Interplay between reactivity and transport phenomena in heterogeneous catalysis

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Chemical reactor

The reactor is the device within which the physicochemical transformations are caused. It can assume **various shapes and modes of operations** and be operated in a number of possible environments of pressure and temperature.
Heterogeneous catalytic reactions by their nature involve a separate phase of catalyst embedded in a phase of reacting species.
The way to the active sites

A

Boundary layer

1

Porous catalyst

2

Active sites

3

A*

Chemical reaction

4

B*

Adsorption/desorption

5

Pore diffusion

6

Film diffusion

7
The way to the active sites

Boundary layer

Porous catalyst

Active sites

Chemical reaction

Adsorption/desorption

Pore diffusion

Film diffusion
The way to the active sites

1. Boundary layer
2. Adsorption/desorption
3. Active sites
4. Chemical reaction
5. Adsorption/desorption
6. Pore diffusion
7. Film diffusion

The **observable reaction rate** may differ substantially from the **intrinsic rate** of chemical transformation under bulk fluid phase conditions.
Catalysts at work

How do transport phenomena and distribution of residence times in the reactor affect the observed reaction rate?
Outline

1) Effect of the distribution of the contact times in the reactor on the observed reaction rate

2) Inter-phase and intra-phase transport phenomena and their impact on the observed reaction rate

3) Show-case: effect of transport phenomena on catalyst reactivity

4) Take-home messages
Reactivity (for this talk)

A → B

\[ r = k c_A \text{ [mol/m}^3 \text{ / s]} \]

\[ k = k_0 \exp \left( -\frac{E}{RT} \right) \]
Outline

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4) Take-home messages
How long molecules stay in the reactor?

PLUG-FLOW-REACTOR:
all molecules have same residence time and concentrations vary only along the length of the tubular reactor.

CONTINUOUS-FLOW STIRRED TANK REACTOR:
due to vigorous agitation, the reactor contents are well mixed, so that effluent composition equals that in the tank.
Residence time distribution in PFR
Residence time distribution in PFR
Residence time distribution in PFR

INLET

OUTLET

$V/Q$
Residence time distribution in CSTR
Residence time distribution in CSTR
Residence time distribution in CSTR

Time

INLET

Q

V

OUTLET

v/Q
PFR Vs. CSTR reactor

INLET

PFR

CSTR

OUTLET

Time

Time

Time
Does RTD affect the observed reactivity?
Do I have to expect different reactivity even if I am running the reaction at constant T, P and same inlet composition?
Effect of RTD on observed reaction rate

\[ \text{A} \rightarrow \text{B} \quad r = k c_A \quad [\text{mol/m}^3/\text{s}] \]

\[ Q = 10 \text{ m}^3/\text{s} \quad V = 5 \text{ m}^3 \]
\[ c_{A,0} = 1 \text{ kmol/m}^3 \quad k = 5 \text{ s}^{-1} @ T = 500K - P = 1 \text{ atm} \]

We want to run the reaction isothermally and pressure drops are negligible

**PLUG FLOW REACTOR**

Every “small” element travels along the reactor without mixing with the rest

\[ \tau = \frac{V}{Q} \]

\[ Q c_A \bigg|_{V} - Q c_A \bigg|_{V+dV} - k c_A dV = 0 \]
Effect of RTD on observed reaction rate

\[ A \rightarrow B \quad r = kc_A \quad [\text{mol/m}^3 / \text{s}] \]

\[ Q = 10 \text{ m}^3/\text{s} \quad V = 5 \text{ m}^3 \]
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We want to run the reaction isothermally and pressure drops are negligible

**PLUG FLOW REACTOR**

Every “small” element travels along the reactor without mixing with the rest

\[ \tau = \frac{V}{Q} \]

Mass balance equation:

\[ \frac{dc_A}{d\tau} = -kc_A \quad \rightarrow \quad c_A = c_{A,0} \exp(-k\tau) \quad \rightarrow \quad \chi = \frac{c_{A,0} - c_A}{c_{A,0}} = 91\% \]
Effect of RTD on observed reaction rate

\[ A \rightarrow B \quad r = k c_A \quad [\text{mol/m}^3 / \text{s}] \]

\[ Q = 10 \text{ m}^3/\text{s} \quad V = 5 \text{ m}^3 \]

\[ c_{A,0} = 1 \text{ kmol/m}^3 \quad k = 5 \text{ s}^{-1} \quad T = 500K \quad P = 1 \text{ atm} \]

We want to run the reaction isothermally and pressure drops are negligible

CONTINUOUS STIRRED TANK REACTOR (CSTR)

Mixing is so fast that concentration of every species is uniform and homogeneous in the reactor

\[ \bar{\tau} = \frac{V}{Q} \]

IN-OUT+PROD = ACC

\[ Q c_{A,0} - Q c_A - k c_A V = 0 \]
Effect of RTD on observed reaction rate

\[ A \rightarrow B \quad r = k c_A \quad [\text{mol/m}^3 / \text{s}] \]

\[ Q = 10 \text{ m}^3/\text{s} \quad V = 5 \text{ m}^3 \]
\[ c_{A,0} = 1 \text{ kmol/m}^3 \quad k = 5 \text{ s}^{-1} \quad @ \ T = 500\text{K} – P = 1 \text{ atm} \]

We want to run the reaction isothermally and pressure drops are negligible

CONTINUOUS STIRRED TANK REACTOR (CSTR)

Mixing is so fast that concentration of every species is uniform and homogeneous in the reactor

\[ \bar{\tau} = \frac{V}{Q} \]

Mass balance equation:

\[ c_{A,0} - c_A - \tau k c_A = 0 \leadsto c_A = \frac{c_{A,0}}{1 + k \tau} \leadsto \chi = \frac{c_{A,0} - c_A}{c_{A,0}} = 71\% \]
Effect of RTD on observed reaction rate

\[ A \rightarrow B \quad r = k c_A \quad [\text{mol/m}^3 / \text{s}] \]

\[ Q = 10 \ \text{m}^3/\text{s} \quad V = 5 \ \text{m}^3 \]
\[ c_{A,0} = 1 \ \text{kmol/m}^3 \quad k = 5 \ \text{s}^{-1} \quad T = 500 \text{K} \quad P = 1 \ \text{atm} \]

We want to run the reaction isothermally and pressure drops are negligible

\[ \chi = \frac{c_{A,0} - c_A}{c_{A,0}} = 91\% \quad \text{PFR} \]
\[ \chi = \frac{c_{A,0} - c_A}{c_{A,0}} = 71\% \quad \text{CSTR} \]
1) Effect of the distribution of the contact times in the reactor on the observed reaction rate

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4) Take-home messages
Inter- and Intra-phase transport phenomena

$A \rightarrow B \quad r = k c_A \quad [\text{mol/m}^3/\text{s}]$
Interphase transport phenomena

\[ A \rightarrow B \quad r = kC_A \quad [\text{mol/m}^3 / \text{s}] \]
Interphase transport phenomena

\[ A \rightarrow B \quad r = kC_A \quad [\text{mol/m}^3 / \text{s}] \]
Interphase transport phenomena

Catalytic slab

$k_A = \frac{D_A}{L}$

$N = k_A \left( C_A - C_{A,s} \right)$

MASS TRANSPORT RATE

$C_{A,s}$

$r = kC_{A,s}$

INTRINSIC REACTION RATE

$kC_{A,s}V = k_A \left( C_A - C_{A,s} \right) S$
Interphase transport phenomena

Catalytic slab

\[ k_A = \frac{D_A}{L} \]

\[ N = k_A \left( C_A - C_{A,S} \right) \]

MASS TRANSPORT RATE

\[ r = kC_{A,S} \]

INTRINSIC REACTION RATE

\[ kC_{A,S} = k_A \left( C_A - C_{A,S} \right) \frac{S}{V} = k^*_A \left( C_A - C_{A,S} \right) \]
Interphase transport phenomena

Catalytic slab

\[ k_A = \frac{D_A}{L} \]

MASS TRANSPORT RATE

\[ N = k_A \left( C_A - C_{A,S} \right) \]

INTRINSIC REACTION RATE

\[ r = kC_{A,S} \]

\[ C_{A,S} = \frac{C_A}{1 + \frac{k}{k_A}} = \frac{C_A}{1 + Da} \]
Interphase transport phenomena

\[ C_{A,S} = \frac{C_A}{1 + \frac{k}{k_A}} = \frac{C_A}{1 + Da} \]

\[ r_{obs} = kC_{A,S} = k \frac{C_A}{1 + \frac{k}{k_A}} = \left( \frac{1}{k} + \frac{1}{k_A^*} \right)^{-1} \]

\[ C_A = k_{obs} C_A \]

- **CHEMICAL REGIME**
  \[ r_{obs} = kC_A \]

- **MASS TRANSFER REGIME**
  \[ r_{obs} = k_A^* C_A \]
Effect on observable reaction rate

Da<<1

\[ r_{obs} = kC_A \]

CHEMICAL REGIME

\[ k_{obs} = k = k_0 \exp\left(\frac{-E}{RT}\right) \]

Da >> 1

\[ r_{obs} = k_A^*C_A \]

MASS TRANSFER REGIME

\[ k_{obs} = k_A^* = k_0 \exp\left(\frac{-E \rightarrow 0}{RT}\right) \]

Transport coefficient has very weak dependence on temperature
Intra-phase transport phenomena

WE CONSIDER NOW THE POSSIBILITY THAT TRANSPORT WITHIN THE SLAB CAN BECOME LIMITING.
Intraphase transport phenomena

\[ -D^\text{eff}_A S \frac{dC_A(y)}{dy} \bigg|_y - \left( -D^\text{eff}_A S \frac{dC_A(y)}{dy} \bigg|_{y+dy} \right) - kC_A(y)Sdy = 0 \]
Intraphase transport phenomena

\[ D_{A}^{\text{eff}} \frac{d^2 C_A(y)}{dy^2} = k C_A(y) \]

\[ \left\{ \begin{align*}
\frac{dC_A}{dy} \bigg|_0 &= 0 \\
C_A(y = L) &= C_{A,S}
\end{align*} \right. \]
Intraphase transport phenomena

\[ D_A^{\text{eff}} \frac{d^2 C_A(y)}{dy^2} = kC_A(y) \]

\[
\begin{cases}
\frac{dC_A}{dy} \bigg|_0 = 0 \\
C_A(y = L) = C_{A,S}
\end{cases}
\]

\[ C_A(y) = \frac{\cosh \left( \phi \frac{y}{L} \right)}{\cosh (\phi)} C_{A,S} \]

where:
\[ \phi = L \sqrt{\frac{k}{D_A^{\text{eff}}}} \approx \frac{\text{reaction rate}}{\text{diffusion rate}} \]

THIELE MODULUS
Intraphase concentration gradients

Figure 18.4 Distribution and average value of reactant concentration within a catalyst pore as a function of the parameter $mL = L \sqrt{k/D}$. 
Figure 18.4 Distribution and average value of reactant concentration within a catalyst pore as a function of the parameter $mL = L \sqrt{k/D}$. So what?
At what extent am I using the catalyst?

\[ \eta = \frac{R_{obs}}{R_S} = \frac{\int V kC_A(V) dV}{kC_{A,S}V} = \frac{\tanh(\phi)}{\phi} \]
Effect on observable reaction rate

\[ \eta = \frac{R_{\text{obs}}}{R_S} = \frac{\int V kC_A(V) dV}{kC_{A,S}V} = \frac{\tanh(\phi)}{\phi} \]

For high values of Thiele modulus (internal mass transfer limitations):

\[ \eta \to \frac{1}{\phi} \]

\[ R_{\text{obs}} = \eta R_S = \frac{1}{\phi} R_S = \frac{1}{\phi} kC_{A,S} = \left( \frac{1}{L} \sqrt{\frac{D_{\text{eff}}^A}{k}} \right) kC_{A,S} = k_{\text{obs}} C_{A,S} \]

\[ k_{\text{obs}} = \left( \frac{1}{L} \sqrt{\frac{D_{\text{eff}}^A}{k}} \right) k = \frac{1}{L} \sqrt{D_{\text{eff}}^A k} \]
Effect on observable reaction rate

\[
\begin{align*}
    k_{\text{obs}} &= \left( \frac{1}{L} \sqrt{\frac{D_A^{\text{eff}}}{k}} \right) k = \frac{1}{L} \sqrt{D_A^{\text{eff}}} k = k_{\text{obs}} \exp \left( -\frac{E_{\text{obs}}}{RT} \right) \\
    k &= k_0 \exp \left( -\frac{E}{RT} \right)
\end{align*}
\]

\[E_{\text{obs}} = \frac{E}{2}\]
Interplay between kinetic and transport

Rate of reaction, log scale

CHEMICAL REGIME

\[ k = k_0 \exp\left(-\frac{E}{RT}\right) \]

slope = \(-\frac{E}{R}\)

INTRINSIC ACTIVATION ENERGY (dashed line)

OBSERVED ACTIVATION ENERGY (solid line)
Interplay between kinetic and transport

Rate of reaction, log scale

$$k = k_0 \exp\left(-\frac{E}{RT}\right)$$

slopes:

- **Intrinsic Activation Energy (dashed line)**: $slope = -\frac{E}{2R}$
- **Observed Activation Energy (solid line)**: $slope = -\frac{E}{R}$
Interplay between kinetic and transport

Rate of reaction, log scale

INTER MASS TRANSFER REGIME

slope $\rightarrow 0$

INTRAPHASE MASS TRANSFER REGIME

slope $= -\frac{E}{2R}$

CHEMICAL REGIME

$k = k_0 \exp\left(-\frac{E}{RT}\right)$

slope $= -\frac{E}{R}$

INTRINSIC ACTIVATION ENERGY (dashed line)

OBSERVED ACTIVATION ENERGY (solid line)
Interplay between kinetic and transport

Homogeneous reaction

Rate of reaction, log scale

1/T

INTER MASS TRANSFER REGIME

INTERPHASE MASS TRANSFER REGIME

CHEMICAL REGIME

slope → 0

slope = $-\frac{E}{2R}$

OBSERVED ACTIVATION ENERGY (solid line)

INTRINSIC ACTIVATION ENERGY (dashed line)

$k = k_0 \exp\left(-\frac{E}{RT}\right)$

slope = $-\frac{E}{R}$

OBSERVED ACTIVATION ENERGY

Homogeneous reaction
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Annular Reactor

- Laminar flow $\Rightarrow$ negligible pressure drops
- High GHSV $\Rightarrow 10^6 - 10^7$ Nl/Kg_{cat}/h
  $\Rightarrow$ distance from chemical equilibrium
- Small annular gap (0.5 mm) and thin catalyst layers
- Regular geometry (easy modeling)
- Thermal equilibrium across the section of the ceramic tube
- Isothermal conditions are easily reached (efficient heat dissipation by radiation, dilution)
Combustion of a fuel-rich H₂ over Rh catalyst in an annular reactor (*)

Governing equations

Fluid Phase

\[
\begin{align*}
\frac{\partial (\rho \omega_i)}{\partial t} + \nabla (\rho U \omega_i) &= \nabla (\rho D_{i} \nabla \omega_i) + \sum_j R_j \nu_{ij} MW_i \\
\frac{c_p}{\partial t} + c_p \nabla (\rho T) &= \nabla (k \nabla T) + \sum_j R_j \Delta H_j \\
\frac{\partial (\rho U)}{\partial t} + \nabla (\rho U U) &= -\nabla p + \nabla (\mu \nabla U) + \rho g \\
\frac{\partial \rho}{\partial t} + \nabla (\rho U) &= 0
\end{align*}
\]

Solid Phase

\[
\begin{align*}
\frac{\partial (\rho^{\text{mix}} \omega_i)}{\partial t} &= \nabla (\rho^{\text{mix}} D_{\text{eff},i} \nabla \omega_i) + \left( \sum_j R_{\text{het},j} \nu_{ij} MW_i \right) \cdot a_{\text{cat}} \\
c_{\text{p, sol}} \frac{\partial (\rho_{\text{sol}} T)}{\partial t} &= \nabla (k_{\text{eff}} \nabla T) + \sum_j R_{\text{het},j} \Delta H_j \cdot a_{\text{cat}} \\
\Gamma_{\text{site}} \frac{\partial \theta_i}{\partial t} &= R_{i, \text{surf}}
\end{align*}
\]
Governing equations

Non-catalytic walls

\[ \nabla \omega_k \bigg|_{\text{inert}} = 0 \]

\[ T \bigg|_{\text{inert}} = f(t, T) \]

\[ \nabla T \bigg|_{\text{inert}} = g(t, T) \]

Catalytic walls

\[ \rho \Gamma_{k, \text{mix}} \left( \nabla \omega_k \right) \bigg|_{\text{catalytic}} = -\alpha_{\text{cat}} \dot{\Omega}_k^{\text{het}} \quad k = 1, \ldots, \text{NG} \]

\[ \lambda \left( \nabla T \right) \bigg|_{\text{catalytic}} = -\alpha_{\text{cat}} \sum_{j=1}^{\text{NR}} \Delta H_j^{\text{het}} \dot{i}_j^{\text{het}} \]

\[ \sigma_{\text{cat}} \frac{\partial \theta_i}{\partial t} = \dot{\Omega}_i^{\text{het}} \quad i = 1, \ldots, \text{NS} \]

Detailed microkinetic models

1. \( \text{H}_2 + 2\text{Rh}(s) \rightarrow 2\text{H}(s) \)
2. \( 2\text{H}(s) \rightarrow \text{H}_2 + 2\text{Rh}(s) \)
3. \( \text{O}_2 + 2\text{Rh}(s) \rightarrow 2\text{O}(s) \)
4. \( 2\text{O}(s) \rightarrow \text{O}_2 + 2\text{Rh}(s) \)
5. \( \text{OH}(s) + \text{Rh}(s) \rightarrow \text{H}(s) + \text{O}(s) \)
6. \( \text{H}(s) + \text{O}(s) \rightarrow \text{OH}(s) + \text{Rh}(s) \)
7. \( \text{H}_2\text{O}(s) + \text{Rh}(s) \rightarrow \text{H}(s) + \text{OH}(s) \)
8. \( \text{H}(s) + \text{OH}(s) \rightarrow \text{H}_2\text{O}(s) + \text{Rh}(s) \)
9. \( \text{H}_2\text{O}(s) + \text{O}(s) \rightarrow 2\text{OH}(s) \)
10. \( 2\text{OH}(s) \rightarrow \text{H}_2\text{O}(s) + \text{O}(s) \)
11. \( \text{OH} + \text{Rh}(s) \rightarrow \text{OH}(s) \)
12. \( \text{OH}(s) \rightarrow \text{OH} + \text{Rh}(s) \)
13. \( \text{H}_2\text{O} + \text{Rh}(s) \rightarrow \text{H}_2\text{O}(s) \)
14. \( \text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O} + \text{Rh}(s) \)
15. \( \text{H} + \text{Rh}(s) \rightarrow \text{H}(s) \)
16. \( \text{H}(s) \rightarrow \text{H} + \text{Rh}(s) \)
17. \( \text{O} + \text{Rh}(s) \rightarrow \text{O}(s) \)
18. \( \text{O}(s) \rightarrow \text{O} + \text{Rh}(s) \)

Adsorbed (surface) species

\[ r_j = A_j \cdot T^\beta_j \cdot \exp \left( -\frac{E_{\text{att},j}(\theta_i)}{RT} \right) \prod_{i=1}^{\text{NC}} (c_i)^{v_{ij}} \]

M. Maestri, Microkinetic analysis of complex chemical processes at surface, in “New strategy for chemical synthesis and catalysis”, Wiley-VCH (2012)
Identification of the calculation domain

- Cylindrical symmetry
- 2D domain
- Lower computational effort

Fluid and solid regions

Annular reactor

Combustion of a fuel-rich $\text{H}_2$ over Rh catalyst in an annular reactor (*)

No resistances in the porous washcoat
Annular reactor

Combustion of a fuel-rich H₂ over Rh catalyst in an annular reactor (*)

No resistances in the porous washcoat
Model results

Combustion of a fuel-rich H₂ over Rh catalyst in an annular reactor
Combustion of a fuel-rich H\(_2\) over Rh catalyst in an annular reactor

Model results

\[ D_{\text{eff}} = k(\varepsilon) \cdot D_{\text{bulk}} \]
Intraphase gradients

Different controlling regimes at different T

- Temperature (°C):
  - 373 K
  - 423 K
  - 523 K
  - 823 K

- Oxygen mass fraction vs. Catalytic Layer Width [μm]

- Oxygen Conversion [%] vs. Temperature [°C]
**Interphase gradients**

![Graph showing O2 conversion percentage against temperature for different H2 mole fractions at 150°C, 400°C, and 500°C.]

- **H2 mole fraction**:
  - 150°C
  - 400°C
  - 500°C

- **O2 mole fraction**:
  - 150°C
  - 400°C
  - 500°C

- **H2O mole fraction**:
  - 150°C
  - 400°C
  - 500°C

Temperature [°C] | H2 mole fraction | O2 mole fraction | H2O mole fraction
---|---|---|---
150°C | [0-0.04] | [0-0.10] | [0-0.05]
400°C | [0-0.04] | [0-0.10] | [0-0.05]
500°C | [0-0.04] | [0-0.10] | [0-0.05]
Outline

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4) Take-home messages
Take-home messages

1) Physical transport may have a strong influence on the rate of the overall process and may introduce additional dependences on the operating conditions.

2) The observable reaction rate may differ substantially from the intrinsic rate of the chemical transformation under bulk fluid phase composition.
Take-home messages

1) Physical transport may have a strong influence on the rate of the overall process and may introduce additional dependences on the operating conditions.

2) The observable reaction rate may differ substantially from the intrinsic rate of the chemical transformation under bulk fluid phase composition.

3) You need to be aware of such interplay and related effects in order to:
   1) understand what you are measuring
   2) understand what you are comparing
   3) scale-up properly and successfully your reaction
   4) force your catalyst to the desired observed functionality (selectivity €€€!! – safe operation)

4) Reactivity measurement is intrinsically a multiscale phenomenon: make sure you minimize the effect of transport (dilution, temperature, geometry).
A first-principles approach to CRE

MIクロスケール
化学結合の形成と破壊

メソスケール
化学事件の相互作用

マクロスケール
反応工学と伝播現象

電子構造理論

kMC

CFD

Length

Time
Thank you for your attention!

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