, EPR)

\[ \text{CH}_3\text{OH} + \text{M} + \text{MO} \rightleftharpoons \text{MOCH}_3 + \text{MOH} \]
\[ \text{MOCH}_3 + 2\text{MO} \rightleftharpoons \text{MOCH}_2\text{OM} + \text{MOH} \]
\[ \text{MOCH}_3 + \text{MO} \rightleftharpoons \text{MOCH}_2 + \text{MOH} \]
Development of the model

Oxidation of CH₄

\[
\text{CH}_4 + 2\text{MO} \rightleftharpoons \text{MOCH}_3 + \text{MOH}
\]

Two possible ways of methane adsorption on the surface

1) initial formation of a precursor state on the surface and consecutive dissociation into methoxy- and hydroxyl groups
2) activation of surface Oxygen to O⁻ and consecutive dissociative adsorption of methane
Development of the model

Mechanism as combination of all steps

\[ \text{CH}_4 + 2\text{MO} \rightleftharpoons \text{MOCH}_3 + \text{MOH} \quad \text{(Step 1)} \]

\[ \text{CH}_3\text{OH} + \text{M} + \text{MO} \rightleftharpoons \text{MOCH}_3 + \text{MOH} \quad \text{(Step 2)} \]

\[ \text{MOCH}_3 + 2\text{MO} \rightleftharpoons \text{MOCH}_2\text{OM} + \text{MOH} \quad \text{(Step 3)} \]

\[ \text{MOCH}_3 + \text{MO} \rightleftharpoons \text{MOCH}_2 + \text{MOH} \quad \text{(Step 4)} \]

\[ \text{H}_2\text{CO} + \text{M} \rightleftharpoons \text{MOCH}_2 \quad \text{(Step 5)} \]

\[ \text{H}_2\text{CO} + \text{MO} \rightleftharpoons \text{MOCH}_2\text{O} \quad \text{(Step 6)} \]

\[ \text{MOCH}_2\text{OM} + 2\text{MO} \rightleftharpoons \text{CO}_2 + 2\text{MOH} + 2\text{M} \quad \text{(Step 7)} \]

\[ \text{MOCH}_2\text{O} + \text{MO} \rightleftharpoons \text{CO} + 2\text{MOH} \quad \text{(Step 8)} \]

\[ 2\text{MOH} \rightleftharpoons \text{H}_2\text{O} + \text{MO} + \text{M} \quad \text{(Step 9)} \]

\[ 2\text{M} + \text{O}_2 \rightleftharpoons 2\text{MO} \quad \text{(Step 10)} \]

\[ \text{CO} + \text{MO} \rightleftharpoons \text{MOCO} \quad \text{(Step 11)} \]

\[ \text{MOCO} \rightleftharpoons \text{CO}_2 + \text{M} \quad \text{(Step 12)} \]
Development of the model

- Combined consideration of the oxidations of carbon monoxide, formaldehyde, methanol, and methane
- Agreement with available literature
- No assumptions about the existence of rate-determining steps or most abundant surface intermediates
- All steps reversible; two pathways for CO$_2$ formation
\[
\begin{align*}
\text{CH}_4 + 2\text{MO} & \rightleftharpoons \text{MOCH}_3 + \text{MOH} \quad \text{(Step 1)} \\
\text{CH}_3\text{OH} + \text{M} + \text{MO} & \rightleftharpoons \text{MOCH}_3 + \text{MOH} \quad \text{(Step 2)} \\
\text{MOCH}_3 + 2\text{MO} & \rightleftharpoons \text{MOCH}_2\text{OM} + \text{MOH} \quad \text{(Step 3)} \\
\text{MOCH}_3 + \text{MO} & \rightleftharpoons \text{MOCH}_2 + \text{MOH} \quad \text{(Step 4)} \\
\text{H}_2\text{CO} + \text{M} & \rightleftharpoons \text{MOCH}_2 \quad \text{(Step 5)} \\
\text{H}_2\text{CO} + \text{MO} & \rightleftharpoons \text{MOCH}_2\text{O} \quad \text{(Step 6)} \\
\text{MOCH}_2\text{OM} + 2\text{MO} & \rightleftharpoons \text{CO}_2 + 2\text{MOH} + 2\text{M} \quad \text{(Step 7)} \\
\text{MOCH}_2\text{O} + \text{MO} & \rightleftharpoons \text{CO} + 2\text{MOH} \quad \text{(Step 8)} \\
2\text{MOH} & \rightleftharpoons \text{H}_2\text{O} + \text{MO} + \text{M} \quad \text{(Step 9)} \\
2\text{M} + \text{O}_2 & \rightleftharpoons 2\text{MO} \quad \text{(Step 10)} \\
\text{CO} + \text{MO} & \rightleftharpoons \text{MOCO} \quad \text{(Step 11)} \\
\text{MOCO} & \rightleftharpoons \text{CO}_2 + \text{M} \quad \text{(Step 12)} \\
\end{align*}
\]

\[
K_{i,eq} = \frac{k_{i,for}}{k_{i,rev}} = \exp\left(\frac{\Delta S_i^0}{k_B}\right) \exp\left(-\frac{\Delta H_i^0}{k_B T}\right)
\]
Calibration of the model

Estimation of preexp. factors

Estimation of ΔH for each elementary step + additional use of Evans-Polanyi correl.

Estimation of bond strength (constrained to physically reasonable limits)

---

Table 8-1. Adjusted Evans–Polanyi Parameters

<table>
<thead>
<tr>
<th>Step</th>
<th>$E_0$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>58 MoO$_3$–SiO$_2$</td>
</tr>
<tr>
<td>4</td>
<td>63 V$_2$O$_5$–SiO$_2$</td>
</tr>
<tr>
<td>3, 5, 6, 7, 9, 10</td>
<td>28</td>
</tr>
<tr>
<td>8</td>
<td>55 MoO$_3$–SiO$_2$</td>
</tr>
<tr>
<td>11, 12</td>
<td>45</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
</tr>
</tbody>
</table>

Note: Catalyst-dependent Evans–Polanyi parameters for Steps 1 and 8 suggest that these may not be elementary reactions.

Table 8-2. Adjusted Bond Strengths (kcal/mol)

<table>
<thead>
<tr>
<th>Bond</th>
<th>MoO$_3$–SiO$_2$</th>
<th>V$_2$O$_5$–SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M=O</td>
<td>92</td>
<td>82</td>
</tr>
<tr>
<td>M–OH</td>
<td>70</td>
<td>61</td>
</tr>
<tr>
<td>M–OCH$_3$</td>
<td>59</td>
<td>56</td>
</tr>
<tr>
<td>M–OCH$_2$</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>MO–CH$_2$O</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>MO–CO</td>
<td>20</td>
<td>27</td>
</tr>
</tbody>
</table>
Comparison of Experiment and Model

Figure 8.1. Calculated and experimental HCHO, CO, and CO₂ selectivities versus CH₄ conversion over MoO₃–SiO₂. Symbols correspond to experimental data, and lines to model predictions.

Figure 8.2. Calculated and experimental HCHO, CO, and CO₂ selectivities versus CH₄ conversion over V₂O₅–SiO₂. Symbols correspond to experimental data, and lines to model predictions.
Comparison of Experiment and Model

Agreement of model and experimental data for different temperatures and different experimental conditions
Active Steps during CH₄ partial oxidation

(a: Molybdena)

1. CH₄ → CH₃OM
2. CH₃OM → CH₂OM
3. CH₂OM → HCHO
4. HCHO → OCH₂OM
5. OCH₂OM → CO
6. CH₃OM → MOCH₂OM
7. MOCH₂OM → CO₂

(b: Vanadia)

1. CH₄ → CH₃OM
2. CH₃OM → CH₂OM
3. CH₂OM → HCHO
4. HCHO → OCH₂OM
5. OCH₂OM → CO
6. CH₃OM → MOCH₂OM
7. MOCH₂OM → CO₂
8. CO → OCH₂OM
9. OCH₂OM → CO
10. MOCH₂OM → CO₂
11. CO → MOCH₂OM
12. MOCH₂OM → CO₂
Molecular Orbital Studies

Coordination number affects the electronic structure of transition metal oxides.

Major effect of cation coordination is the energy of the d bands.

The number of d-orbitals with high energy number increases with coordination.

Figure 8-7. Effect of coordination number on the d-orbital energies in vanadium oxides.
Analysis of Adsorption

\[ \text{CH}_4 + 2\text{MO} \rightleftharpoons \text{MOCH}_3 + \text{MOH} \]

Figure 8-8. Electronic correlation diagram for VO$_4^{3-}$.

Figure 8-9. Electronic correlation diagram for CH$_3$ adsorption on VO$_4^{3-}$. 
Microkinetic Analysis

Combination of available *experimental* data, *theoretical* principles and appropriate correlations relevant to the catalytic process in a *quantitative* fashion
Literature

R.D. Cortright, J.A. Dumesic

J.A. Dumesic, D.F. Rudd, L.M. Aparicio, J.E. Rekoske
„The Microkinetics of Heterogeneous Catalysis“

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„Microkinetic simulation of catalytic reactions“

O. Hinrichsen