Recap: two-site processes

Two-site processes occur when you have a surface process that requires two adjacent sites.

For example:

- Dissociative adsorption

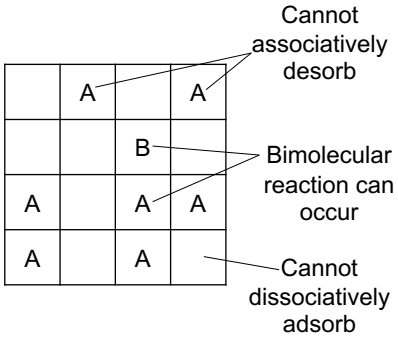
$$A_2 + ** \underset{k_{des}}{\overset{k_{ads}}{\rightleftharpoons}} A{**}A$$

- Associative desorption

- 2 molecule surface reaction:

$$\underbrace{A^* + B^*}_{\text{To be consistent with above, you could write this as A**B}} \not\rightarrow \text{products} + 2^*$$

(when it's X* + Y* or Y* + Y* or 2*, it probably means X**Y, Y**Y or **)



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Recap: two-site processes

For all of these processes, we will need [**], [X**Y] or [Y**Y] for the kinetics.

Let's look at [**]:

What is the probability (P_{**}) that we will find two adjacent sites at a given site?

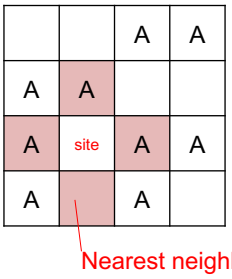
$$P_{**} = \vartheta_*(z\,\vartheta_*)$$

Nb of nearest neighbors

We then "apply" this probability to every site (= multiply it by $[*]_0$) and divide by two to avoid double counting:

$$[**] = \frac{[*]_0}{2}\vartheta_*(z\vartheta_*) = \frac{z}{2}\frac{[*]_0[*]^2}{[*]_0^2} = \frac{2[*]^2}{[*]_0}$$

Notice that the units are correct, we still have concentration units!



The factor 2 in the denominator avoids double counting. It distinguishes between these two questions:

"how many sets of two free sites are there?"

"how many sites have at least 1 free site next to them?" → Double counting

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Recap: two-site processes

Now we just use the definitions of [**], [X**Y] or [Y**Y] in the kinetics:

- For dissociative/associative adsorption/desorption:

$A_2 + ** \underset{k_{\text{des}}}{\overset{k_{\text{ads}}}{\rightleftharpoons}} A**A$ $\qquad r = k_{ads}[A_2][**] - k_{des}[A ** A]$

We plug in our expression: $r = k_{ads}[A_2]\frac{2[*]^2}{[*]_0} - k_{des}\frac{2[A*]^2}{[*]_0}$

We put the factor 2 in the constant: $r = k_{ads}[A_2]\frac{[*]^2}{[*]_0} - k_{des}\frac{[A*]^2}{[*]_0}$

- For a surface reaction (Langmuir Hinshelwood):

$A* + B* \not\rightarrow \text{products} + 2*$

$$r = k_3[A ** B] = k_3\frac{[A*][B*]}{[*]_0} = k_3[*]_0\,\vartheta_A\,\vartheta_B$$

$$r = \frac{k_3\,K_{ads,A}\,K_{ads,B}\,[*]_0[A]\,[B]}{\left(1 + K_{ads,A}[A] + K_{ads,B}[B]\right)^2}$$

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Recap: finding a rate equation

Derivation the rate equation:

- 1. Find the RDS and (if applicable) the MARI
- 2. Write r=RDS
- 3. Find an eq. or SSA relation to calculate concentrations in the RDS
  - 3.1 If the RDS consumes the MARI, [MARI] is obtained from an eq. relation.
  - 3.2 If both steps are irreversible, use the SSA.

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Recap: finding a rate equation

How do I find a MARI?

- Don't assume you have to! It's an approximation and lots of RX don't have MARIs
- Look for clues:
  - In the rate equation: e.g.: $r = \frac{cst1\ P_{PO} - cst2\ P_{PHOH}/P_{H_2}}{1 + cst3\ P_{H_2}^{0.5}}$
  - In the conditions*: high P, high/low conversion.…
  - In your chemical intuition (the most risky)

e.g.:

(1) $A + * \underset{}{\overset{K_1}{\rightleftharpoons}} A*$

(2) $A* \xrightarrow{k_2} B*$

(3) $B* \underset{}{\overset{K_3}{\rightleftharpoons}} B + *$

At high or low conversion, or at high P_A or P_B, we can force A* or B* to be the MARI

*You choose them so you can force a MARI…

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Outline of the course

Objective: Be able to analyze and understand a heterogeneous reaction (mechanism, kinetics etc…) from experimental data .

- 1. Basic concepts (about 4 weeks)
  - Kinetics (elementary reactions and transition state theory) **Chapter 1 and 2 (partial)**
  - Ideal reactors **Chapter 3 (partial)**
  - Non-ideal reactors **Chapter 8 (most of it)**
  - The Steady-State Approximation (SSA) **Chapter 4 (most of it)**
- 2. Heterogeneous catalysis (about 4 weeks)
  - What are heterogeneous catalysts?
  - Bulk and surface structures in heterogeneous catalysts
  - Surface reactivity
  - Elementary step kinetics
  - Kinetics of Overall Reactions

  } **Chapter 5**
- **3. Transport effects in heterogeneous catalysis** (about 4-5 weeks)
  - External transport
  - **Internal transport**
  - Combined internal and external transport
  - Analyzing rate data

  } **Chapter 6**

+ 1 week of computer exercises

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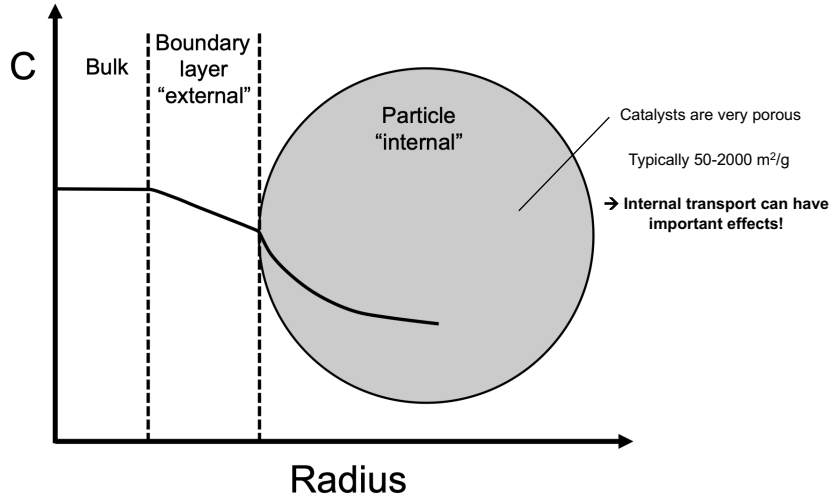
3 Transport effects in heterogeneous catalysis

Overview of the system:



Catalysts are very porous

Typically 50-2000 m^2/g

→ **Internal transport can have important effects!**

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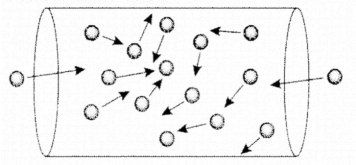
3 Transport effects in heterogeneous catalysis

3.3.1 Types of pores and pore networks

- Molecular diffusion



In large pores (>1000 nm for molecules ~100 g/mol), molecules will hit themselves much more than the wall (=bulk diffusion)

- Knudsen diffusion

In smaller pores ($5<R_p<1000$ nm for molecules ~100 g/mol), molecules will increasingly hit the wall more than themselves

Knudsen diffusion coefficient [cm^2s^{-1}]

Pore radius [cm]

$$D_{KA} = 9.7\ 10^3 R_{po} \left(\frac{T}{M_A}\right)^{1/2}$$

T° [K]

Molecular weight [g/mol]

For a gas, D_{AB}~0.1 cm^2s^{-1}. For D_{KA} to be comparable, for a molecule where M_A~100 g/mol and T°=300 K, we need:

$0.1=10^4\ R_{po}\ (3)^{1/2}$ → R_{po} ~ 10^{-5} cm = 100 nm

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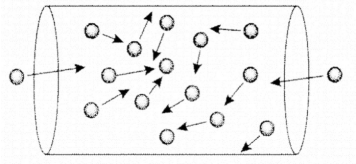
3 Transport effects in heterogeneous catalysis

3.3.1 Types of pores and pore networks

- Molecular diffusion

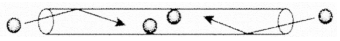


In large pores (>1000 nm for molecules ~100 g/mol), molecules will hit themselves much more than the wall (=bulk diffusion)

- Knudsen diffusion

In smaller pores ($5<R_p<1000$ nm for molecules ~100 g/mol), molecules will increasingly hit the wall more than themselves

- Single file diffusion



Only one molecule can pass through the pore at a time (2-5 nm, depending on the molecule)

- Shape-selective/very small pore

The pore is smaller than a molecule (< 2nm)

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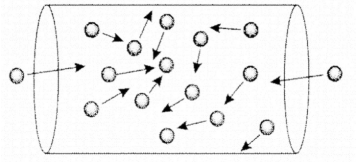
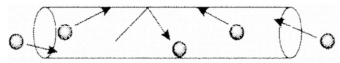
3 Transport effects in heterogeneous catalysis

3.3.1 Types of pores and pore networks

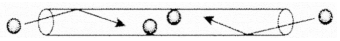
- Molecular diffusion



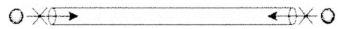
- Knudsen diffusion

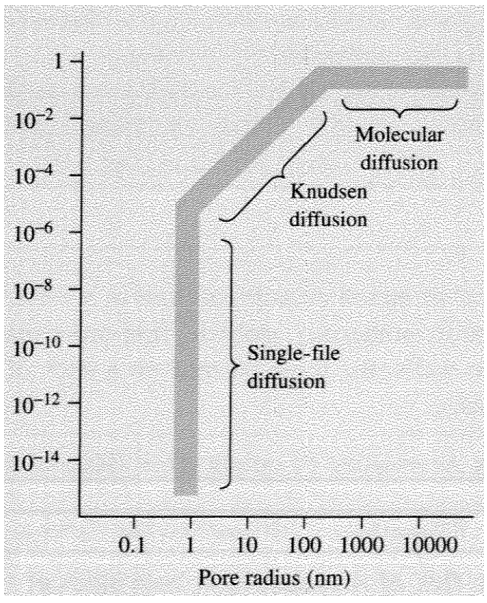


- Single file diffusion



- Shape-selective/very small pore





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