Some Typical Catalysts

**Noble Metals**: mostly Pt, Rh and Pd
Typical uses: oxidation, hydrogenation and dehydrogenation, HCN.

**Transition Metal Oxides**: in particular $V_2O_5$, $MnO_2$, $Cu_2O$, $Fe_2O_3$
Typical uses: oxidative dehydrogenation, methanol, styrene, DeNOx

**Zeolites (aluminosilicates)**: crystalline clays with very regular pore structure with pore diameters between 5 and 10 Å (“molecular sieves”). The extremely small pores allow only certain molecules to reach the catalytically active sites, making these catalysts typically very selective.
Typical uses: isomerisation, FCC, (also non-catalytic: detergents, baby diapers…)

Many catalysts are used as **supported catalysts** by depositing them on high-surface area materials such as silica, alumina or activated carbon, to
(1) reduce the amount of (expensive) active catalyst *(why does this work?)* and
(2) increase the surface area for materials with otherwise low surface areas.

**Silica & alumina**: Both oxides have rather large surface areas (several 100 m$^2$/g) and are used as catalysts as well as support materials. While silica ($SiO_2$) is typically amorphous, alumina ($Al_2O_3$) is crystalline with a number of different phases ($\alpha$, $\beta$ and $\gamma$ being the most common).
Typical uses: hydrocarbon cracking and support for noble metals (many examples…).
Some Typical Catalysts
Catalyst Supports

Most heterogeneous catalysts are composed of the active component and a support material.

Typical supports:
- Nickel clusters
- SiO₂
- Highly dispersed metal on metal oxide

Why do you think supports are being used for many heterogeneous catalysts?

Desired qualities:
- high
- high
- high
Some Catalyst Shapes

most catalyst particles are laced with channels called pores

- large channels (> 50 nm): m
- mid-size channels (2-50 nm): m
- smaller channels (< 2 nm): m
The development of catalysts is still largely a **black art** rather than a scientific endeavor...

...almost all industrial catalysts have been found by painstaking trial-and-error procedures rather than thoughtful scientific design!

Most technical catalysts contain a large number of components (as support, active components, structural and/or mechanical stabilizers etc).

Catalyst “recipes” are among the best kept secrets in the chemical industry.
Catalyst Deactivation...

...by this definition, catalysts are truly magnificent inventions!

(Maybe only surpassed by a certain computer operating system...)

Three main deactivation mechanisms (also called: 'aging')
Cat. Deactivation: Time Scales

- $C_3$ dehydrogenation
- Hydrocracking
- Reforming
- Hydrogenations
- Aldehydes
- Acetylene
- Oxychlorination
- Formaldehyde
- $NH_3$ oxidation
- TWC
- FCC
- Fat hardening
- HDS
- EO
- MA
- SCR
Catalysts Deactivation: Sintering

Sintering takes place on several length scales:

- **Agglomeration**
  - Monomer dispersion → 2-D cluster → 3-D cluster

**Mechanisms for agglomeration:**
- Particle migration & coalescence
- Interparticle transport

**Catalyst pore:**
- Pore occlusion over time
Cat. Deactivation: Sinter Kinetics

- occurs always (strong function of temperature, though!)
- irreversible
- sintering typically follows 2\textsuperscript{nd} order kinetics

\[
- \frac{d(a_s)}{dt} = k_s a_s^2 \quad \Rightarrow \quad a_s(t) = \frac{1}{1 + k_s t}
\]

with: \[ k_s = A_s \exp(-E_s / T) \]

reaction rate becomes:

\[
-r_A = (k C_A) a_s = \frac{k C_A}{1 + k_s t}
\]

strategy to overcome loss of activity is generally to raise temperature:
Sintering: Some Examples

Specific surface area of some typical catalyst support materials versus temperature

Pt-particles on catalyst support after 5h at different temperatures
Catalyst Deactivation: Coking

Coking = deposition of carbon  (very common in hydrocarbon reactions)

as surface accumulates carbon, reactants must diffuse through carbon layer

=> diffusion resistance builds

Counter-measures:
• buildup delayed by high $H_2$ partial pressures or $H_2O$-addition
• reversible by burning off carbon (catalyst regeneration)
  but: ...

modeled by a variety of kinetics

increasing temperature used to offset decline in $a_z$ between regenerations
Catalyst Deactivation: Poisoning

desired reaction sequence

\[ A + S \leftrightarrow \]
\[ A\cdot S \leftrightarrow \]
\[ B\cdot S \leftrightarrow \]

undesired reaction

\[ P + S \leftrightarrow \]

surface complex \( P\cdot S \) does not react further

- generally irreversible
- modeled by power law kinetics

Poison \( P \) typically trace contaminant in feed

=> catalytic reactors do not (really) operate at steady-state !!
Cat. Deactivation: Example

Catalytic reforming:

deactivation due to coking

Alloying the catalyst quite successful!

Typical technical catalysts comprise many components, only a few of which are catalytically active, the rest are stabilizers of some form (anti-sintering, anti-coking, anti-poisoning, ...)

Catalyst Pt (0.2%) / Al₂O₃

\[ C_{12}H_{26} \rightleftharpoons C_{12}H_{24} + H_2 \]

\[
\begin{align*}
\rho_{H_2} &= 1.35 \text{ bar} \\
\rho_{HC} &= 0.10 \text{ bar} \\
LHSV &= 1 \text{ h}^{-1} \\
T &= 745 \text{ K}
\end{align*}
\]
More Ways to Die...

A final common reason for catalyst exchange is ____________

Even in a simple fixed-bed reactor (we will learn more about other types later), catalysts break up:

1. during filling of the reactor:
   - mechanical impact when 'pouring' the catalyst pellets into the reactor

2. during start-up and shut-down cycles:
   - At start-up the hot tubular reactor expands and the catalyst settles.
   - At shut-down the reactor contracts and leads to some catalyst breakage.

Such breakdown can ______________________ through the tube by up to 10% a year. Hence, the catalyst shape as well as the support material is designed to resist break up. However, this increased strength can lead to reduced activity and so a compromise may be required.