Gerhard Ertl received the 2007 Chemistry Nobel Prize for converting catalysis from art to science.
Progress of a chemical reaction

Haber-Bosch Ammonia Synthesis

\[ \text{N}_2 + 3 \text{H}_2 \rightleftharpoons 3 \text{NH}_3 \]

A significant fraction of our energy consumption goes into producing ammonia for fertilizers. Plants need nitrogen in a form that can be biologically converted into proteins or DNA (see the N in the peptide bond, Lect. 15, Slides 15,19 and N in the base pairs of DNA, Slide 20). Only a few plants can fix \( \text{N}_2 \) from air with the help of symbiotic bacteria, all others need fertilizers where the strong triple bond in \( \text{N}_2 \) is already broken up (ammonia \( \rightarrow \) nitrites \( \rightarrow \) nitrates).

The Haber-Bosch synthesis uses iron oxide as catalyst, together with high temperature (400\(^0\)C) and high pressure (200 atmospheres) to drive the reaction to the right side.

Bacteria in the roots of certain plants can achieve the same result at room temperature and atmospheric pressure with a bio-catalyst (=enzyme) called nitrogenase.
\[ \text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3 \]
World population and ammonia production

- **Population**
  - 1920: 1.0 \times 10^9
  - 2000: 7.0 \times 10^9

- **Production**
  - 1920: 0 \times 10^6 t/aN
  - 2000: 140 \times 10^6 t/aN
(Haber-Bosch process)

Technical conditions: $T \approx 400^\circ C$, $p \approx 300$ bar
promoted iron catalyst

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>K</th>
<th>Al</th>
<th>Ca</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BASF S6-10 catalyst (at. %)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Bulk composition</strong></td>
<td>40.5</td>
<td>0.35</td>
<td>2.0</td>
<td>1.7</td>
<td>53.2</td>
</tr>
<tr>
<td><strong>Surface –</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>unreduced</td>
<td>8.6</td>
<td>36.2</td>
<td>10.7</td>
<td>4.7</td>
<td>40.0</td>
</tr>
<tr>
<td>reduced</td>
<td>11.0</td>
<td>27.0</td>
<td>17.0</td>
<td>4.0</td>
<td>41.0</td>
</tr>
<tr>
<td>cat. active spot</td>
<td>30.1</td>
<td>29.0</td>
<td>6.7</td>
<td>1.0</td>
<td>33.2</td>
</tr>
</tbody>
</table>
Surface Geometry is Crucial

Dissociative nitrogen adsorption on Fe single crystal surfaces

\[
\begin{align*}
\text{Fe (111)} & \quad \text{Fe (100), } T = 693\text{K} \\
\text{Fe (110)}
\end{align*}
\]

\[y = \frac{1}{x} \times 10^7 \text{[L]} \]

\[N_2 \text{ exposure} \]

An energy diagram showing the progression of the reaction from the reactants $\text{N}_2$ and $\text{H}_2$ to the product $\text{NH}_3$. Energies are given in units of kJ/mol. (Adapted from Ertl 1983)
Catalytic Converters

Car exhaust emission (USA)

- CO
- NO\(_x\)
- HC

mg/mile


year
Catalytic oxidation of CO

(Pt at low coverages)
Small Au particles on Oxides as Catalysts
Size is Critical

Catalytic activity for the \( CO \rightarrow CO_2 \) reaction versus particle size:
(a) Au on TiO\(_2\)(110)
(b) Au on Mo(112)-TiO\(_x\)


This looks like the medieval alchemist’s dream, turning one element into another. Gold particles behave like platinum if their size is right. The explanation is still debated. It could be that the oxygen removes an electron from gold and thereby changes the number of electrons to that of platinum (which is to the left of gold in the Periodic Table).
Enzymes: Biological Catalysts

Substrate entering active site of enzyme

Enzyme/substrate complex

Enzyme/products complex

Products leaving active site of enzyme
Nitrogenase, Nature’s Efficient Way of Converting $\text{N}_2$ to $\text{NH}_3$

Only the catalytically active part of this enzyme (=biocatalyst) is shown. It contains the $\text{Fe}_6\text{Mo}$ metal complex surrounded by $\text{S}$ atoms.

Figure 1. (a) Nitrogenase FeMo cofactor from the crystal structure 1M\text{I}N.\textsuperscript{7} (b) Calculated model system. The color scheme is dark blue (molybdenum), orange (iron), yellow (sulfur), red (oxygen), light blue (nitrogen), gray (carbon), and black (hydrogen).
Calculated Reaction Pathway for Ammonia Synthesis via Nitrogenase

$$\text{N}_2 + 6\ H \leftrightarrow 2\ \text{NH}_3$$
Getting Rid of Sulfur in Oil Refineries

Sulfur in gasoline creates acid rain containing sulfuric acid.

\( \text{MoS}_2 \) catalysts are used to hydrogenate the sulfur and produce volatile \( \text{H}_2\text{S} \). Companies, such as Haldor Topsoe in Denmark systematically optimize them.

Control of the cluster size helps optimizing a catalyst. 

Catalysis Today 130, 86 (2008)
MoS$_2$ itself is an inert layered compound similar to graphite. STM experiments show that the edges and corners of MoS$_2$ nanocrystals are in fact reactive. Placing 3d transition metal atoms (Co, Ni) at the edges enhances the catalytic activity.
Inexpensive Catalysts for \( \text{H}_2 \) Fuel Cells

Go from rare 4d, 5d transition metals to common 3d metals, as nature does.

Figure 1. Active site of an iron-based catalyst might look like this. Within a carbon particle are gaps between small graphitic crystallites. Nitrogen can bond to newly formed extensions (blue) at the edge of the crystallites. An iron cation (red) is held by the surrounding N atoms. (Figure courtesy of Jean-Pol Dodelet, Institut National de la Recherche Scientifique.)

Figure 2. Performance of catalysts in hydrogen fuel cells. The curves plot the cell voltage, corrected for the Ohmic drop in the cell, against the density of the current on the electrode surfaces, at 80 °C and 1.5 bar. The black curve is a ready-to-use Pt-based cathode with a Pt loading of 400 \( \mu \)g/cm\(^2\). The red and blue curves are Fe-based catalysts having total Fe loadings of 90 and 17 \( \mu \)g/cm\(^2\), respectively. (Adapted from ref. 2.)
Computer Design of an Optimized Catalyst for Producing $H_2$ in an Electrolytic Cell

(This could be for production of $H_2$ for fuel cells, possibly with solar electricity.)

Trade-off for a catalyst: If the reactant (here $H$) binds too weakly to the surface, it does not stick long enough to react (forming $H_2$), but if it binds too strongly, it will occupy all available surface sites and poison the reaction. The optimum for this reaction is a binding energy $\Delta G_H \approx 0$ (yellow dots).

**Figure 3** Computational high-throughput screening for $|\Delta G_H|$ on 256 pure metals and surface alloys. The rows indicate the identity of the pure metal substrates, and the columns indicate the identity of the solute embedded in the surface layer of the substrate. Thus, a point at the intersection of the ‘Rh’ row with the ‘Pd’ column, for example, would correspond to a surface alloy with Pd embedded in the (111) surface layer of a pure Rh host. The solute coverage is 1/3 ML in all cases, and the adsorbed hydrogen coverage is also 1/3 ML. The diagonal of the plot corresponds to the hydrogen-adsorption free-energy on the pure metals.

A Second Criterion: Chemical Stability

(Here the most pessimistic of a variety of unwanted reactions is chosen, such as corrosion, oxidation, surface segregation. Pure Pt is very stable, but does not have optimum catalytic activity. A BiPt surface alloy combines maximum activity with sufficient stability.)
Experimental Test of an Optimized BiPt Surface Alloy for Producing H$_2$ in an Electrolytic Cell

The *in silico* design of functional materials actually works!

*Figure 5* Hydrogen evolution after each stage of BiPt surface alloy synthesis on a fluorine-doped tin-oxide substrate. (1) Pt film after deposition and anneal (2) immediately after Bi UPD (3) after second anneal to form the BiPt surface alloy.