Reactions at solid surfaces: 
From atoms to complexity

Gerhard Ertl
Fritz Haber Institut der Max Planck-Gesellschaft
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Jöns Jakob Berzelius
1779 – 1848
Wilhelm Ostwald
1853 – 1932

Nobel Prize 1909
A + B → C

\[ r = -\frac{d[A]}{dt} = k[A][B] \]

\[ k = k_0 e^{-E^*/RT} \]
Progress of a chemical reaction

- without catalyst
- with catalyst

Energy

$E^*$

$\Delta E$
Heterogeneous catalysis

Steady-state reaction rate:

\[ \frac{dn_i}{dt} = \frac{dn_i'}{dt} + \frac{dn_j}{dt} \]

\[ r = f(p_i, p_j, T, \text{catalyst}) \]

i: reactants

j: products
Fritz Haber
1868 - 1934
Nobel Prize 1918
$\text{N}_2 + 3\ \text{H}_2 \rightarrow 2\ \text{NH}_3$

Haber & LeRossignol, 1909
Carl Bosch
1874 - 1940
Nobel Prize 1931
World population and ammonia production

P.H. Emmett (1974):

"The experimental work of the past 50 years leads to the conclusion that the rate-limiting step in ammonia synthesis over iron catalysts is the chemisorption of nitrogen. The question as to whether the nitrogen species involved is molecular or atomic is still not conclusively resolved, though, in my opinion, the direct participation of nitrogen in an atomic form seems more likely than in molecular form."

Catalytic synthesis of ammonia

(Haber-Bosch process)

Technical conditions: \( T \approx 400\,^{\circ}\text{C}, \, p \approx 300\,\text{bar} \)

promoted iron catalyst

BASF S6-10 catalyst (at. %)

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>K</th>
<th>Al</th>
<th>Ca</th>
<th>O</th>
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<tbody>
<tr>
<td>Bulk composition</td>
<td>40.5</td>
<td>0.35</td>
<td>2.0</td>
<td>1.7</td>
<td>53.2</td>
</tr>
<tr>
<td>Surface –</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>unreduced</td>
<td>8.6</td>
<td>36.2</td>
<td>10.7</td>
<td>4.7</td>
<td>40.0</td>
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<tr>
<td>reduced</td>
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<td>27.0</td>
<td>17.0</td>
<td>4.0</td>
<td>41.0</td>
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<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>

Irving Langmuir
1881 – 1957
Nobel Prize 1932
“Most finely divided catalysts must have structures of great complexity. In order to simplify our theoretical consideration of reactions at surfaces, let us confine our attention to reactions on plane surfaces. If the principles in this case are well understood, it should then be possible to extend the theory to the case of porous bodies. In general, we should look upon the surface as consisting of a checkerboard ...”

Al (111)

1.3 nm × 0.9 nm

4.6 nm × 7.1 nm
O/Pt(111)

Oxygen atoms adsorbed on Pt (111) after exposure to 2 L O₂ at 165 K

5.3 nm × 5.5 nm

O/Ru (0001) $T = 300 \text{ K}$

QuickTime™ and a decompressor are needed to see this picture.

J. Winterlin & R. Schuster
Dissociative nitrogen adsorption on Fe single crystal surfaces

Mechanism of catalytic ammonia synthesis

\[ \text{N}_2 \leftrightarrow \text{N}_2^{ad} \leftrightarrow 2\text{N}^{ad} \]

\[ \text{H}_2 \leftrightarrow 2\text{H}^{ad} \]

\[ \text{N}^{ad} + \text{H}^{ad} \leftrightarrow \text{NH}^{ad} \]

\[ \text{NH}^{ad} + \text{H}^{ad} \leftrightarrow \text{NH}_2^{ad} \]

\[ \text{NH}_2^{ad} + \text{H}^{ad} \leftrightarrow \text{NH}_3^{ad} \leftrightarrow \text{NH}_3 \]

Delta H = 46 kJ/mol

1129 kJ/mol 1400 ~960

\[ \text{N}^{ad} + 3\text{H} \]

\[ \text{NH} + 2\text{H} \]

\[ \text{NH}^2 + \text{H} \]

\[ \Delta H = 46 \text{ kJ/mol} \]

Catalytic synthesis of ammonia: Microkinetics

\[ \text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 \]

promoted iron catalyst

P. Stoltze and J.K. Nørskov,


*J. Catal.* **110** (1988), 1
Car exhaust emission (USA)

CO

NO\textsubscript{x}

HC

mg/mile


year
Rh(111)-(√3×√3)R30°-CO

Rh(111)-(2×2)-O

Rh(111)-(2×2)-(O+1 CO)

S. Schwegmann, H. Over, V. De Renzi, G. Ertl, Surf Sci. 375 (1997), 91
Catalytic oxidation of CO

\[ 2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 \]

\[
\begin{align*}
\text{CO} + * & \rightleftharpoons \text{CO}_{\text{ad}} \\
\text{O}_2 + 2* & \rightleftharpoons \text{O}_{2,\text{ad}} \rightarrow 2\text{O}_{\text{ad}} \\
\text{O}_{\text{ad}} + \text{CO}_{\text{ad}} & \rightarrow \text{CO}_2 + 2* 
\end{align*}
\]

\(E_{\text{LH}} = 100\)  \(\Delta H = 283 \text{ kJ/mol}\)

(Pt at low coverages)
\[
\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 / \text{Pt}(110)
\]

\[T = 470 \text{K}; \quad p_{\text{CO}} = 3 \times 10^{-5} \text{mbar}; \quad p_{\text{O}_2} = 2.0 \rightarrow 2.7 \times 10^{-4} \text{mbar}\]

*M. Eiswirth and G. Ertl, Surface Sci. 177 (1986), 90*
Lotka-Volterra Model

\[ \frac{dx}{dt} = \alpha_1 x - \alpha_2 xy \]

\[ \frac{dy}{dt} = \beta_1 xy - \beta_2 y \]
$\theta_{\text{CO}} \leq 0.5 \text{ ML}$

0.2 ML $\leq \theta_{\text{CO}} \leq$ 0.5 ML

1×2 missing row

CO / Pt(110)
CO + $\frac{1}{2}$O$_2$ $\rightarrow$ CO$_2$ / Pt(110)


T = 540K; $p_{O_2} = 6.7 \times 10^{-5}$ mbar; $p_{CO} = 3 \times 10^{-5}$ mbar
Heartbeats of ultra thin catalyst

F. Cirak, J.E. Cisternas, A.M. Cuitino, G. Ertl, P.Holmes, I. Kevrekidis, M.Ortiz, H.H. Rotermund, M.Schunack, J. Wolff,
Science 300 (2003), 1932

Ultra thin (200 nm thick) Pt(110) catalyst during CO oxidation, 5 mm sample diameter, $T = 528$ K, $p_{O_2} = 1 \times 10^{-2}$ mbar, $p_{CO} = 1.85 \times 10^{-3}$ mbar
2 CO + O₂  ⇒  2 CO₂ / Pt(110)

Target patterns

\[ p_{O_2} = 3.2 \times 10^{-4} \text{ mbar} \]
\[ p_{CO} = 3 \times 10^{-5} \text{ mbar} \]
\[ T = 427 K \]

\[ \phi = 500 \mu m \]
Spiral waves during CO-oxidation on Pt(110)

PEEM images with 500 µm diameter,
steady-state conditions: $p_{O_2} = 4 \times 10^{-4}$ mbar, $p_{CO} = 4.3 \times 10^{-5}$ mbar, $T = 448$ K

Chemical turbulence

Photoemission electron microscope (PEEM) imaging. Dark regions are predominantly oxygen covered, bright regions are mainly CO covered.

Real time, image size 360 x 360 μm

Temperature T = 548 K, oxygen partial pressure \( p_{o2} = 4 \times 10^{-4} \) mbar, CO partial pressure \( p_{co} = 1.2 \times 10^{-4} \) mbar.
Global delayed feedback

M. Kim, M. Bertram, M. Pollmann, A. von Oertzen; A.S. Mikhailov, H.H. Rotermund, and G. Ertl,
*Science* **292** (2001), 1357
CO oxidation reaction on Pt(110)

- Suppression of spiral-wave turbulence and development of intermittent turbulence with cascades of reproducing bubbles
Retina