Reactions at solid surfaces: From atoms to complexity

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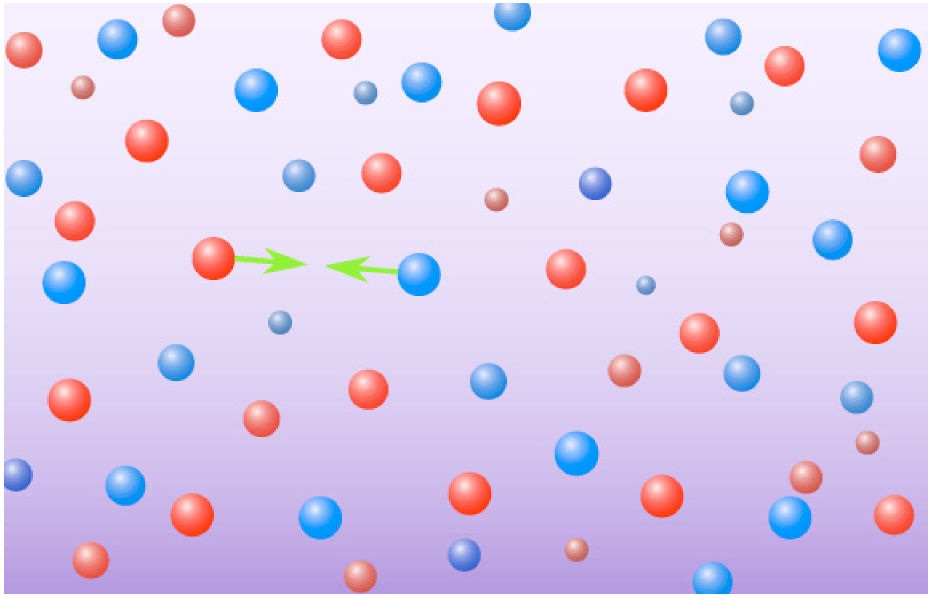
Fritz Haber Institut der Max Planck-Gesellschaft
Berlin, Germany

Jac. Berzelius.

Jöns Jakob Berzelius
1779 – 1848

Wilhelm Ostwald
1853 – 1932

Nobel Prize 1909

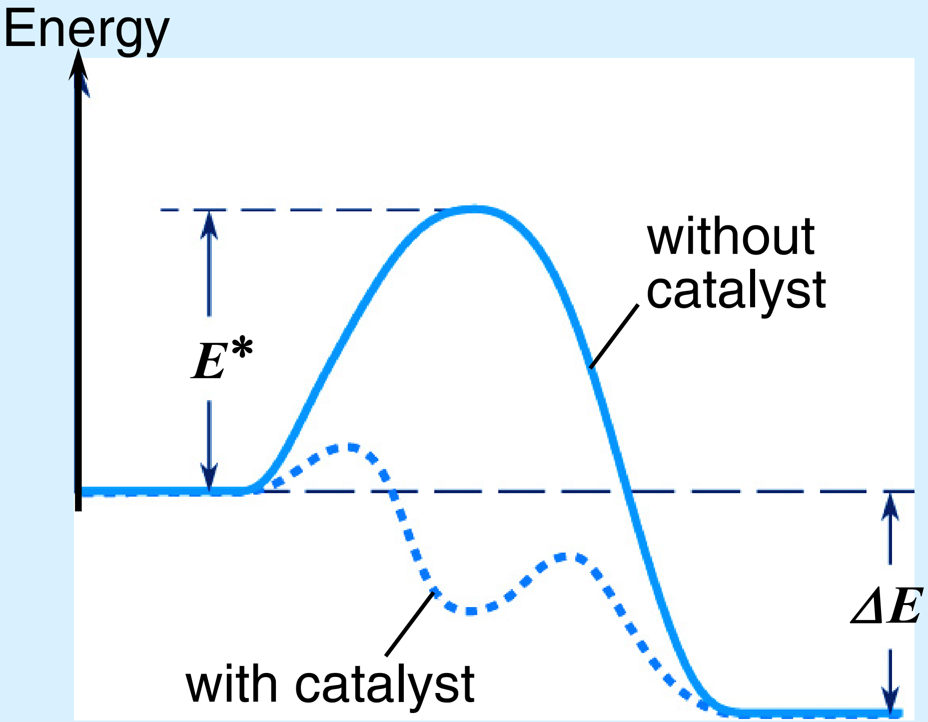


$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}$$

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

$$k = k_0 e^{-E^*/RT}$$

Progress of a chemical reaction



Heterogeneous catalysis

$$\frac{dn_i}{dt} \longrightarrow \boxed{} \longrightarrow \frac{dn_i'}{dt} \quad \frac{dn_j}{dt}$$

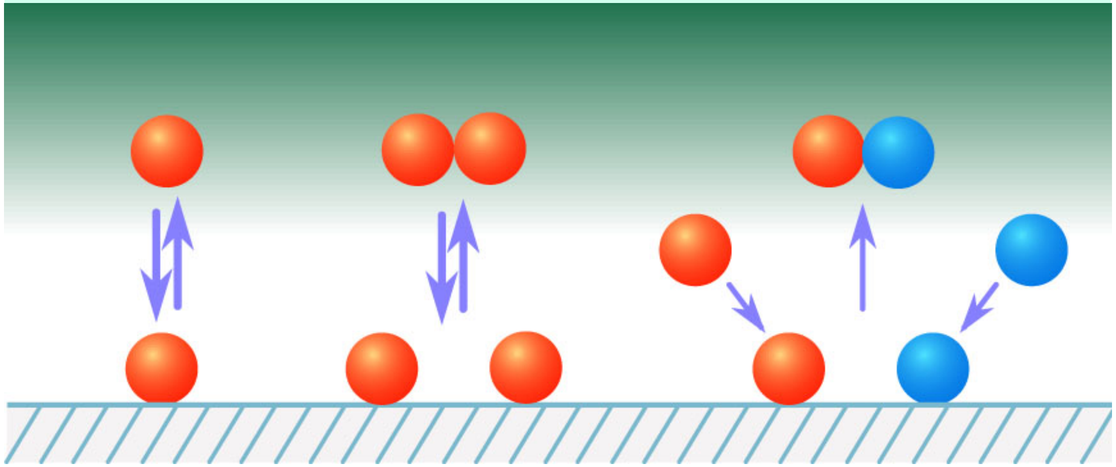
Reactor

i: reactants

j: products

Steady-state reaction rate:

$$\frac{dn_j}{dt} = r = f\,(p_i, p_j, T, \text{catalyst})$$

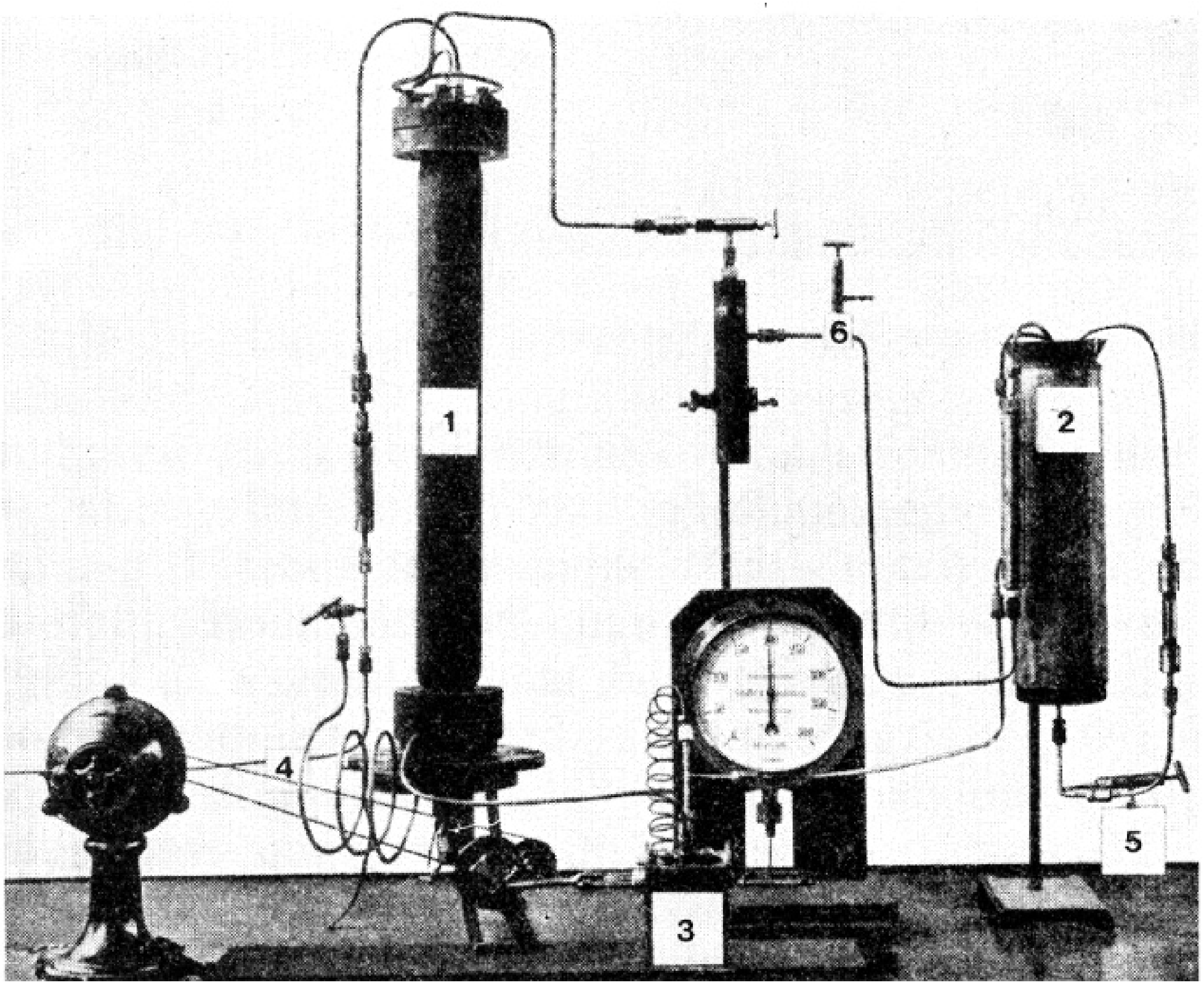


Fritz Haber

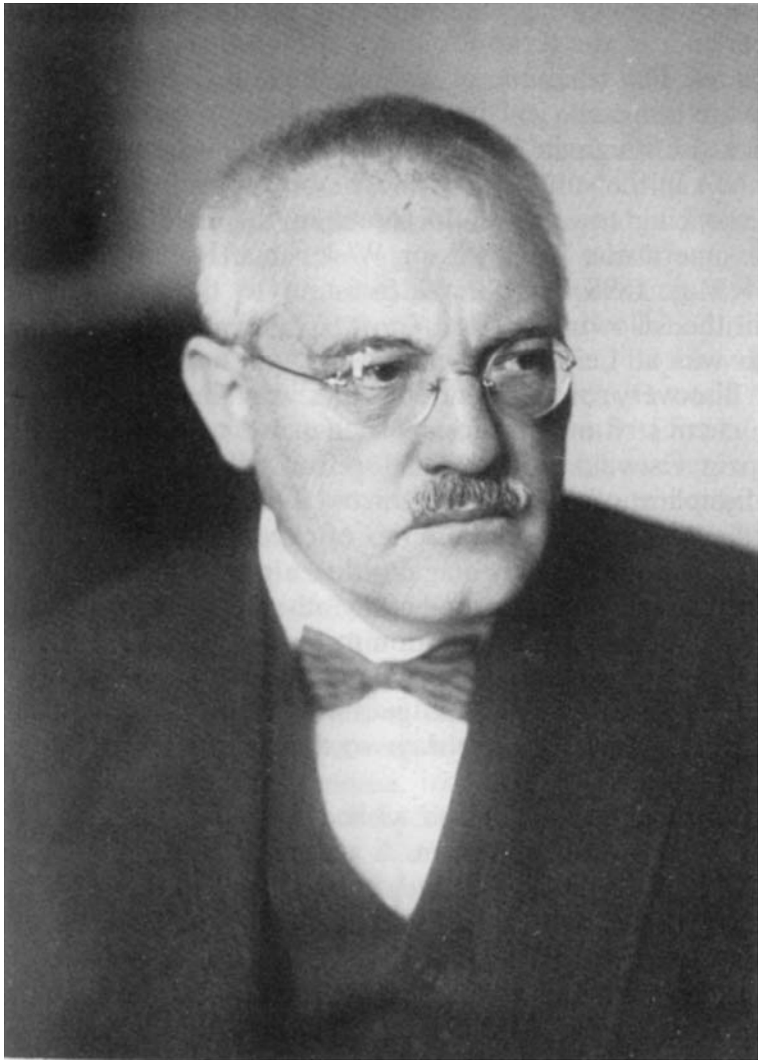
1868 - 1934

Nobel Prize 1918

$$N_2 + 3\,H_2 \rightarrow 2\ NH_3$$



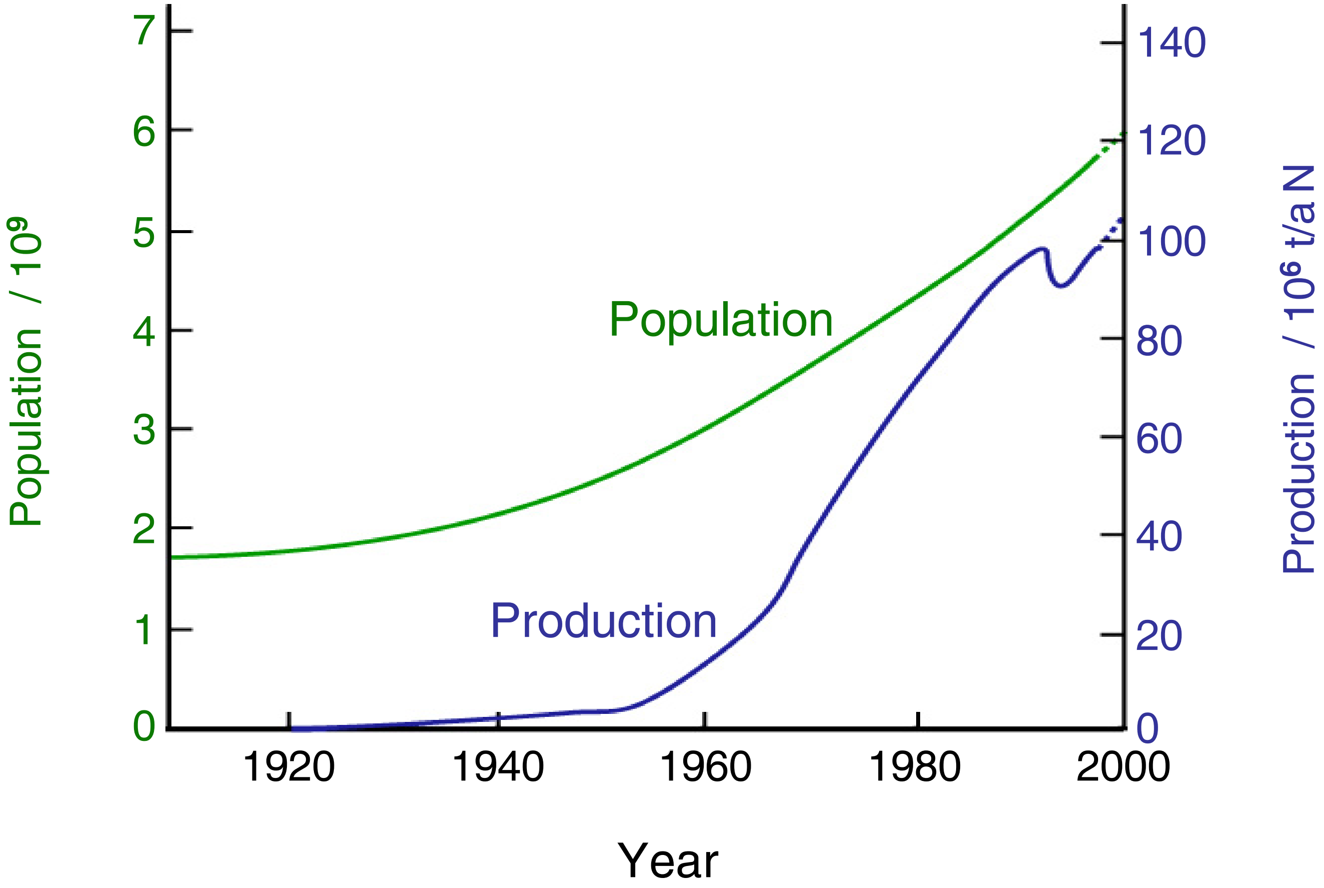
Haber & LeRossignol, 1909



Carl Bosch
1874 - 1940

Nobel Prize 1931

World population and ammonia production



M. Appl, "Ammonia", Wiley–VCH (1999)

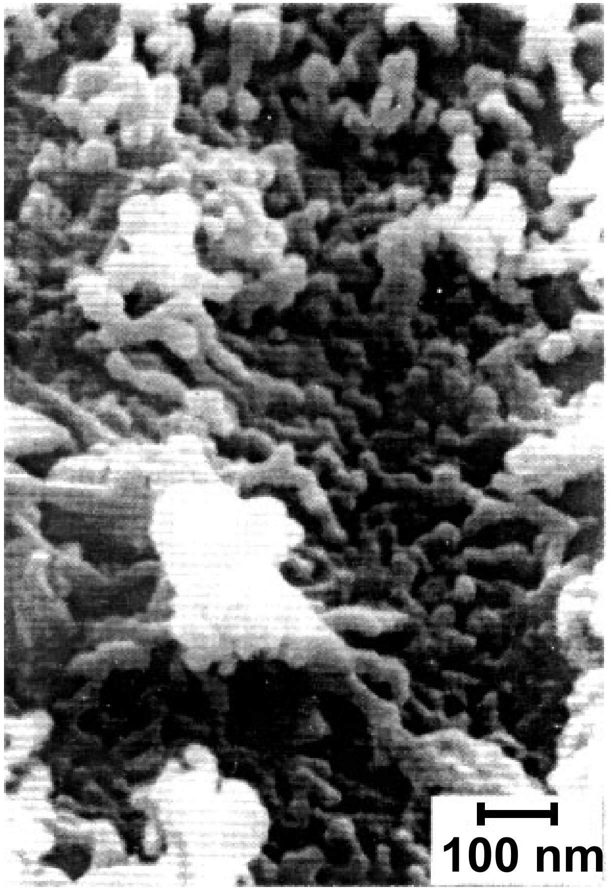
P.H. Emmett (1974):

„ *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.“*

The physical basis of heterogeneous catalysis (E. Drauglis & R.I. Jaffee, eds.),
Plenum Press, New York, 1975, p. 3

Catalytic synthesis of ammonia

(Haber- Bosch process)

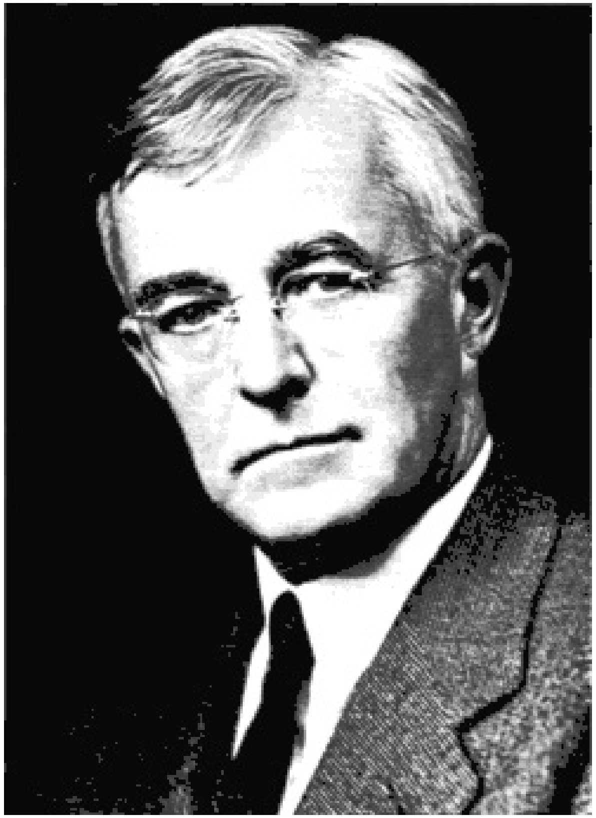


Technical conditions: **T ≈ 400°C, p ≈ 300 bar**
promoted iron catalyst

BASF S6-10 catalyst (at. %)

	Fe	**K**	**Al**	**Ca**	**O**
Bulk composition	40.5	0.35	2.0	1.7	53.2
Surface –					
unreduced	8.6	36.2	10.7	4.7	40.0
reduced	11.0	27.0	17.0	4.0	41.0
cat. active spot	30.1	29.0	6.7	1.0	33.2

G. Ertl, D. Prigge, R. Schlögl & D. Weiss, J.Catal. **79** *(1983), 359*



Irving Langmuir

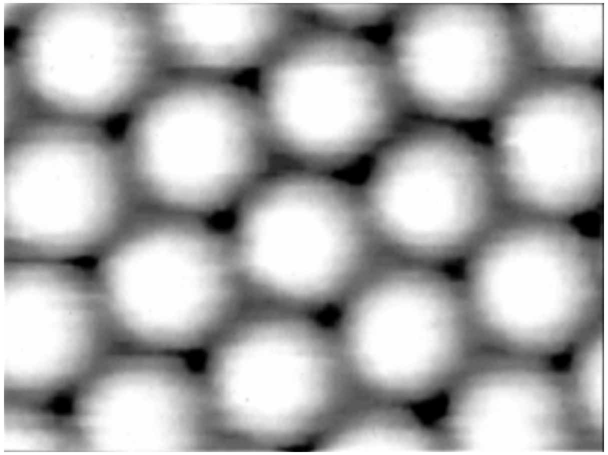
Irving Langmuir
1881 – 1957
Nobel Prize 1932

“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 ...”

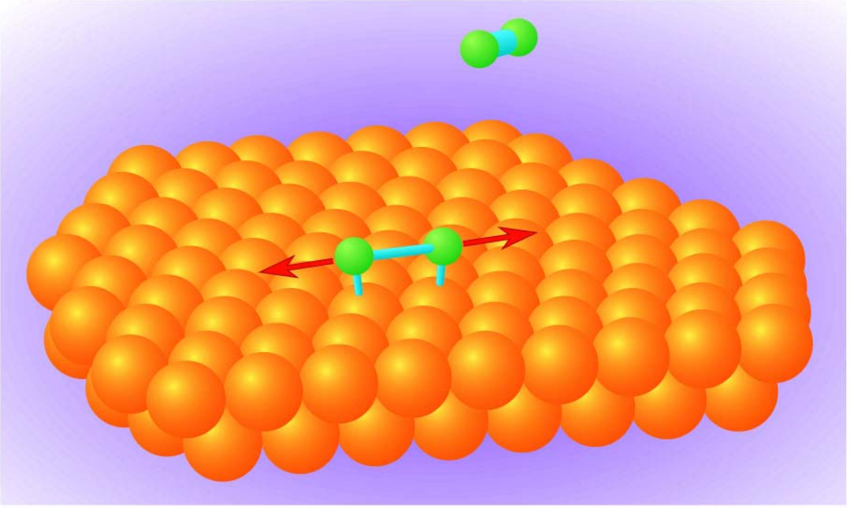
I. Langmuir, *Trans. Faraday Soc.* **17** (1922), 607

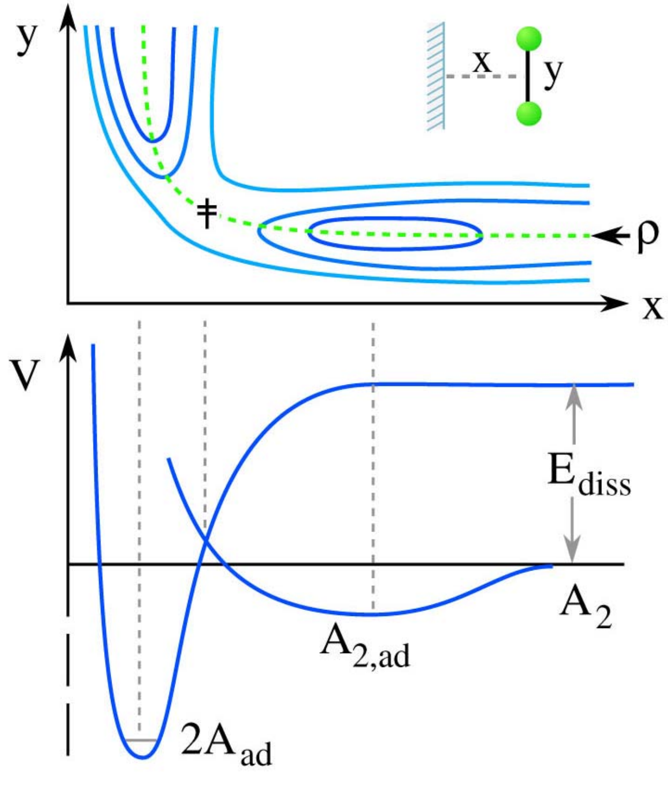
Al (111)

4.6 nm × 7.1 nm



1.3 nm × 0.9 nm




y
x
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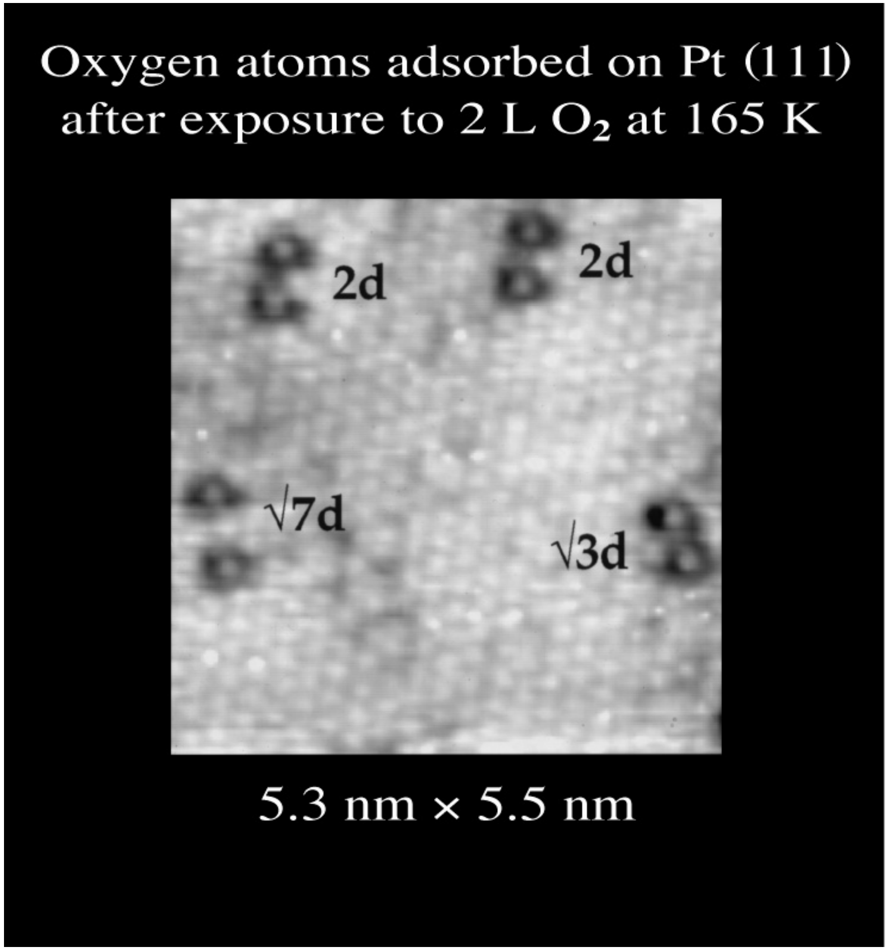
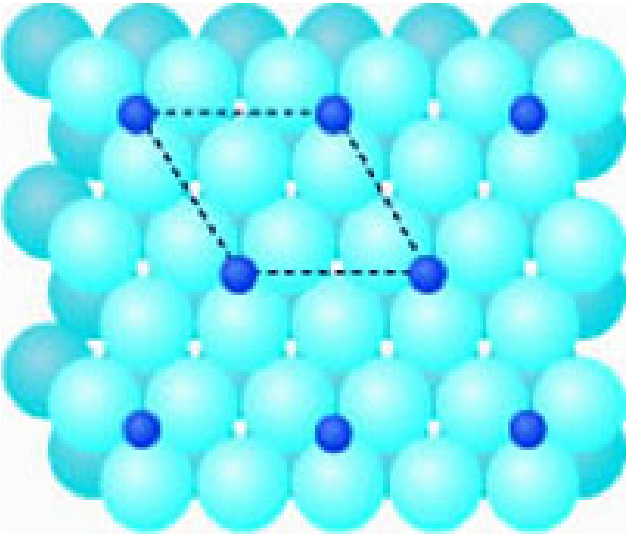
V
E_diss
A_2
A_2,ad
2A_ad

O / Pt (111)



Oxygen atoms adsorbed on Pt (111) after exposure to 2 L O_2 at 165 K

5.3 nm × 5.5 nm



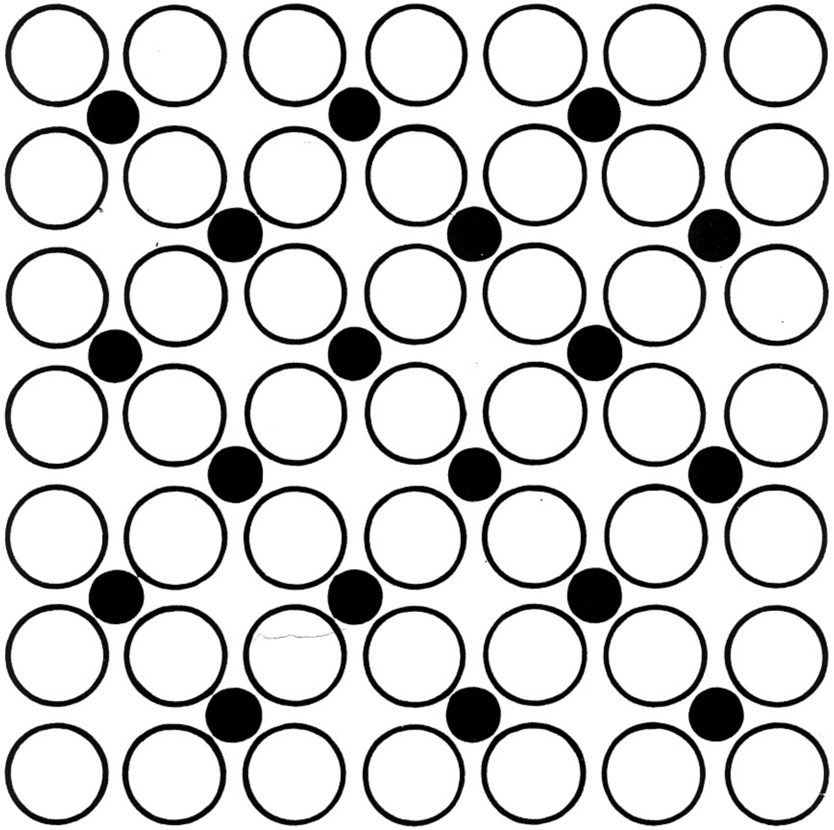
J. Wintterlin, R. Schuster, and G. Ertl, Phys.Rev.Lett. 77 (1996), 123.

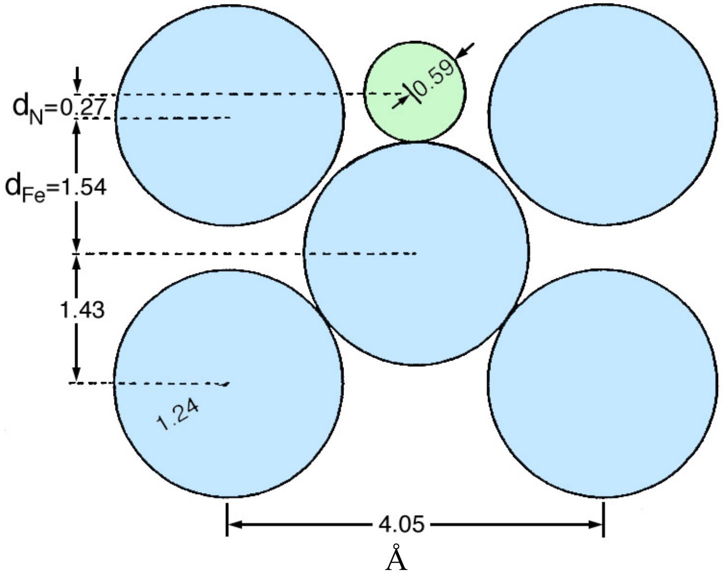
O/Ru (0001) T = 300 K

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

J. Wintterlin & R. Schuster

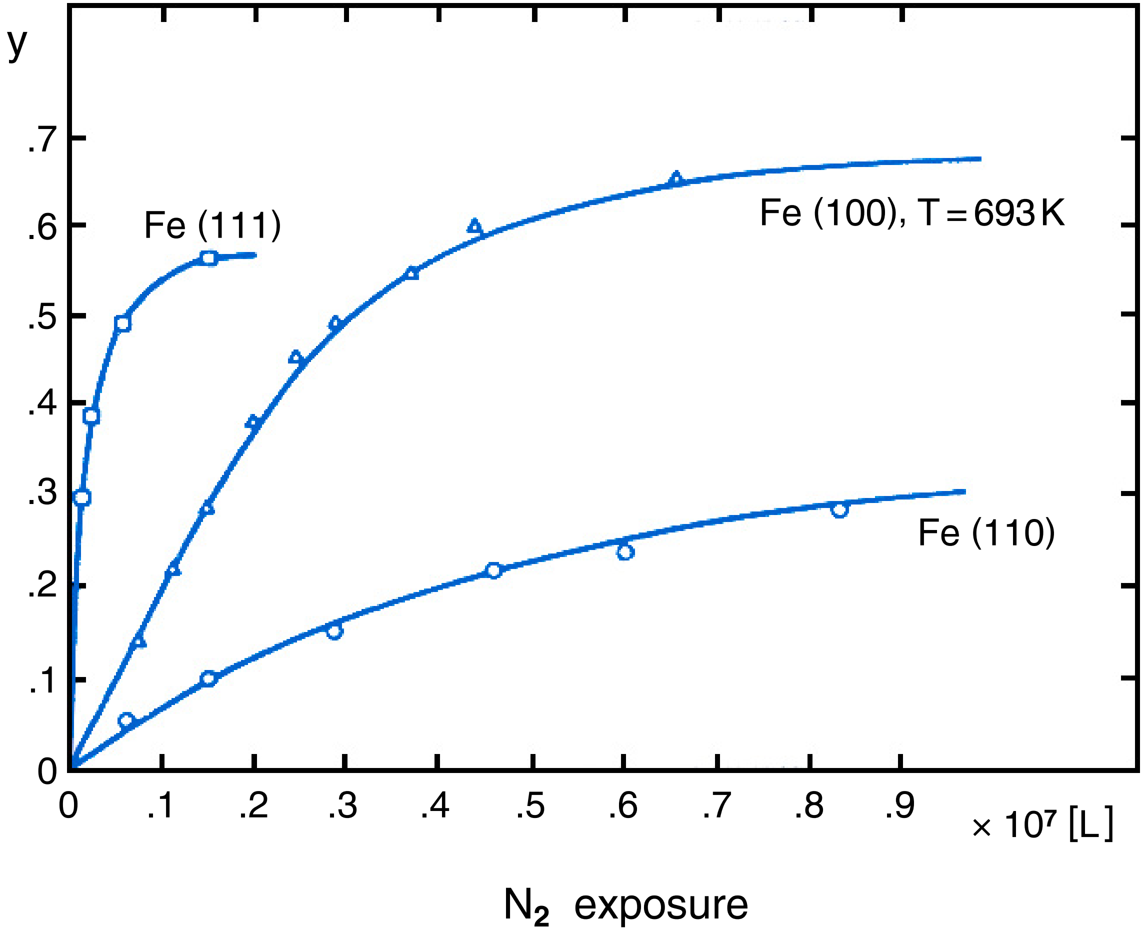
N / Fe (100)

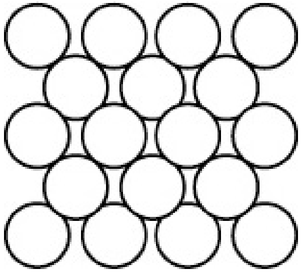




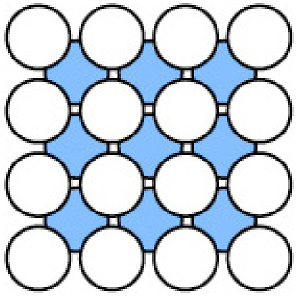
R. Imbihl, R.J. Behm, G. Ertl, W. Moritz, Surface Sci. **123** *(1982), 129.*

Dissociative nitrogen adsorption on Fe single crystal surfaces

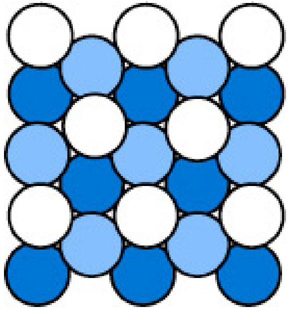




Fe (110)



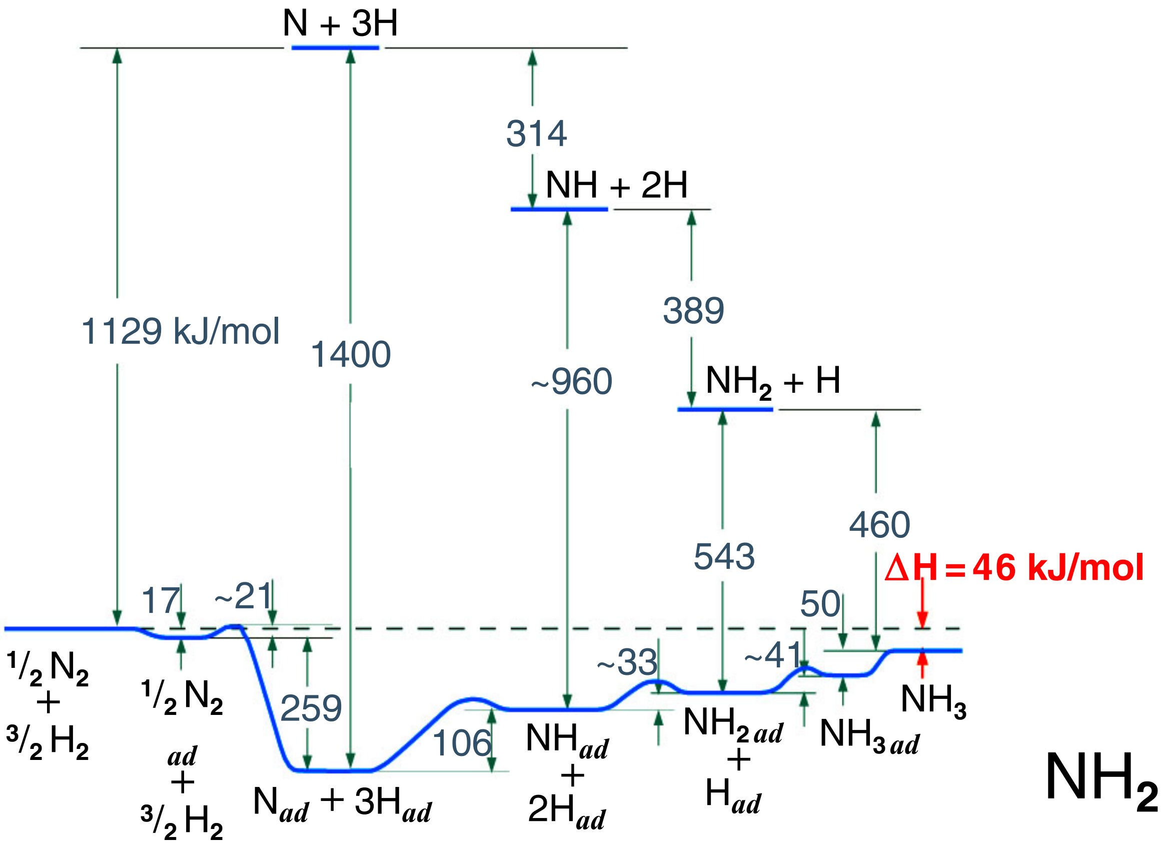
Fe (100)



Fe (111)

F. Bozso, G. Ertl, M. Grunze & M. Weiss, J. Catal. **49** *(1977), 18;* **50** *(1977), 519*

Mechanism of catalytic ammonia synthesis



$$N_2 \rightleftarrows N_{2\,ad} \rightleftarrows 2N_{ad}$$

$$H_2 \rightleftarrows 2H_{ad}$$

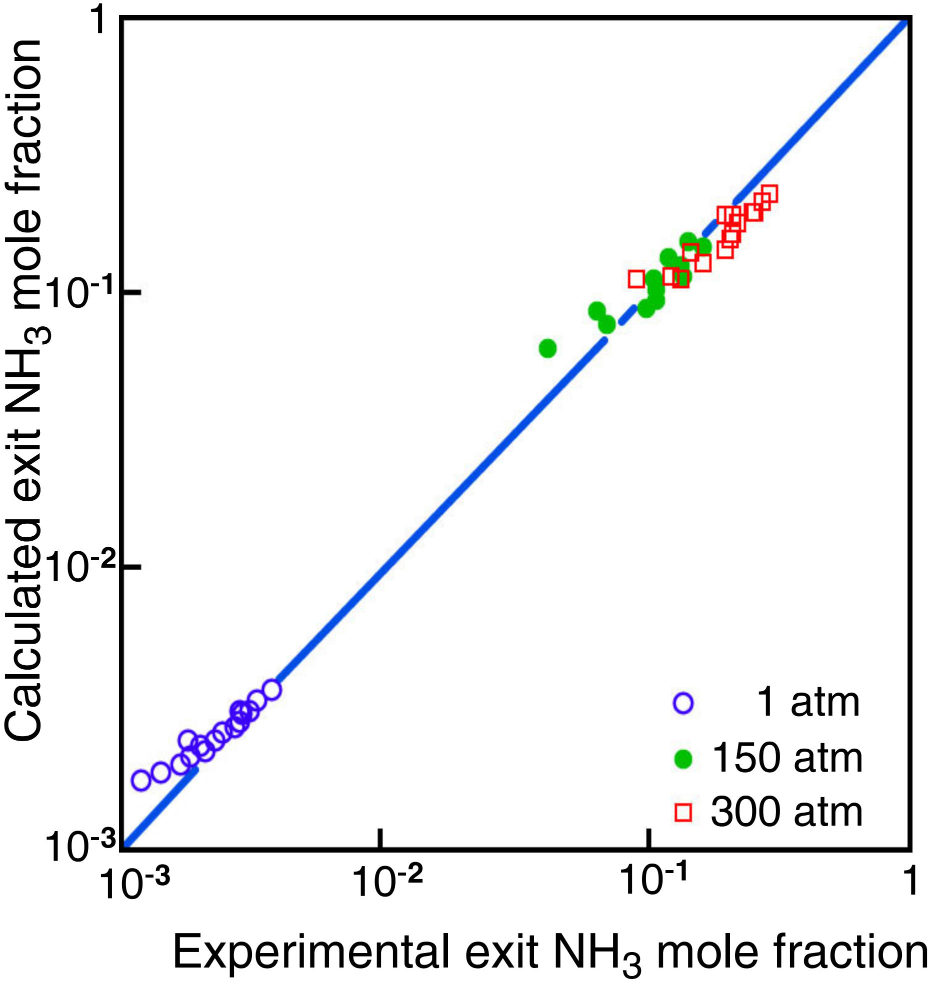
$$N_{ad} + H_{ad} \rightleftarrows NH_{ad}$$

$$NH_{ad} + H_{ad} \rightleftarrows NH_{2\,ad}$$

$$NH_{2\,ad} + H_{ad} \rightleftarrows NH_{3\,ad} \rightleftarrows NH_3$$

G. Ertl, Catal.Rev.Sci.Eng. **21** *(1980), 201*

Catalytic synthesis of ammonia: Microkinetics



$$N_2 + 3\,H_2 \rightleftarrows 2\,NH_3$$

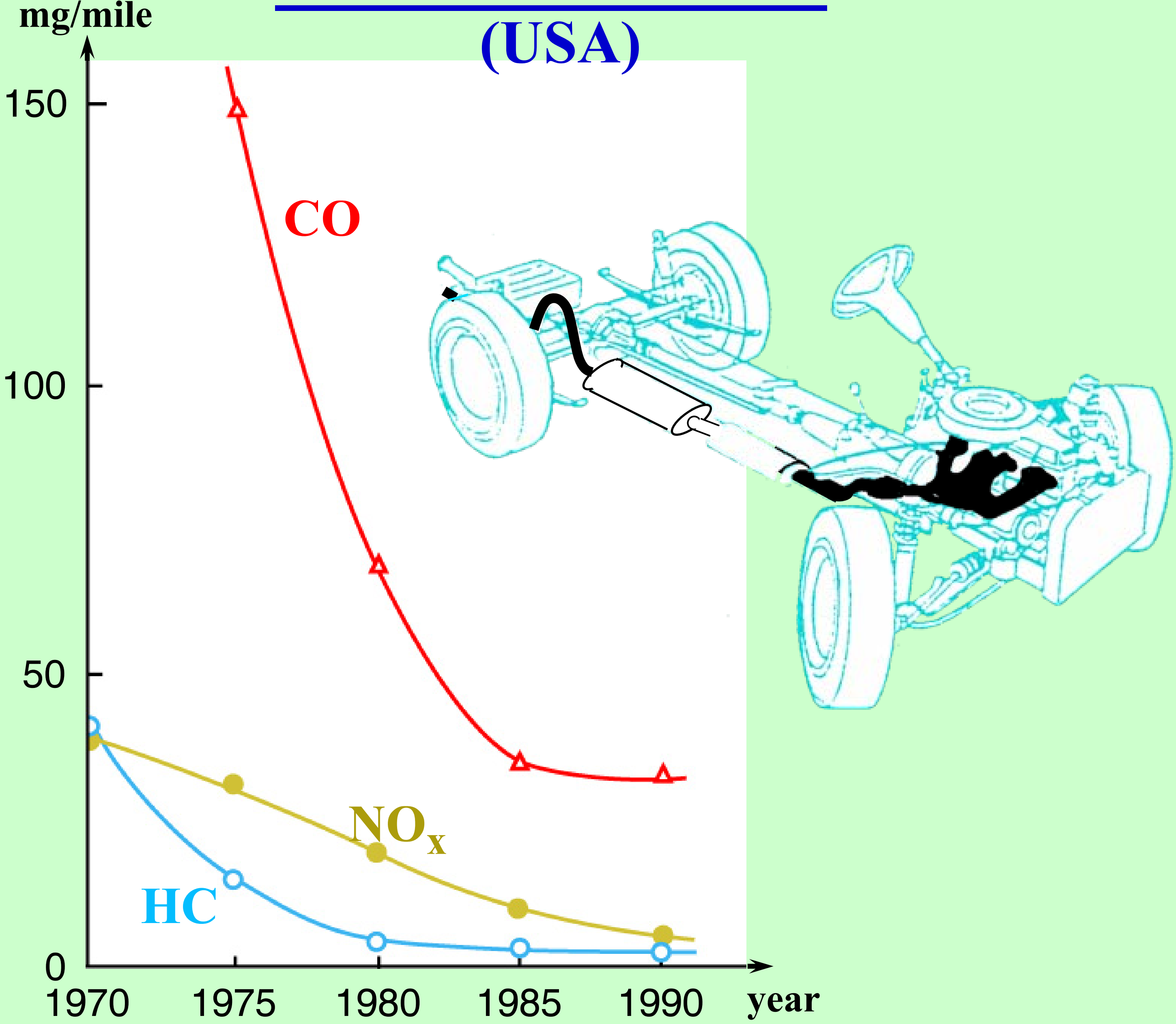
promoted iron catalyst

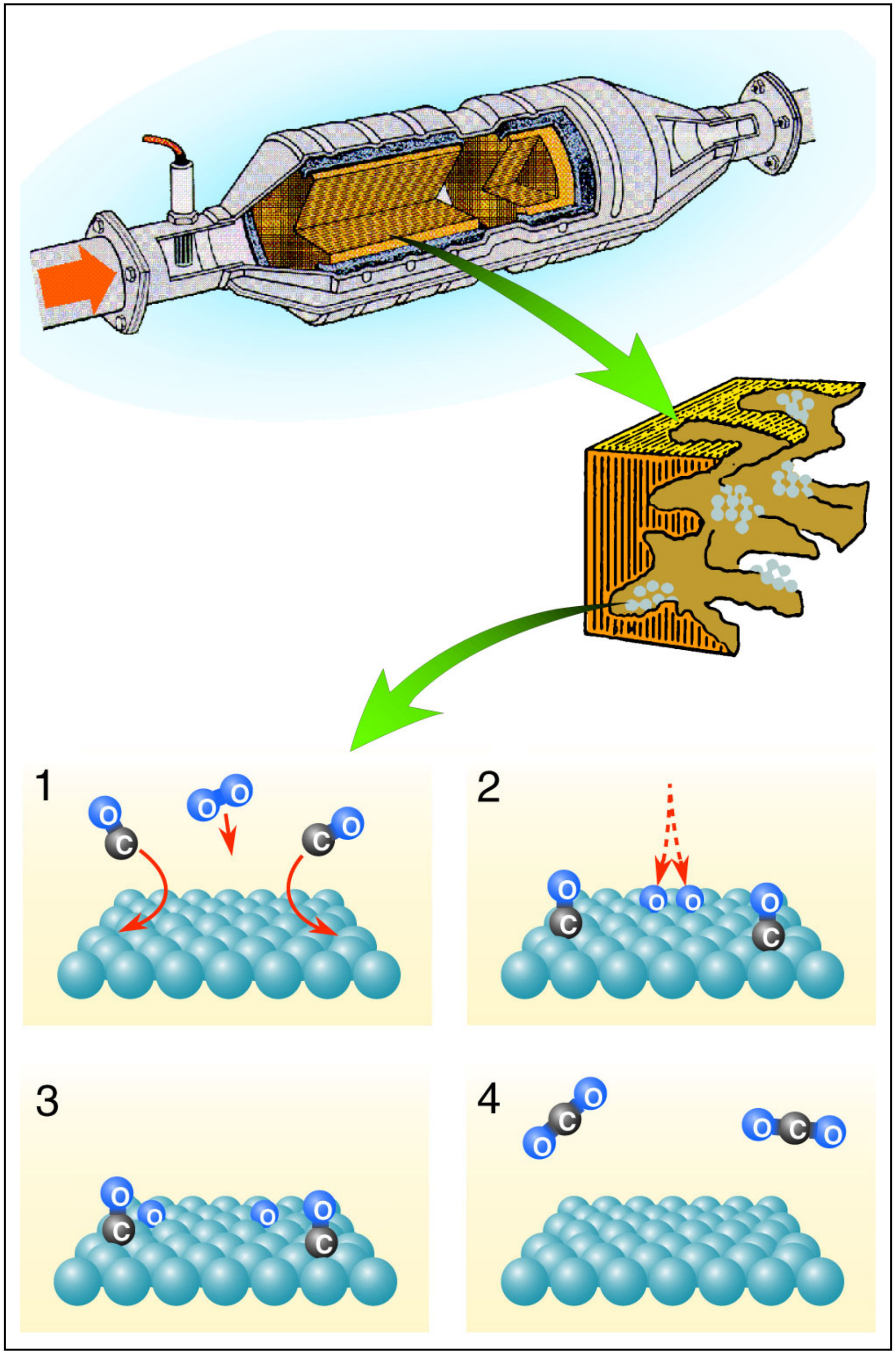
P. Stoltze and J.K. Nørskov,

Phys. Rev. Lett. ***55*** *(1985), 2502*

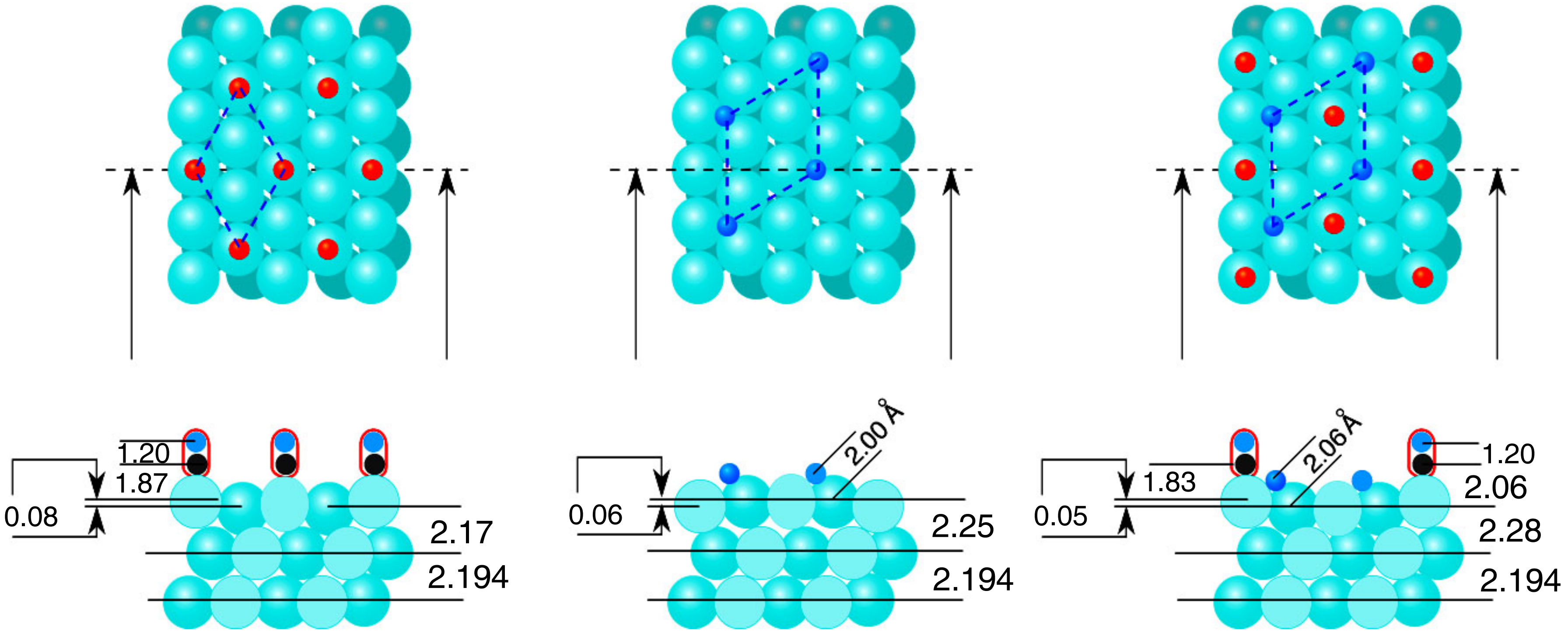
J. Catal. ***110*** *(1988), 1*

Car exhaust emission
(USA)



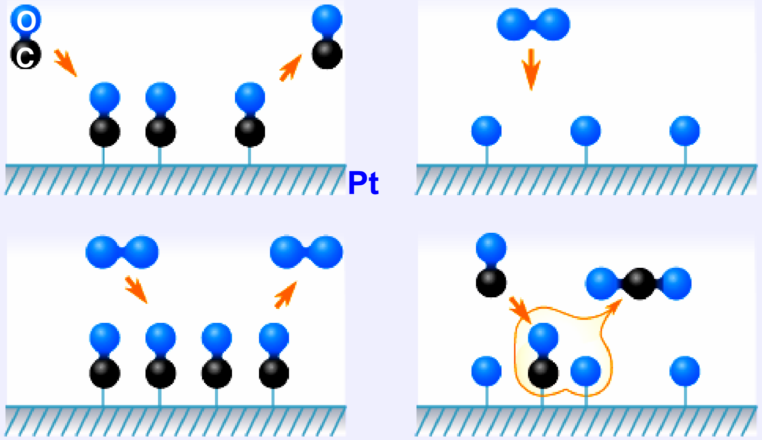

1
O
C
O O
C O
2
O
C
O O
O
C
3
O
C
O
O
O
C
4
O C O
O C O

Rh(111)-($\sqrt{3}\times\sqrt{3}$)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

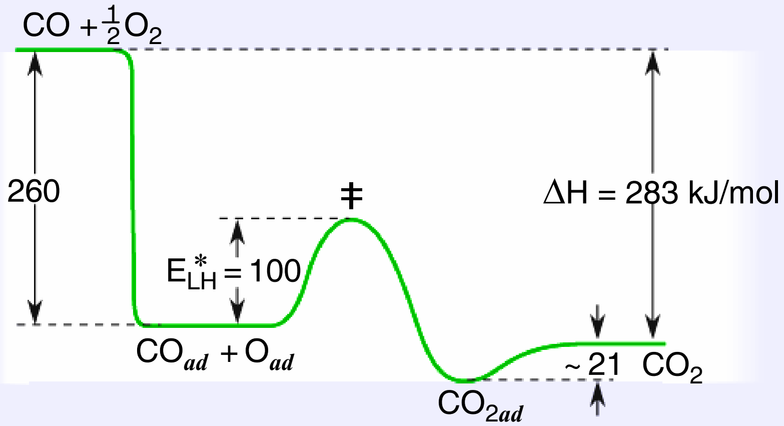


$$2CO + O_2 \longrightarrow 2CO_2$$

$$CO + * \rightleftharpoons CO_{ad}$$

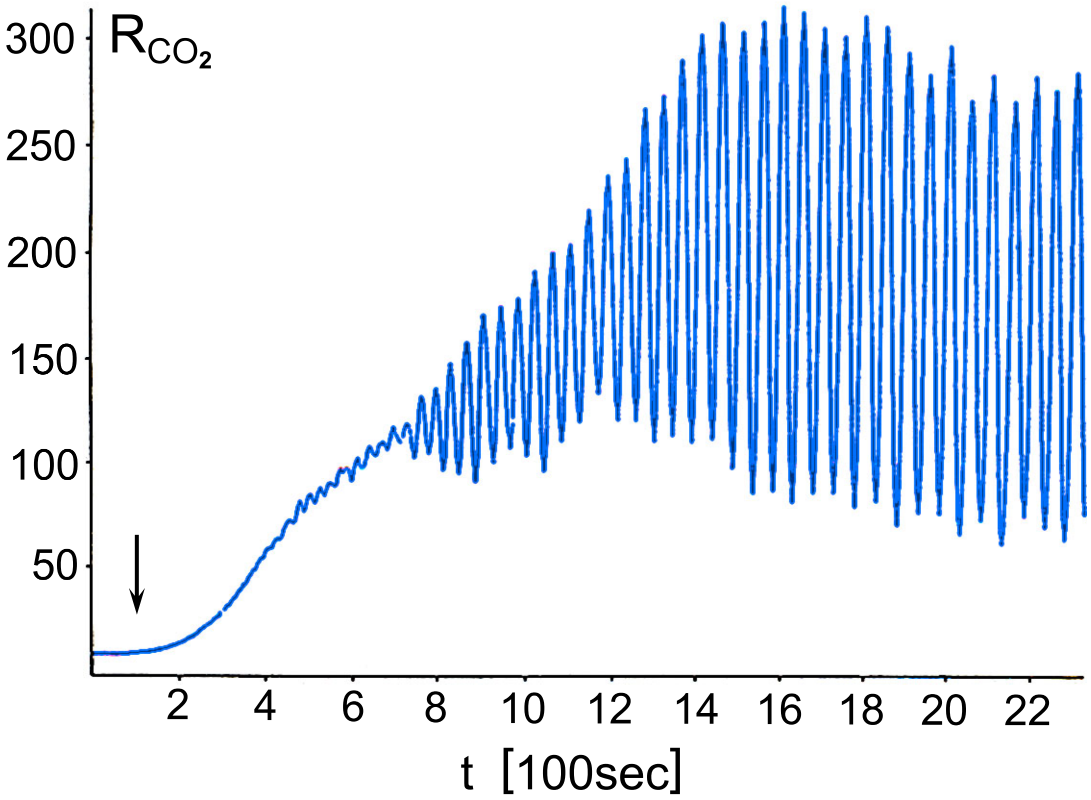
$$O_2 + 2* \rightleftharpoons O_{2,ad} \longrightarrow 2O_{ad}$$

$$O_{ad} + CO_{ad} \longrightarrow CO_2 + 2*$$



(Pt at low coverages)

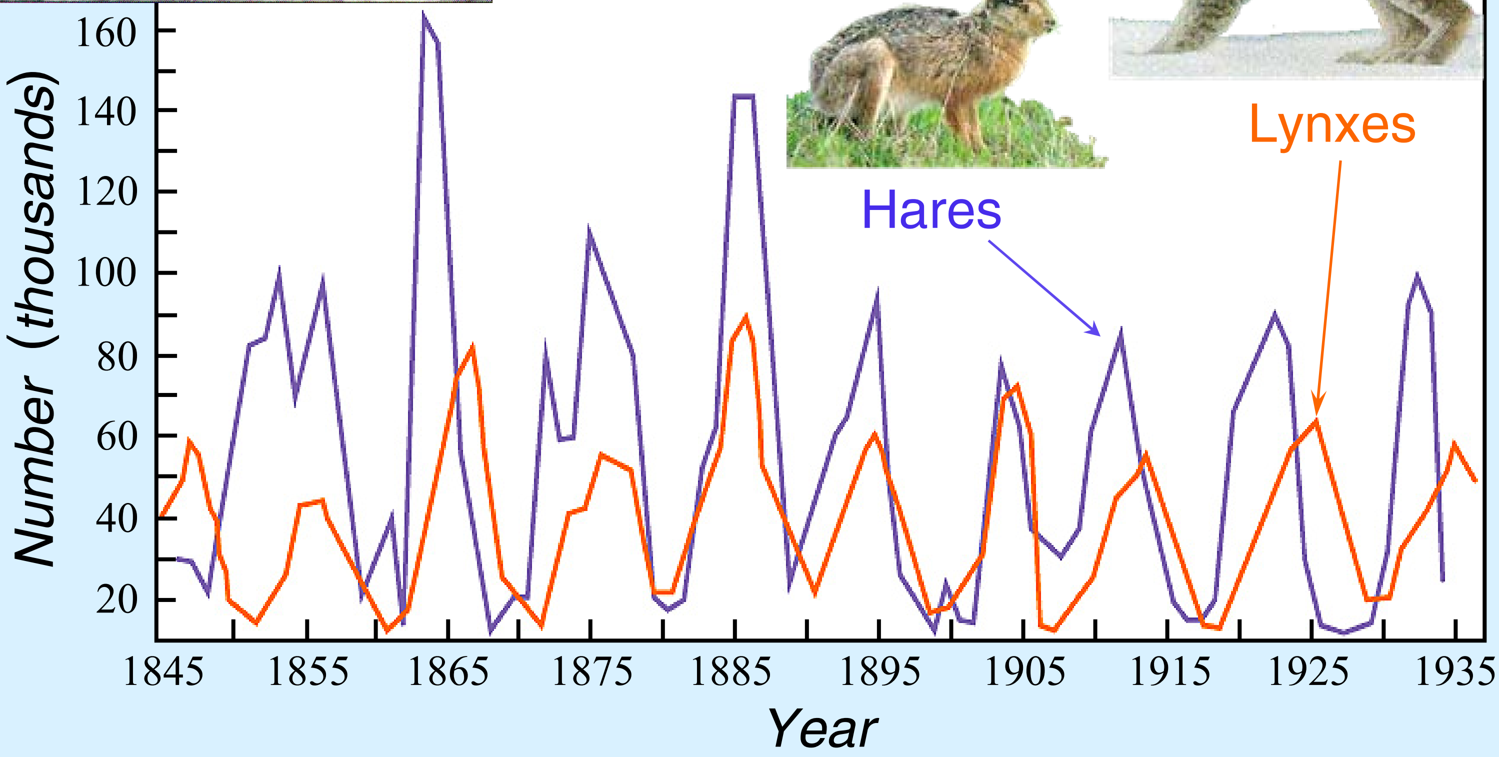
$CO + \frac{1}{2}O_2 \rightarrow CO_2$ / Pt(110)



T = 470 K; $p_{CO} = 3\times10^{-5}$ mbar; $p_{O_2} = 2.0 \rightarrow 2.7\times10^{-4}$ mbar

*M. Eiswirth and G. Ertl, Surface Sci. **177** (1986), 90*

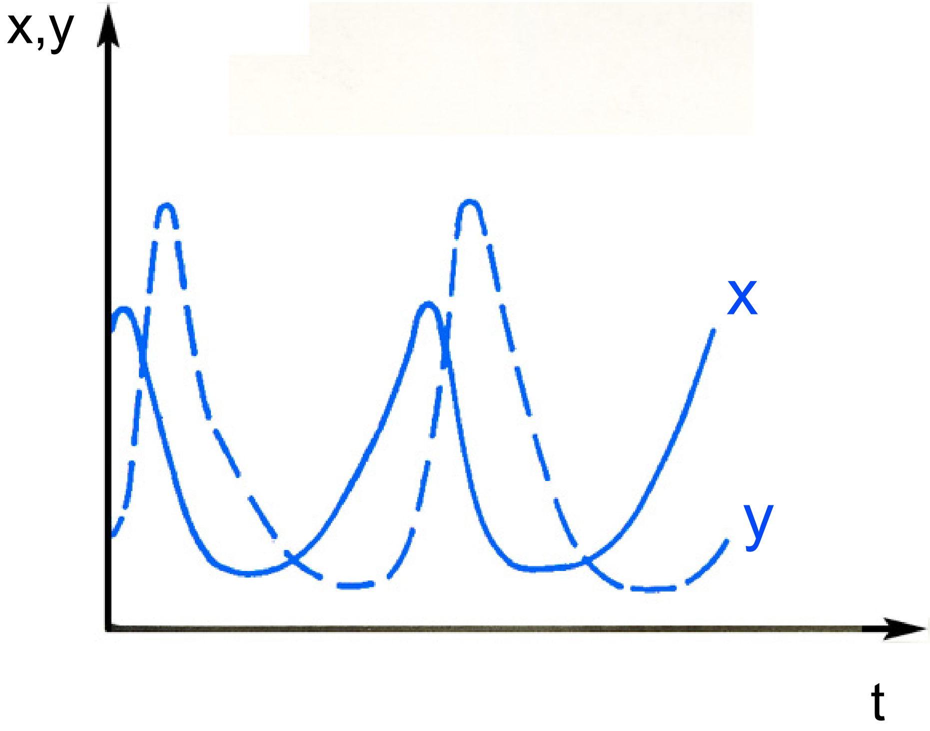

HUDSON'S BAY COMPANY


Hares
Lynxes
Number (thousands)
160
140
120
100
80
60
40
20
1845
1855
1865
1875
1885
1895
1905
1915
1925
1935
Year

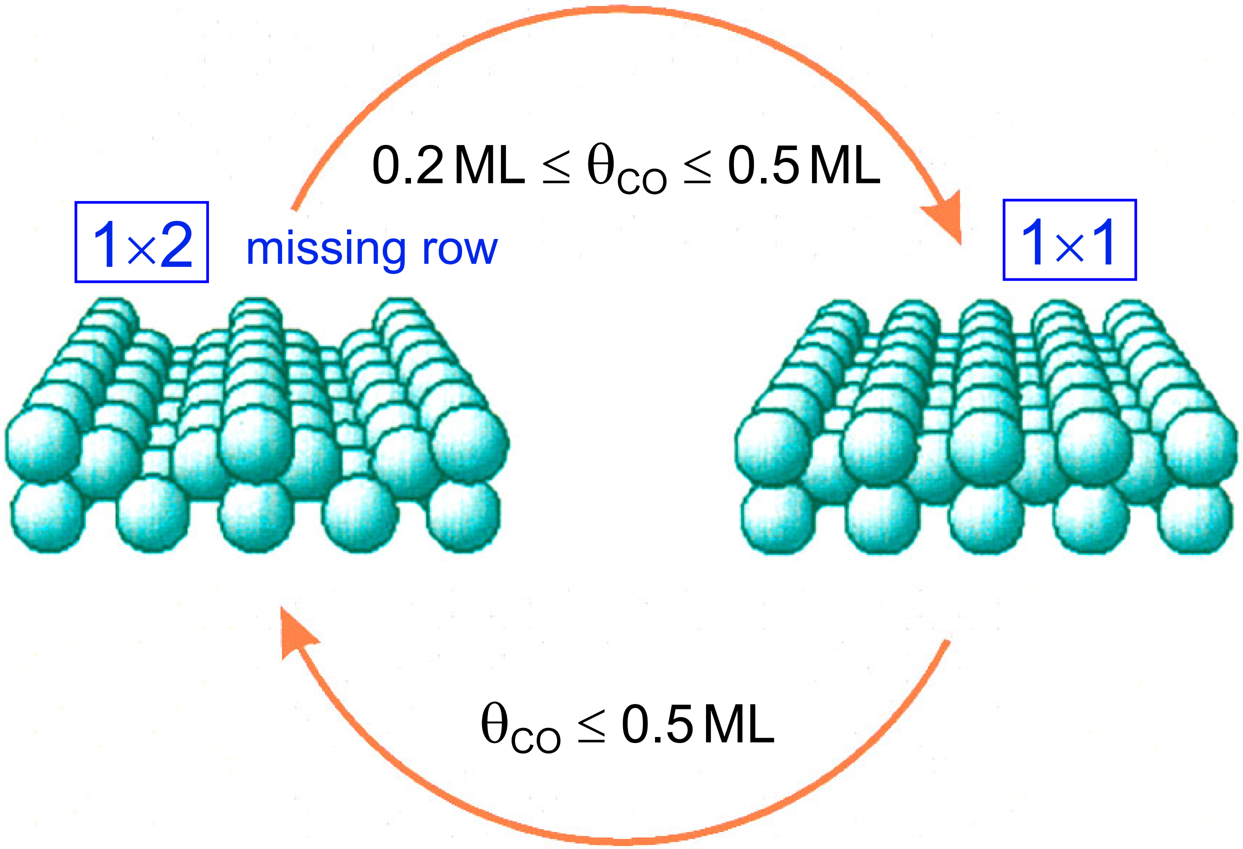
Lotka-Volterra Model

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

$$\frac{dy}{dt} = \beta_1 xy - \beta_2 y$$



CO / Pt(110)



$0.2\,\mathrm{ML} \leq \theta_{CO} \leq 0.5\,\mathrm{ML}$

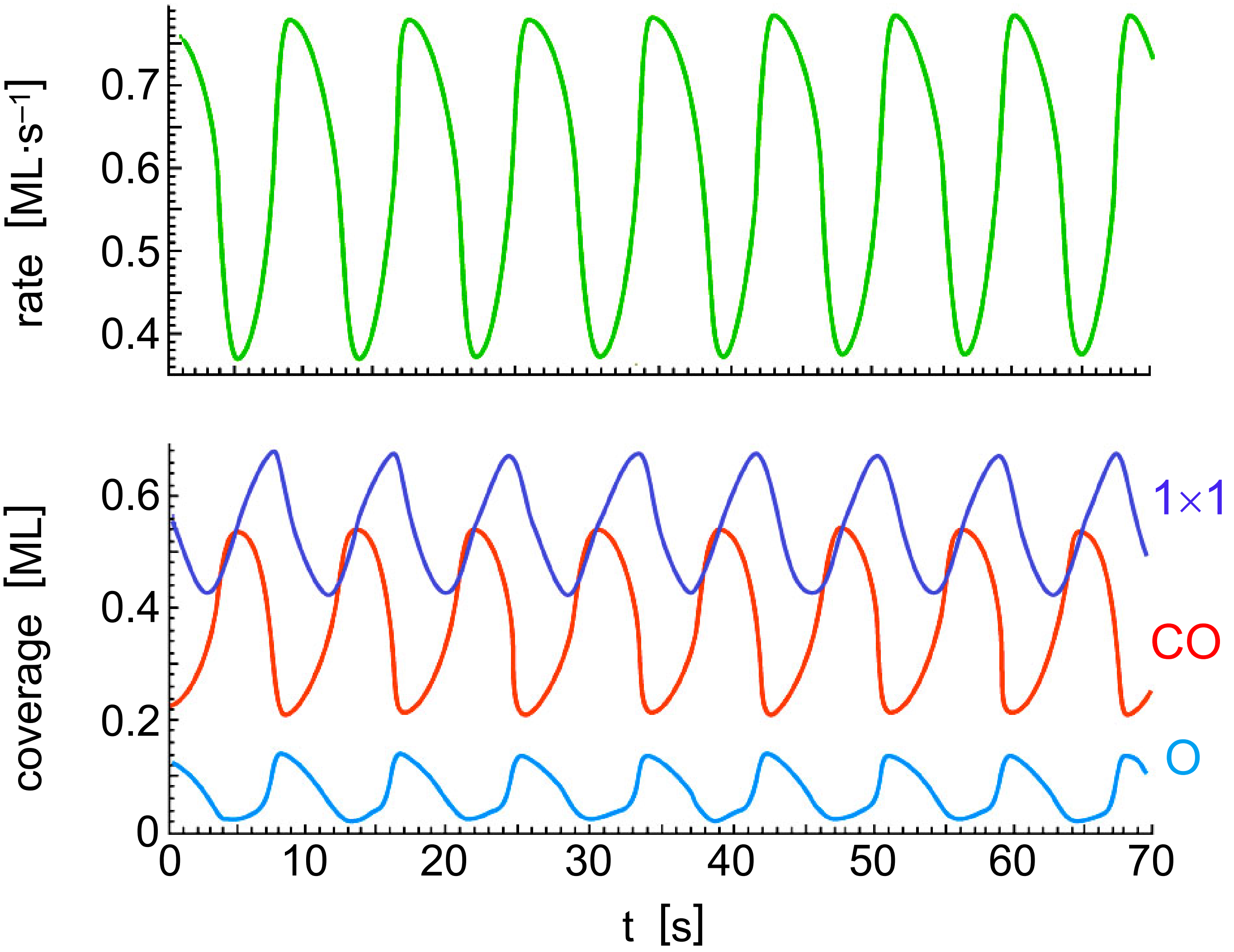
1×2 missing row

1×1

$\theta_{CO} \leq 0.5\,\mathrm{ML}$

$CO + \frac{1}{2}O_2 \rightarrow CO_2$ / Pt(110)

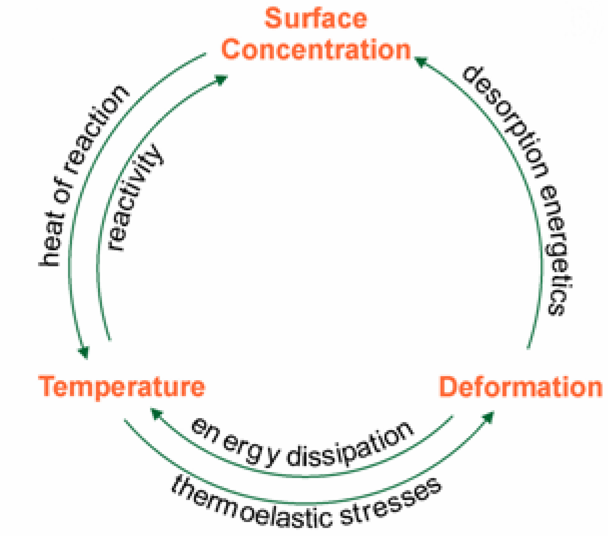
K. Krischer, M.Eiswirth & G. Ertl, *J.Chem.Phys.* ***96*** *(1992), 9161 (Theory)*



T = 540 K; p_{O_2} = 6.7×10^{-5} mbar; p_{CO} = 3×10^{-5} mbar

Heartbeats of ultra thin catalyst

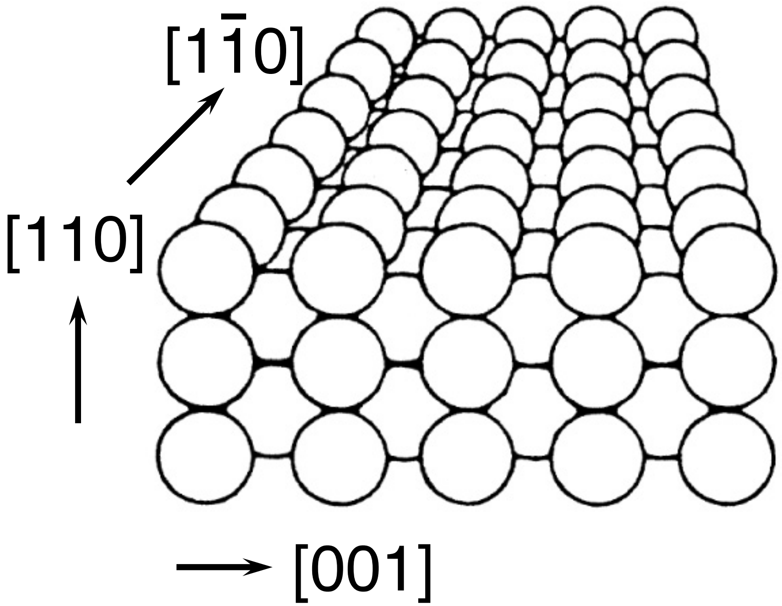
QuickTime™ and a
decompressor
are needed to see this picture.



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_{O2} = 1 x 10^{-2} mbar, p_{CO} = 1.85 x 10^{-3} mbar



$2\,CO + O_2 \Rightarrow 2\,CO_2$ / Pt(110)

Target patterns

$p_{O_2} = 3.2 \times 10^{-4}$ mbar

$p_{CO} = 3 \times 10^{-5}$ mbar

$T = 427$ K

Ø = 500 µm

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

S. Nettesheim, A. von Oertzen, H.H. Rotermund, G. Ertl, J.Chem.Phys. ***98*** *(1993), 9977*

Chemical turbulence

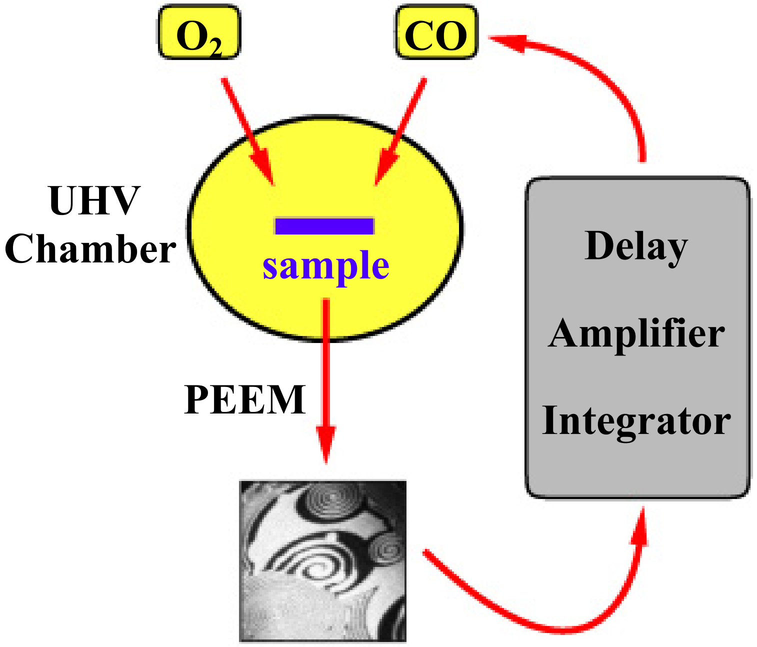
QuickTime™ and a
Photo decompressor
are needed to see this picture.

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



O_2

CO

UHV Chamber

sample

PEEM

Delay

Amplifier

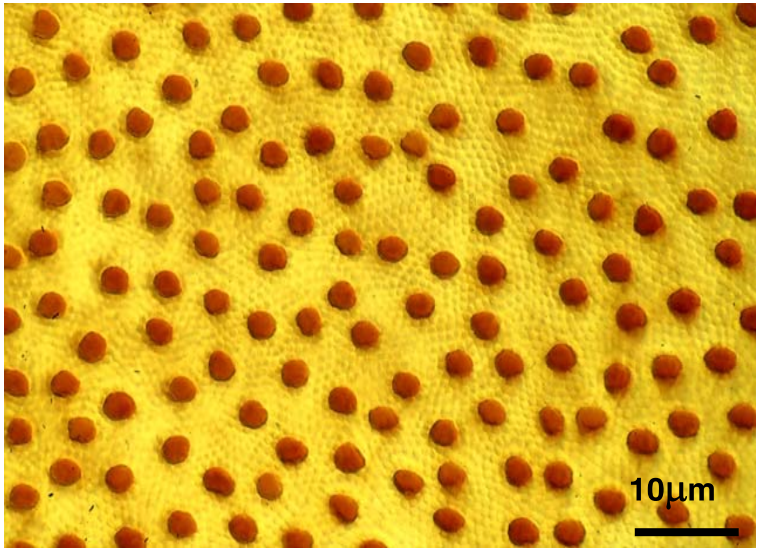
Integrator

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)

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

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



Retina