Homogeneous vs. heterogeneous catalysis

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Heterogeneous Catalysis

Homogeneous Catalysis

Biocatalysis
General features:

- Different reaction phases possible: „classic“ gas/solid; liquid/solid or liquid/liquid systems.
- High industrial relevance (about 85% of all catalytic processes are heterogeneously catalysed).
- In general wide range of operating conditions (high temperatures/pressures).
- Specialised set of analytic methods required (e.g. X-ray methods, Operando spectros.).
- **Major advantage**: Ease of separation of reactants/products/catalysts.

**Homogeneous Catalysis**

General features:

- Liquid phase reactions dominate the field.
- Industrially less relevant; but complex organic or asymmetric transformations possible!
- Reaction conditions milder than required for heterogeneous reactions (-78 °C - ~200 °C).
- Investigation of reactions by spectroscopic methods (NMR, MS, IR, UV-Vis) directly in solution possible.
- Fine-tuning of catalyst properties using different ligands/additives easy possible.
- **Major challenge**: Separation of products and catalysts/additives.
Heterogeneous Catalysis

Technical setup:

Mechanism:

Langmuir-Hinshelwood

Eley-Rideal

## Heterogeneous Catalysis

### Major industrial processes using heterogeneous catalysis

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<th>Process</th>
<th>Catalyst</th>
<th>Reactants</th>
<th>Products</th>
<th>Application</th>
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<td>NH₃</td>
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<tr>
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<td>Cu/ZnO/Al₂O₃</td>
<td>CO, CO₂, H₂</td>
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<tr>
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<td>C₅-C₁₁ hydrocarbons</td>
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<td>Cracking</td>
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<td>Long alkanes, C₁₂⁺</td>
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<td>Ethylene</td>
<td>Polyethylene</td>
<td>Polymers</td>
</tr>
</tbody>
</table>
Heterogeneous Catalysis

Major industrial processes using heterogeneous catalysis

An example from daily life: the three-way catalyst

- Ceramic monolith
- $\gamma$-alumina washcoat
- Pt/Pd/Rh catalyst

Catalytic converter

$\text{CO} + \frac{1}{2}\text{O}_2 \xrightarrow{\text{Pt, Pd}} \text{CO}_2$

$\text{HC's} + \text{O}_2 \xrightarrow{\text{Pt, Pd}} \text{CO}_2 + \text{H}_2\text{O}$

$\text{CO} + \text{NO} \xrightarrow{\text{Rh}} \text{CO}_2 + \frac{1}{2}\text{N}_2$

$\text{H}_2 + \text{NO} \xrightarrow{\text{Rh}} \text{H}_2\text{O} + \frac{1}{2}\text{N}_2$
**Homogeneous vs. heterogeneous catalysis**

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**Heterogeneous Catalysis**

**Setup:**

The Ruhrchemie/ Rhône-Poulenc Hydroformylation (the *oxo process*)

Ligand L is "tppts":

\[
\begin{align*}
&\text{Na}_3\text{SO}_3 \\
&\text{Ph} - \text{P} - \text{SO}_3\text{Na} \\
&\text{Ph} - \text{SO}_3\text{Na}
\end{align*}
\]

General procedure:

Homogeneous Catalysis

Mechanism for Pd-catalysed reactions - cross-coupling and carbonylation:
Major industrial processes using homogeneous catalysis

The Monsanto process / Cativa Process
Acetic acid
Catalyst system: Rh / Ir complexes

The Shell Higher Olefins Process (SHOP)
Oligomerization of ethen to medium and long-chain α-olefins (C₄-C₂₀)
Catalysts: Ni(II)-complexes

The Wacker Oxidation Process
Oxidation of olefins to carbonyl compounds
Catalyst system: Pd(II)- and Cu(I)-salts, oxygen

The Ciba-Geigy Metolachlor Process
Enantioselective Hydrogenation of an imine
Catalyst system: Josiphos-Ir complexes

The DuPont Adiponitril Synthesis
Hydrocyanation of butadiene to hexanenitrile
Catalyst system: Ni(0)-complexes
The Cativa process: Synthesis of acetic acid

Interplay: homogeneous and heterogeneous catalysis

Traditional synthesis

2-Methylpropylbenzene

Homogeneous Catalysis

Heterogeneous Catalysis

Heterogeneous Catalysis

Homogeneous Catalysis

Biocatalysis
Final example: Artificial metalloenzymes

Merging the advantages of different types of catalysis – here: enzymatic and transition metal catalysis

Synthesis of dihydroisoquinolones from benzamides and olefins:

\[
\text{Benzamide} + \text{Olefins} \rightarrow \text{Dihydroisoquinolone}
\]

Ward, Rovis et al.: up to 95% yield, up to 91.9 e.r.

Metalloenzyme by Ward and Rovis et al.:

streptavidin (Sec mutant)

biotinylated Cp*Rh complex
incorporated as co-factor

Chiral environment
by streptavidin

Highlight: M. Hapke, C. C. Tzschucke, Angew. Chem. 2013, 52, 3317
Manuskript der Vorlesung unter:

http://www.catalysis.de/Cycloadditionen.42.0.html