„It is in the preparation of catalysts that the chemist is most likely to revert to type and to employ alchemical methods. From all evidence, it seems that the work should be approached with humility and supplication, and the production of a good catalyst received with rejoicing and thanksgiving.“

**Types of Catalysts**

**Terminology:** J. Haber, Pure & Appl. Chem. 63, 1227 (1991)

<table>
<thead>
<tr>
<th>Bulk Catalysts</th>
<th>Supported Catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal oxides</td>
<td>Often noble metals</td>
</tr>
<tr>
<td>Metals (skeletal catalysts)</td>
<td>Systems which cannot be dispersed by other methods</td>
</tr>
<tr>
<td>Noble metal gauze</td>
<td></td>
</tr>
</tbody>
</table>

Dispersion = \( \frac{\text{number of surface atoms}}{\text{total number of atoms}} \)

*Rule of thumb for specific surface area with respect to particle size:*

\[
\begin{align*}
\cdot & \quad 1 \ \mu \text{m} \sim 1 \ \text{m}^2/\text{g} \\
\cdot & \quad \text{one magnitude higher/lower particle size corresponds to one magnitude lower/higher specific surface area}
\end{align*}
\]

**Targets for Catalyst Preparation**

- Activity
- Selectivity
- Stability
  - coking
  - poisoning by reactands
  - sintering
  - poisoning by impurities
- Morphology
- Mechanical strength/resistance
- Thermal properties
- Regeneration
- Reproducibility
- No patent / patentable
- Costs
Bulk Catalysts: Fused Catalysts

- Important for preparation of metal alloys for gauzes
- High dispersion of elements (in melt)
- Ostwald process (Pt/Rh)
- Andrussov process (Pt or Pt/Rh)
- Sulfuric acid catalyst (\(V_2O_5/M_2S_2O_7\))
- Typically high costs of energy, process control difficult

Bulk Catalysts: Raney Catalysts

- Principle: Formation of alloy in a melt, then extraction of one component
- usually: Ni/Al alloy, extraction of Al with alkali hydroxide solution
- Other systems known, technically Raney-Cu is used for the reduction of organic nitro compounds and nitriles
**Bulk Catalysts: Precipitated Catalysts**

- **Precipitated Catalysts**
  - Nucleation is decisive

- **Problems:**
  - Quality varies because of changing concentrations
  - Inclusion of ions: decomposable counter ions, NO$_3^-$, NH$_4^+$, oxalate, citrate...
  - Local supersaturation: homogeneous precipitation, e.g. with urea
  - Component with low $K_{sp}$ precipitates first in co-precipitation
  - Precipitation at high supersaturation or continuously

**Figure:**

- Source
- Crystals
- Nucleation
- Saturation concentration
- Time

(simplified!)

---

**Bulk Catalysts: Precipitated Catalysts**

- Nowadays increasing use of organic solvents, e.g. in production of VPO ($\text{VO}_2\text{P}_2\text{O}_7$) catalysts or Ziegler (zirconocene/MAO/SiO$_2$-catalyst) catalysts
- Precipitation of defined precursor compounds followed by thermal decomposition or transformation into final catalyst

**Examples:**

- Ni/Al$_2$O$_3$
  - Hydrotalcites, such as Ni$_6$Al$_2$(OH)$_{16}$CO$_3$·4H$_2$O, have different calcination and reduction behavior than mixtures of components due to dispersion of elements on atomic level

- Methanol catalyst (Cu/ZnO)
  - Depending on precipitation conditions many different phases with strongly varying catalytic properties can be obtained in dependence of conditions during transformation into catalyst
Bulk Catalysts: Sol-Gel Materials

- Sol-Gel process produces typically highly porous materials with high specific surface areas
- Precursors mostly metal alkoxides, but could as well be simply salts

\[
\begin{align*}
\text{Hydrolysis:} & \quad \text{M-OR + H}_2\text{O} \rightarrow \text{MOH + ROH} \\
\text{Condensation:} & \quad \text{MOH + XO-M} \rightarrow \text{M-O-M + XOH} \quad X = \text{H, R}
\end{align*}
\]

- Both steps proceed simultaneously, relative reaction rate important for product properties

  - if hydrolysis faster than condensation: less branched material
  - if hydrolysis slower than condensation: highly branched material


Sol-Gel Formation

1. Sol Formation

2. Gelation

Advantage: High degree of control over product properties, easy preparation of mixed oxides with atomic dispersion of elements
Gelation of Silica

Gel Drying / Aerogels

Menisci form at pore openings, constant rate period
Menisci recede into solid, shrinkage stops
Accessible pore system

$P$ vs $T$
- solid
- liquid
- normal drying
- critical point
- supercritical drying

Seite 6
Bulk Catalysts: Hydrothermal Synthesis

- Discrimination against precipitation sometimes difficult; typically higher temperature, often pressure, longer reaction time than for precipitation
- Crucial for zeolite synthesis (crystalline, microporous aluminosilicates)

Lab autoclaves
50 - 250 ml

Stirred autoclave
1.5 - 2.5 l

Industrial stirred reactors
50 - 5000 l

Zeolites

\[ M^{x+}_{m/x} \left[ Al_{1x}Si_{n}O_{2(m+n)} \right] \cdot pH_{2}O \]
Zeolites

LTA (4.1 Å)  BEA (6.6 x 6.7 Å)

GIS (4.5 x 3.1)

MFI (5.5 x 5.1 Å)

LTL (7.7 Å)

MOR (7.0 x 6.5 Å)

Zeolite Synthesis

Oxide source

Template

GEL

Mineralizer

H₂O

salt, oxide hydroxide

amine, alkyl ammonium alcohol

seeds sometimes

reaction ordinate (time / temperature)

T = 80 – 200°C
p = 1 – 50 bar
T = 1h - 20 days

Heating unit

Autoclaves

Temperature control
Bulk Catalysts:
Hydrothermal Synthesis

- Discrimination against precipitation sometimes difficult; typically higher temperature, often pressure, longer reaction time than for precipitation
- Crucial for zeolite synthesis (crystalline, microporous aluminosilicates)
- Crystallization from silicon and aluminum containing solutions, mainly under alkaline conditions
- Minimum Si/Al ratio is 1
- Often “template” required (organic additive, e.g. tetraalkylammonium ions), mainly for high silica zeolites
- Many parameters affect zeolite synthesis
  - reagents
  - pH
  - mixing sequence
  - temperature
  - heating rate
  - concentrations
  - template
  - ...

Bulk Catalysts: Solid State Reactions

- Transformation of defined Precursors s.o.
- Also reaction of mixtures of oxides obtained by milling
  - Example: Styrene catalyst milling of KOH + FeO_x + CrO_y, then calcination at 900 - 1300 K
- Solid state ion exchange
  - Example: zeolites, 600-700 K
Bulk Catalysts: Other Methods

- Flame hydrolysis (Aerosil...)
- Sputter processes
- Spezial processes for Carbides, Nitrides
- ...

Supported Catalysts: Supports

- $\gamma$, $\eta$- or $\alpha$ - Al$_2$O$_3$, SiO$_2$, TiO$_2$, ZrO$_2$, MgO, C
- Surface functionality typically -OH for Oxides, oxo-functionality for Carbons
- Oxidic surfaces in electrolytes generally charged

$$
\text{M-OH} + \text{H}^+ \rightarrow \text{M-O}^+ + \text{H}_2\text{O}
$$

$\Rightarrow$ decisive for loading, since no adsorption if wrongly charged!

PZC (Point of zero charge) = particle is not charged at this pH

G.A. Parks, Chem. Rev. 65, 177 (1965)

Rule of thumb:

<table>
<thead>
<tr>
<th>$\text{M}_2\text{O}$</th>
<th>PZC</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>MO</td>
<td>8.5</td>
<td>PZC &lt; 12.5</td>
</tr>
<tr>
<td>$\text{M}_2\text{O}_3$</td>
<td>6.5</td>
<td>PZC &lt; 10.4</td>
</tr>
<tr>
<td>MO$_2$</td>
<td>0</td>
<td>PZC &lt; 7.5</td>
</tr>
<tr>
<td>$\text{M}_2\text{O}_5$</td>
<td>PZC &lt; 0.5</td>
<td></td>
</tr>
</tbody>
</table>
Distribution of Active Component on Support

**macroskopisch**
- homogeneous
- egg shell
- egg white
- egg yolk

**mikroskopisch**
- Non-wetting
- wetting
- spreading

Examples for spreading: V$_2$O$_5$ on TiO$_2$, MoO$_3$ on Al$_2$O$_3$ or on TiO$_2$, not on SiO$_2$

---

Supported Catalysts: Preparation

- **Wet Impregnation, Ion Exchange, Equilibrium Adsorption**
  - Often discriminated but in principle all very similar
  - Principles:
    - Wet Impregnation (incipient wetness/dry impregnation)
      - Support with as much solution to just imbue support; porous material with as much solution that pores are just filled, then drying
      - Drying rate can strongly affect metal distribution
    - Ion Exchange and Equilibrium Adsorption
      - Basically the same: ion exchange if structural charges present (zeolites)
      - Support with excess solution, wait until equilibrium reached, filtration, drying
  - But: During Wet Impregnation also always Adsorption
  - During drying after Ion Exchange/Adsorption also always Wet impregnation
Supported Catalysts: Problems

**Ion Exchange**

» Achievable loading is limited by ion exchange capacity or saturation concentration of solution

- Multiple exchange / loading

» Ion exchange strongly binds ions which can result in irreversible occupation of first exchange sites; might result in inhomogeneous loading

- Taking advantage of competitive ions, such as NH$_4^+$ at Ion Exchange of [Pt(NH$_3$)$_2$]$^{2+}$ in zeolites

**Supported Catalysts: Precipitation-Deposition**

- Support is dispersed in solution, then precipitation is started by addition of precipitation agent
- Problem can be:
  - Precipitation off support
  - Precipitation only on external surface of porous supports

Precipitation-Deposition ideally in concentration range between saturation concentration and nucleation threshold; if interaction between support and species in solution good, then only precipitation on support.
Supported Catalysts: Precipitation-Deposition

Ideal precipitation if precipitation is initiated at the same time in whole solution (homogeneous precipitation)

\[
P\text{H: } \begin{align*}
\text{Urea} & \quad \text{CO}(\text{NH}_2)_2 & \quad \rightleftharpoons & \quad \text{NH}_4^+ + \text{CNO}^- \\
\text{CNO}^- + 3 \text{H}_2\text{O} & \quad \rightleftharpoons & \quad \text{NH}_4^+ + 2 \text{OH}^- + \text{CO}_2 \\
\text{NaNO}_2 & \quad 3 \text{NO}_2^- + \text{H}_2\text{O} & \quad \rightleftharpoons & \quad 2 \text{NO} + \text{NO}_3^- + 2 \text{OH}^- \text{ (no air!)}
\end{align*}
\]

Oxidation state:

Fe\text{II} more soluble than Fe\text{III}, Mn\text{II} more than Mn\text{III}/Mn(IV), Mn\text{VI} may get oxidized in solution (e.g. O\text{2} from air)

Removal of complexation agents:

desorption of NH\text{3} from ammine complexes,
oxidation of inorganic complexing agents with H\text{2}O\text{2}

Supported Catalysts: Grafting

- Grafting (or Anchoring): Deposition involving the formation of a strong (“covalent”) bond between support and active element (J. Haber, Pure&Appl.Chem). Results in defined, good isolated species on surface

- Typically reaction of OH-group with active species. If Silanol reacts, water usually does as well
  \[\rightarrow \text{exclusion of water}\]

- mostly metal organic reactions
  \[
  \text{S-OH} + \text{MX}_n \quad \rightarrow \quad \text{S-O-M-X}_{n-y} + y \text{HX}
  \]
  \[
  \text{S-OH} + \text{M(CO)}_n \quad \rightarrow \quad \text{S-O-MHCO}_{n+2} + 2 \text{CO}
  \]

- further modification by elimination or decomposition of of remaining ligands

- Typical reactions
  - Chlorides and oxychlorides of transition metals
  - Metal alkoxides from gas phase
  - Metal allyles (Mo, Cr) or carbonyles mostly from pentane etc.
Activation / Calcination

• Irrespective of the preparation method of solid, additional steps, such as thermal treatment, are necessary after combination of components

• Easiest Case: Activation under reaction conditions. Relatively rare, in most cases customer wants equilibrated catalyst

• Calcination
  » Can be decisive for properties of catalyst
  » Many possible processes (decomposition of precursor, spreading, sintering, formation of new phases from active material and support, destruction)
  » Specific for each system
  » depends on gas phase; often air, but also inert gas or controlled water vapor atmosphere

Reduction

• One of the most important steps in preparation of metal catalysts

• Starts typically from oxide (after calcination), for noble metals from chloro compounds or oxychloride

• Reduction mostly with H$_2$
  » often: Dispersion higher with higher reduction rate
  » However, can be inverted if nucleation is limiting factor
  » Reducibility might be different to bulk material

• SMSI (strong metal support interaction) might occur
  » Mainly for TiO$_2$, ZrO$_2$
  » H$_2$ sorption suppressed
  » Explanation: electronic effect, alloy, decoration of noble metal with sub-oxides (Ti$_4$O$_7$)
Shaping of Catalysts

- Very important, but basically empirical knowledge
- Often additives, such as oil, graphite, steatite, talc, wasser glass, starch for activated carbon (binder). (additive best protected know-how of producers)
- Shape defines pressure drop in reactor

monoliths < rings < spheres < pellets < extrudates < broken material

Forces between Particles

Chemical Bonds  Solvent Bridges  Capillarity  Solids bridges

Very strong

Covalent bonds

Depends very much on conditions of solvent evaporation and crystallizing solid in bridge

Strong

Capillary forces

Can be repulsive, if charging of particles with same sign occurs; different for conductors and insulators

Variable

Solid bridges

Depends very much on conditions of solvent evaporation and crystallizing solid in bridge

Very strong

Covalent bonds

Comment

Magnitude depends on the interaction potentials

Full saturation of granule with liquid

Methods of Shaping

- Breaking / Milling
- Spray Drying results in small particles (7 - 700 µm)
- Tabletting: Pressing in moulds
- Extrusion: Principle of “Spätzlemaschine”
  » press for highly viscous media
  » screw for less viscous / thixotropic media
- Oil drop coagulation
- Pelletier pan: Snow ball principle
Rotary Tablet Press


Industrial Tableting Machine
Extrusion

Extruders
Extrudates / Monoliths

Bad extrusion characteristics

Good extrusion characteristics

Granulation / Pelletizing

Fig. 1. Schematic of granulation processes: (a) Traditional view (after Savy and Faremaux [16]); (b) Modern approach [1].
Industrial Spherudizer

Novel Approaches in Catalysis

High Throughput Experimentation
Catalyst Development
- “Rational” and “trial & error” approach
- Usually manual manufacturing
- Limited reproducibility
- Sequential testing
- Insufficient data for model development

Transition technology to speed up conventional catalysis research is clearly needed
High Throughput Experimentation

HTE Goal - Decreasing Time to Market

<table>
<thead>
<tr>
<th>Conventional</th>
<th>HTE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab Scale</td>
<td>Lab Scale / Pilot Plant</td>
</tr>
<tr>
<td>Pilot Plant</td>
<td>Production</td>
</tr>
<tr>
<td>Micro reactor</td>
<td>10-100g catalyst</td>
</tr>
</tbody>
</table>
Many standard synthetic operations implemented with high reproducibility and throughput.

Complex formulations possible.

Deficits in the field of precipitation.

High Throughput Synthesis

Packard and Gilson robots for impregnation/precipitation (hte and MPI)

Impregnated, coated and precipitated catalysts (hte)

Mettler and Chemspeed dispensers for precipitation (hte)

High-viscosity dispensers (Corma)

Stage-I and -II tools for hydrothermal synthesis (hte)

Development of reactor technology

- gas inlet from top
- separated outlets into capillaries
- multiport valves
- various analytical techniques possible


Details of MPI Reactors

- reaction gas inlet
- reactor top
- distribution disc
- reactor body
- viton seal
- catalyst cartridge

Reproducibility of System

**Reaction conditions**
- pressure: 45 bar
- temperature: 245 °C

Position

MeOH %

ICI
Quarz
Stage-II Reactor Technology

48-well reactor with integrated stepper motor
Gas flow selection
Parallel slice reactor
16-well hp reactor
16-well pretreatment unit

Automated Synthesis
Combinatorial Chemistry

Molecular compounds

Inorganic compounds

Read-out by XRF

High integration: Single bead reactor

Many Thanks for your Attention!