Outline of the course

1. Basic concepts
   - Kinetics (elementary reactions and transition state theory)
     - Definitions: what is a reaction?
     - Elementary reaction kinetics
       - Basics
       - Transition state theory

$$r = \underbrace{\frac{kT}{h}\exp\left[\frac{\Delta S_0^{\ddagger}}{R}\right]}_{A}\exp\left[-\frac{\Delta H_0^{\ddagger}}{RT}\right]C_A C_B \qquad E_a$$

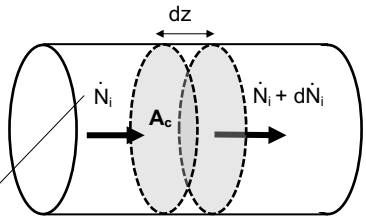
   - Ideal reactors
     - Batch
     - CSTR
     - PFR
     - Measuring r
   - Non-ideal flow in reactors: how to deal with it/what effect on the reaction?
     - Empirically (RTD, RTD effect on kinetics)
     - With a model (model RTD, model dispersion effect on kinetics)
   - The Steady-State Approximation (SSA) : how to deal with a fast intermediate reaction? → essential for catalysis
     - Overview of the SSA
     - When does it apply? After t_r

2

Recap on non-ideal flow

1.4.4 Effect of axial dispersion

Let's model a reactor:



For a PFR:

$$\dot{N}_i = \underbrace{uA_C C_i}_{\text{Convection term}}$$

Acc. = In – out + source

$$0 = \underbrace{\dot{N}_i - \left(\dot{N}_i + d\dot{N}_i\right)}_{d\dot{N}_i} + v_i r A_C dz$$

$$0 = -u\frac{dC_i}{dz} + v_i r dz$$

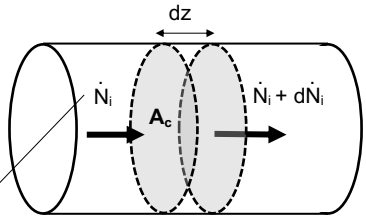
For a 1st order RX: $\dfrac{dC_i}{d(z/u)} = \dfrac{dC_i}{d\tau} = -kC_i$

3

Recap on non-ideal flow

1.4.4 Effect of axial dispersion

Let's model a reactor:



For a real reactor:

$$\dot{N}_i = \underbrace{uA_C C_i}_{\text{Convection term}} - \underbrace{A_C D_A \frac{dC_i}{dz}}_{\text{Dispersion term}}$$

It's not just diffusion, which describes random molecular motion. Here it's also random motion of fluid packets (i.e. "diffusion plus")

Acc. = In – out + source

$$0 = \underbrace{\dot{N}_i - \left(\dot{N}_i + d\dot{N}_i\right)}_{d\dot{N}_i} + v_i r A_C dz$$

$$0 = -u\, d\left(C_i - D_A \frac{dC_i}{dz}\right) + dz v_i\, r_i$$

For a 1st order RX: $u\frac{dC_i}{dz} - D_A\frac{d^2C_i}{dz^2} = -kC_i$

4

Recap on non-ideal flow

1.4.4 Effect of axial dispersion

$$u\frac{dC_i}{dz} - D_A\frac{d^2C_i}{dz^2} = -kC_i$$

Let's use the dimensionless length: $Z = z/L$

$$\frac{u}{L}\frac{dC_i}{dZ} - \frac{D_A}{L^2}\frac{d^2C_i}{dZ^2} = -kC_i$$

Let's use the dimensionless length: $C_i' = C_i/C_{i,0}$

$$\frac{u}{L}\frac{dC_i'}{dZ} - \frac{D_A}{L^2}\frac{d^2C_i'}{dZ^2} = -kC_i'$$

Multiplying by $L/u = \tau$:

$$\frac{dC_i'}{dZ} - \frac{D_A}{uL}\frac{d^2C_i'}{dZ^2} = -k\tau C_i'$$

$$\frac{D_A/L}{u} = \frac{1}{Pe_a} = \frac{Dispersive\ flow}{Convective\ flow}$$

$$k\tau = Da_1 = \frac{Residence\ time}{Characteristic\ RX\ time}$$

5

Recap on non-ideal flow

1.4.4 Effect of axial dispersion

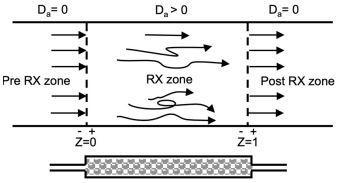
This is a 2nd order ordinary differential equation:

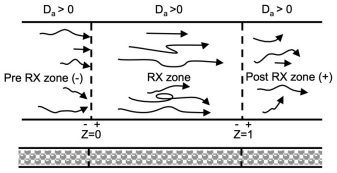
$$\frac{dC_i'}{dZ} - \frac{1}{Pe_a}\frac{d^2C_i'}{dZ^2} = -Da_1 C_i'$$

We need boundary conditions to solve this!

2 possibilities:

- Open-open conditions
- Closed-closed conditions





6

Recap on non-ideal flow

1.4.4 Effect of axial dispersion

This is a 2nd order ordinary differential equation:

$$\frac{dC_i'}{dZ} - \frac{1}{Pe_a}\frac{d^2C_i'}{dZ^2} = -Da_1 C_i'$$

We need boundary conditions to solve this!

2 possibilities:

- Open-open conditions
- Closed-closed conditions

Both types of conditions lead to different functions *C(z)* but the same result at the exit of the reactor (in dimensionless concentration terms for Z=z/L=1):

$$C'_{i,Z=1} = \frac{4q\exp(P\,e_a/2)}{(1+q)^2\exp(Pe_a\,q/2) - (1-q)^2\exp(-Pe_a\,q/2)}$$

With: $q = \sqrt{1 + 4D\,a_1/P\,e_a}$

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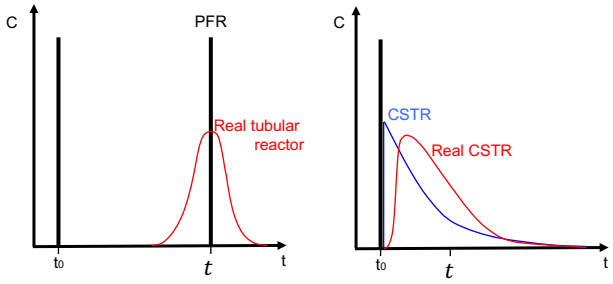
Recap on non-ideal flow

1.4.1 Residence time distribution (RTD)

RTD is represented mathematically by E(t)

It represents the **fraction per time of molecules exiting the reactor at time *t***.

With tracer studies:



Mathematical definition of *E(t)*: (not just $C(t)/C_0$)

$$E(t) = \frac{C(t)}{\int_0^\infty C(t')dt'}$$

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Recap on non-ideal flow

1.4.2 RTD effect on kinetics

We can use a distribution function *E(t)* to calculate properties that can be expressed by time dependent functions:

$$f = \int_0^\infty f(t)E(t)dt$$

One such time-dependent functions is *C(t)* (calculated with the batch reactor expression):

$$C_i = \int_0^\infty C_i(t)E(t)dt$$

⚠ This is only exact for reactions of order 1. For reaction orders n>1, this expression is not exact (but a pretty close approximation).

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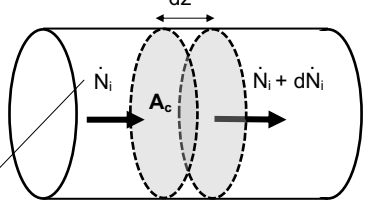
Recap on non-ideal flow

1.4.3 Dispersion models

If having E(t) is not enough for all reactions, let's model a real reactor **with a tracer**:



For a real reactor:

$$\dot{N}_i = \underbrace{uA_C C_i}_{\text{Convection term}} - \underbrace{A_C D_A \frac{dC_i}{dz}}_{\text{Dispersion term}}$$

Acc. = In – out + source

$$\delta V \frac{\partial C_i}{\partial t} = \underbrace{\dot{N}_i - (\dot{N}_i + \partial \dot{N}_i)}_{\partial \dot{N}_i} + 0$$

$$\rightarrow \frac{\partial C_i}{\partial t} = -u \frac{1}{\partial z} \partial \left(C_i + D_A \frac{\partial C_i}{\partial z} \right)$$

$$\frac{\partial C_i}{\partial t} = -u \frac{\partial C_i}{\partial z} + D_A \frac{\partial^2 C_i}{\partial z^2} \xrightarrow[\text{method}]{\text{PDE solving}} \frac{C_i}{C_i^0} = \left(\frac{Pe_a}{4\pi\theta} \right)^{\frac{1}{2}} \exp\left(-\frac{(1-\theta)^2 Pe_a}{4\theta} \right) = E(\theta)$$

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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

  About 6-7 pages per week
- 3. Transport effects in heterogeneous catalysis (about 4-5 weeks)
  - External transport
  - Internal transport
  - Combined internal and external transport
  - Analyzing rate data

  Chapter 6

  About 6-7 pages per week

+ 1 week of computer exercises

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2.2 Bulk and surface structures in heterogeneous catalysts

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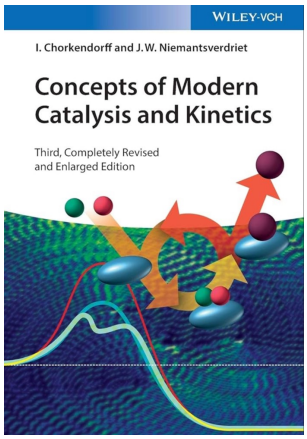
Main source for these slides:



Available for free from EPFL computers:

http://onlinelibrary.wiley.com/book/10.1002/3527602658

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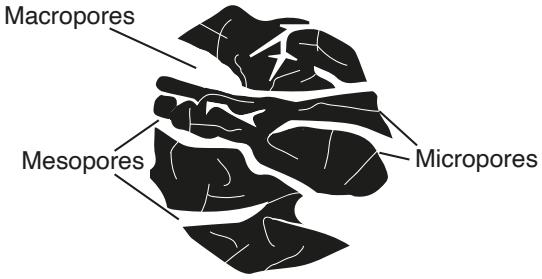
What are heterogeneous catalysts?

For heterogeneous catalysts everything happens on the surfaces (where the solid interacts with the fluid).

→ Porosity is needed to maximize surface area!

A typical catalyst particle:



Macropores: >50 nm

Mesopores: 2-50 nm

Micropores: <2 nm

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What are heterogeneous catalysts?

For heterogeneous catalysts everything happens on the surfaces (where the solid interacts with the fluid).

→ Porosity is needed to maximize surface area!

Catalysts look like porous solids.

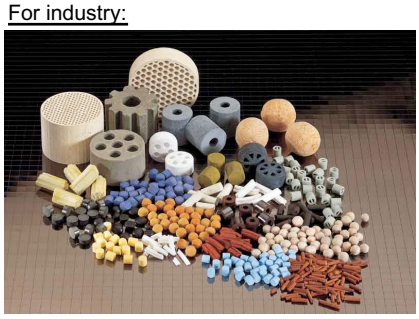
In the lab:


Ru/C


MCM-41
(mesoporous SiO_2)


ZSM-5
(zeolite)

For industry:


Photos: Süd Chemie, Alibaba.com

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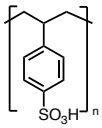
Types of heterogeneous catalysts

Bulk catalysts

Single material forms the entire catalytic particle. Catalysis happens on its surface.

For example:

- Metal oxides
  →Zeolites, Al_2O_3, TiO_2, SiO_2…
- Metal sulfides, carbides, nitrides…etc.
  →MoS_2, WS_2, NiN, WC, Mo_2C…
- Functionalized resins
  →Amberlyst…



Supported catalysts

Some metals are too expensive to form bulk catalysts → supported catalysts are used.

Especially important for noble metals (Pt, Au, Ru, Rh..etc…)

Typical supports

In addition, typical supports include inert materials such as activated carbon, graphitic carbon or SiC

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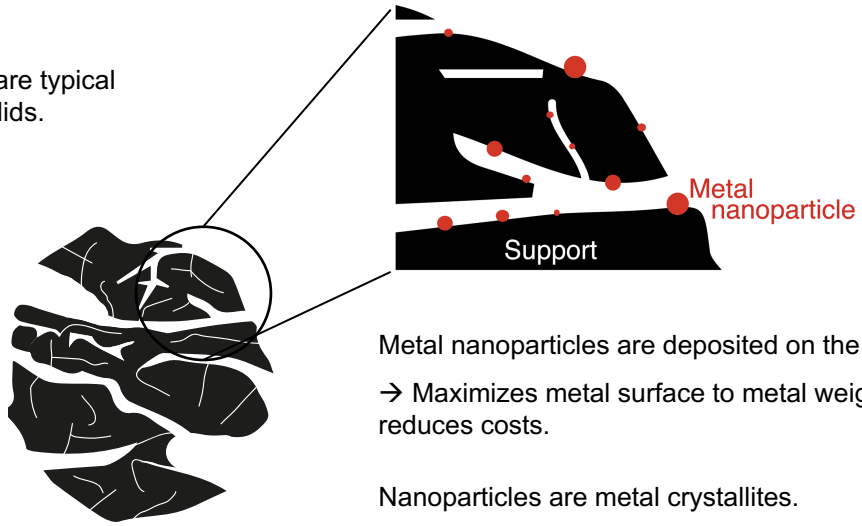
Supported metal catalysts

Supports are typical porous solids.



Metal nanoparticles are deposited on the support.

→ Maximizes metal surface to metal weight, which reduces costs.

Nanoparticles are metal crystallites.

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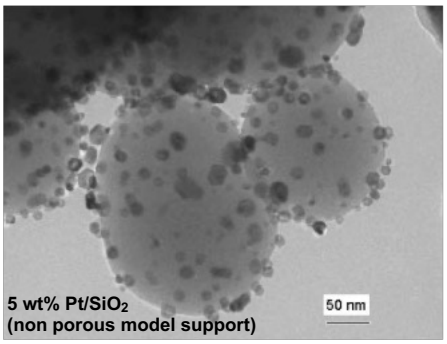
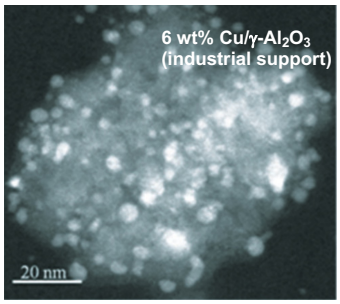
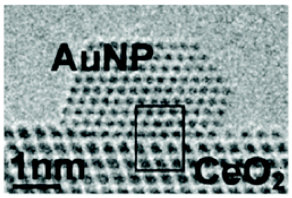
Supported metal catalysts







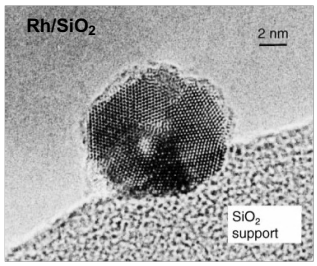


Photo source: Datye, *Topics in Catalysis*, 2000, O'Neill et al. *Angew. Chem.* 2013 and Jinschek Chem. Comm. 2014.

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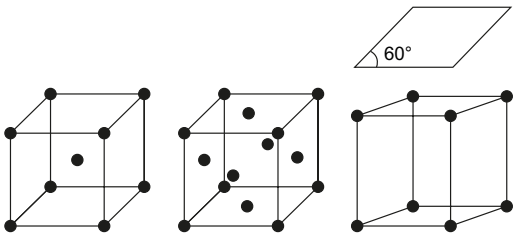
Supported metal catalysts

Crystal structures

The crystals forming the nanoparticles can have various packing arrangements.

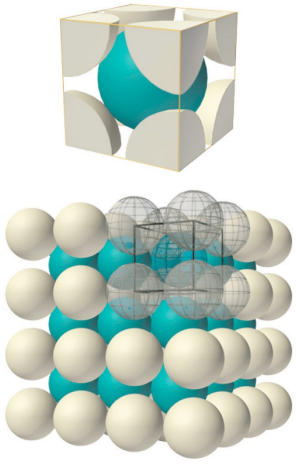
For catalytically relevant transition metals:



Body-centered Cubic (BCC)

Face-centered Cubic (FCC)

Hexagonal closely packed (HCP)



BCC

Photo source: Averill and Eldredge, *Principles of general chemistry*, Prentice Hall, 2007.

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Supported metal catalysts

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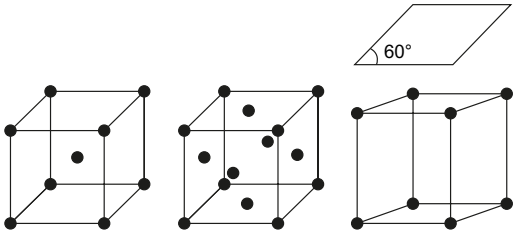

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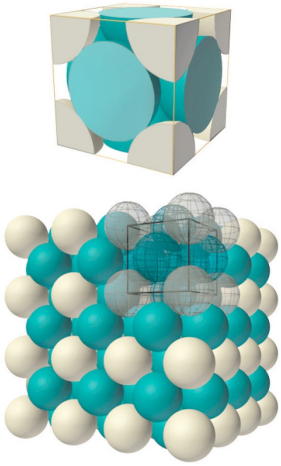

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20

Supported metal catalysts

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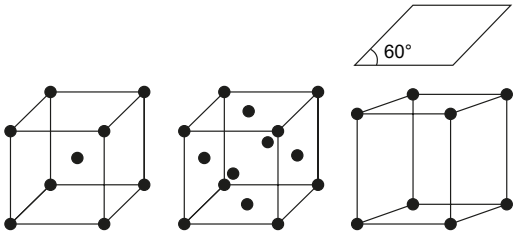

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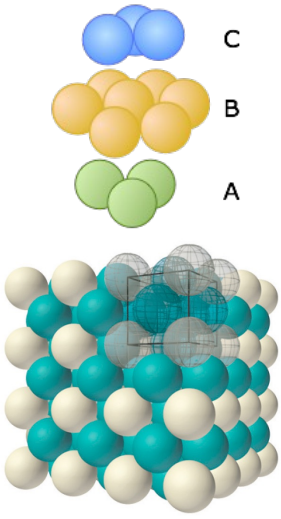

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Supported metal catalysts

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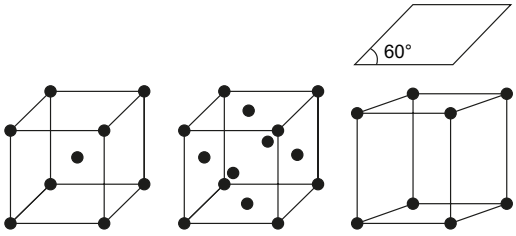

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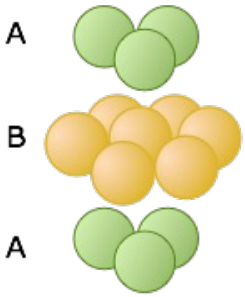

Hexagonal closely packed (HCP)

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Supported metal catalysts

Crystal structures

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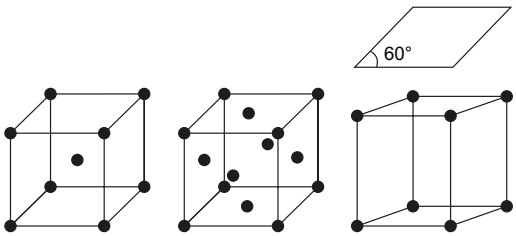

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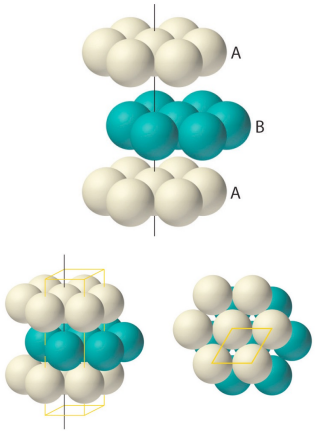

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Supported metal catalysts

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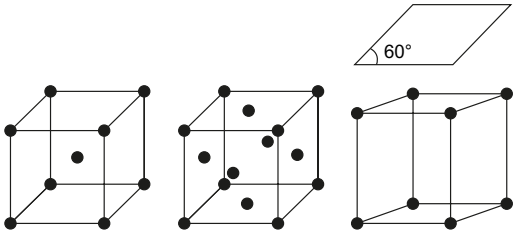

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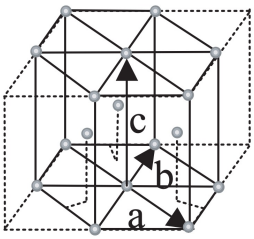

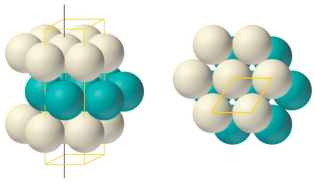

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Supported metal catalysts

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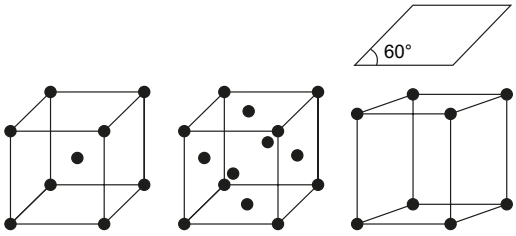

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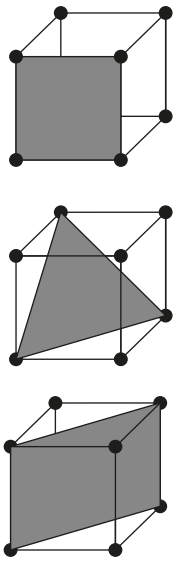

Crystal surfaces are defined by the plain that cuts through their unit cell

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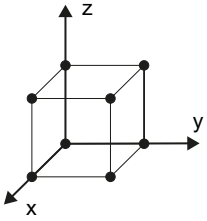
Supported metal catalysts

Crystal structures

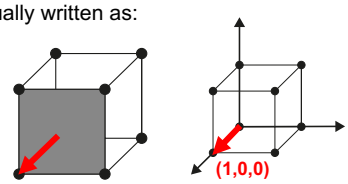
Crystal surfaces are described by the vector normal **H** to the intersecting plain, defined by:

$$\boldsymbol{H} = h\boldsymbol{x} + k\boldsymbol{y} + l\boldsymbol{z}$$

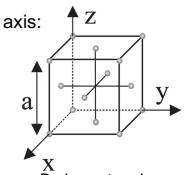


The indices *h*, *k*, *l* are known as the **Miller indices**. They are usually written as:

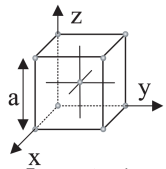
$$(h, k, l)$$



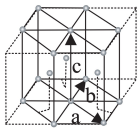
Unit cells with their axis:



Body-centered Cubic (BCC)



Face-centered Cubic (FCC)



Hexagonal

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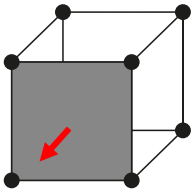
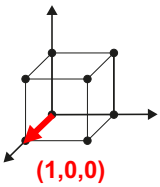
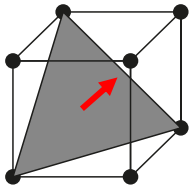
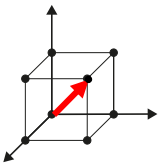
Crystal structures

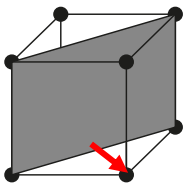
What are the miller indices of these structure (3 main basal crystal plains)?

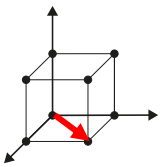












Note: the points where the plain crosses each axis is the inverse of the miller index (h, k, l):

$$(1/h, 1/k, 1/l)$$

For the 3 planes above:

$(1, \infty, \infty)$ $(1,1,1)$ $(1,1, \infty)$

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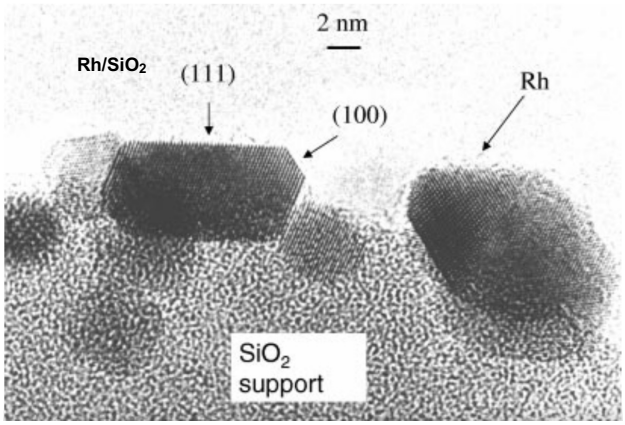
Supported metal catalysts

Crystal structures

These planes are key because they are actually what you find on a catalyst nanoparticle and it's what interacts with the reactant!

Rhodium forms a face-centered cubic (FCC) crystal:



Not all surfaces have the same reactivity!

Photo source: Datye, *Topics in Catalysis*, 2000.

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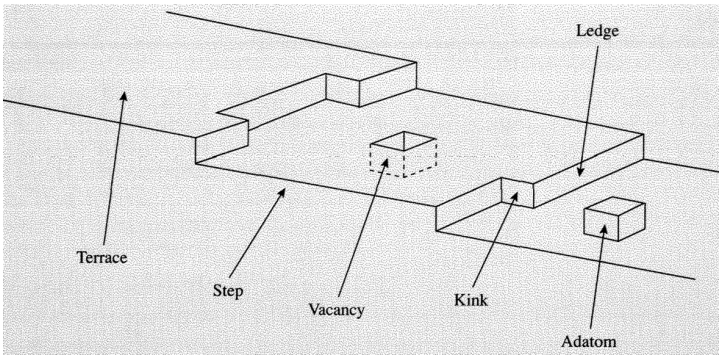
Supported metal catalysts

Crystal structures

A crystal surface contains several different sites. It's not uniform (even if it's perfect)!

Schematic of a typical crystal:



Every single type of site could be equivalent or a defined site type (on a single crystal surface) could be responsible for catalyzing a reaction.

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Metal Oxides

General structure

Metal oxides are a major catalyst category (usually as bulk catalysts or supports). There biggest feature is their participation in both Lewis and Brønsted acid-base reactions because of the presence of the metal (acid) and the oxygen (Brønsted base).

Schematic of a typical surface:

oxide surface: $M^{\delta+} - O^{\delta-} - M^{\delta+} - O^{\delta-} - M^{\delta+}$

Lewis Acid — electron acceptor

Bronsted Base — proton acceptor

Typical reactions:

heterolytic adsorption of:

H_2: H^+ H^- on $M^{\delta+} - O^{\delta-} - M^{\delta+} - O^{\delta-} - M^{\delta+}$

H_2O: H^+ on $O^{\delta-}$ (Bronsted acid), H^- on $M^{\delta+}$ (Bronsted base)

C_2H_6 ; CH_3OH: C_2H_5 and H on $M^{\delta+}$, H on $O^{\delta-}$, CH_3 (methoxy group) on O

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Metal Oxides

Principle oxides: Silica and alumina

Silica and alumina have sites with Bronsted acidity and basicity:

$$M\text{–}OH + H^+ = M\text{–}OH_2^+$$

$$M\text{–}OH + OH^- = M\text{–}O^- + H_2O$$

Because of this, the surface charge is determined by pH.

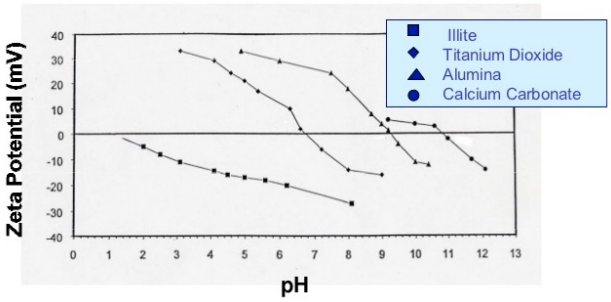

Photo source: Colloid consultants, 2011.

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Metal Oxides

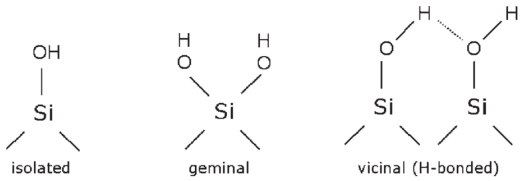
Principle oxides: Silica and alumina

Silica and alumina have sites with Bronsted acidity and basicity:

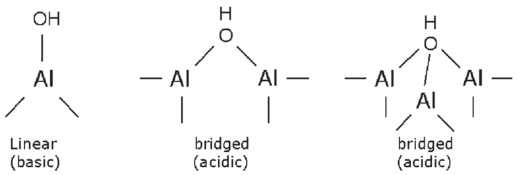
$$M\text{–}OH + H^+ = M\text{–}OH_2^+$$

$$M\text{–}OH + OH^- = M\text{–}O^- + H_2O$$

Silica:



Alumina:



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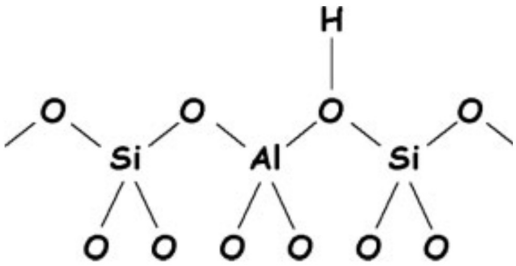
Metal Oxides

Principle oxides: Silica and alumina

Mixture of alumina and sillica be amorphous or crystalline. The crystalline species are referred to as aluminosillicates and include zeolites (hydrated aluminosylicates) and are hugely important for catalysis.

These mixtures are important notably because of their acidity:



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Metal Oxides

Principle oxides: Silica and alumina

Zeolites:

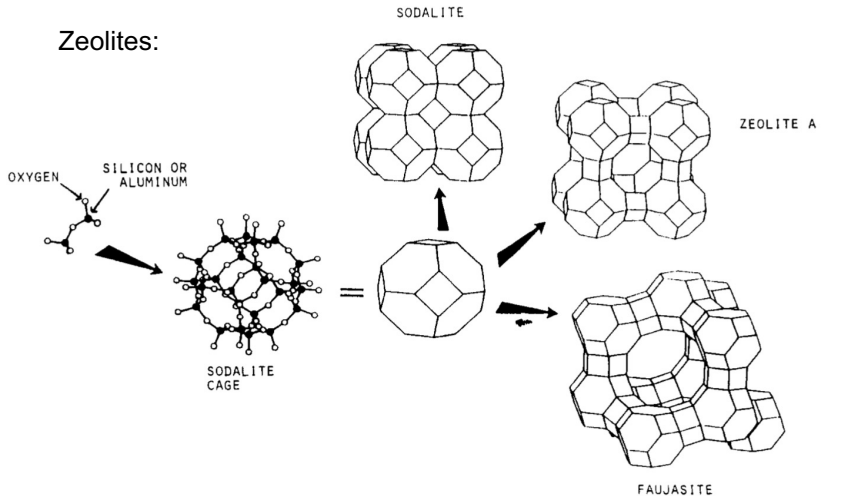

Photo source: Davis, *Ind. Eng. Chem*, 1991.

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Metal Oxides

Principle oxides: Silica and alumina

Zeolites:

The regular crystal structure provides a narrow pore size distribution:

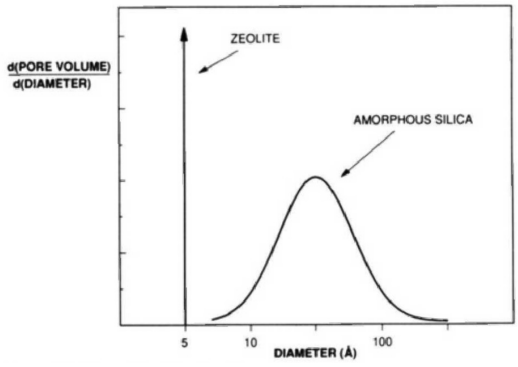
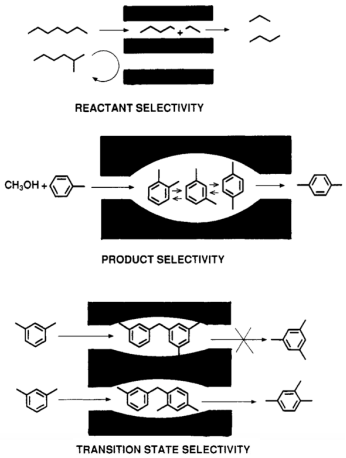


Photo source: Davis, *Ind. Eng. Chem*, 1991.

Narrow pore sizes provides shape selectivity:



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