Molecules at surfaces and mechanism of catalysis

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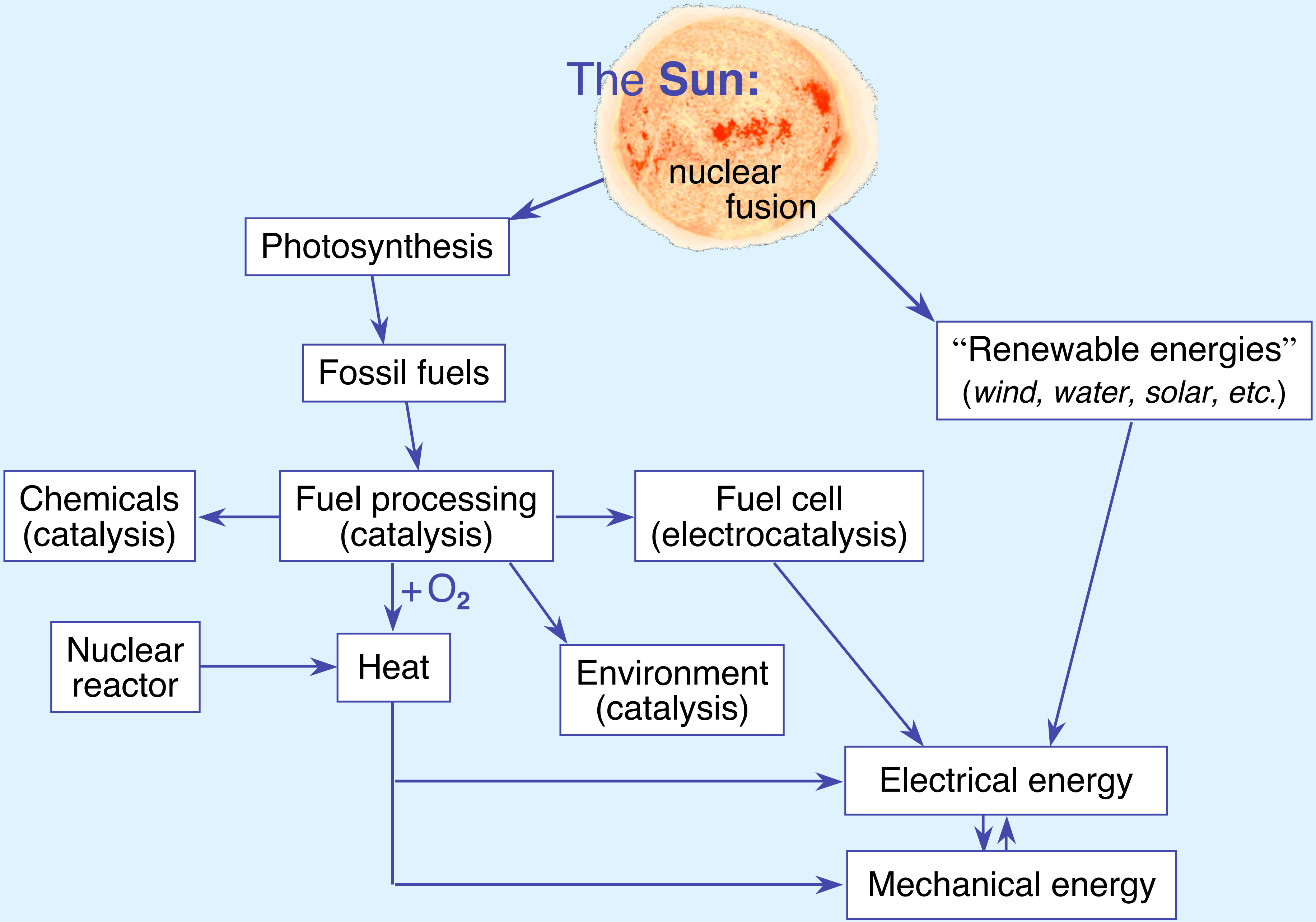
Transformation of energy and matter

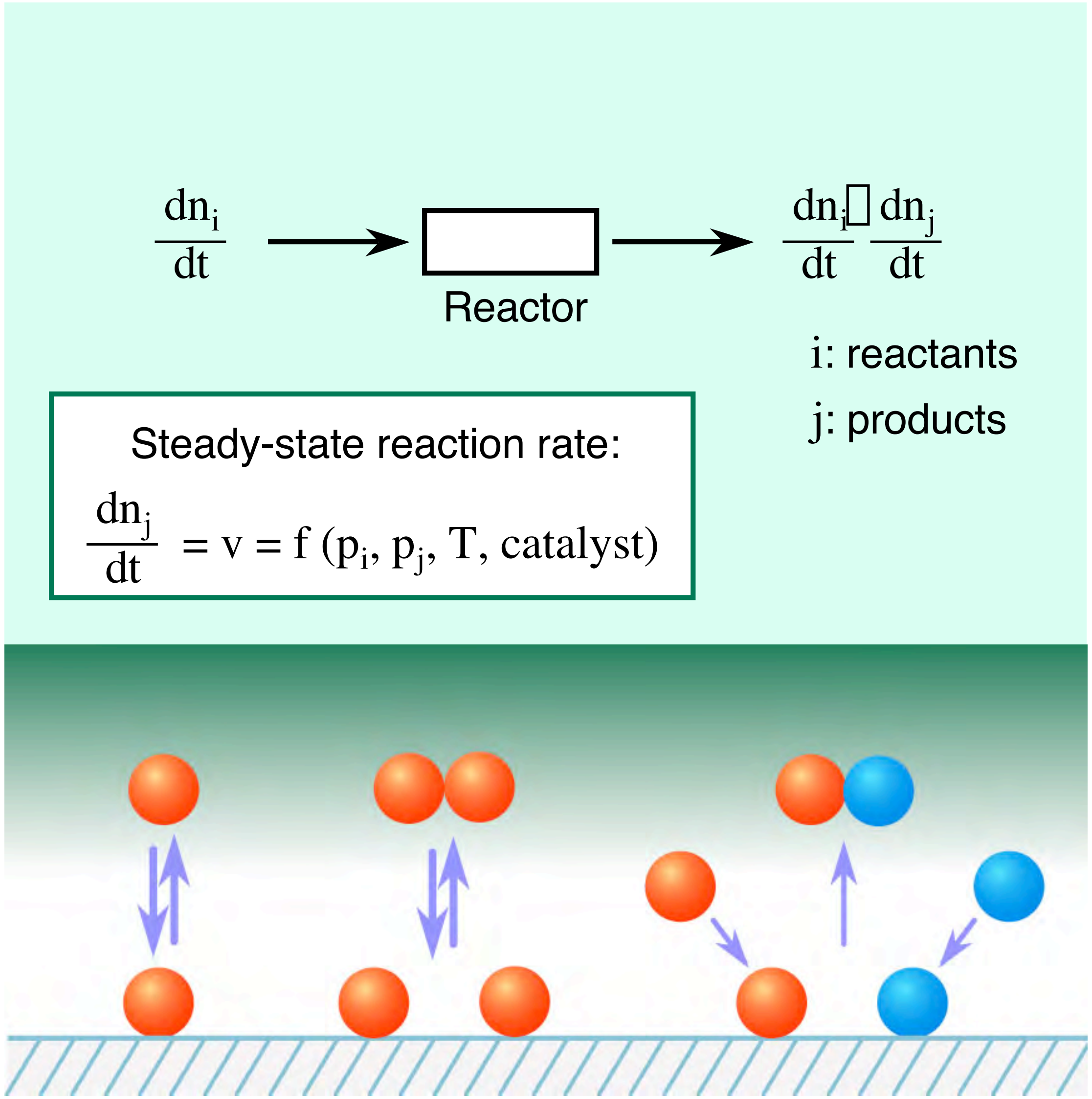


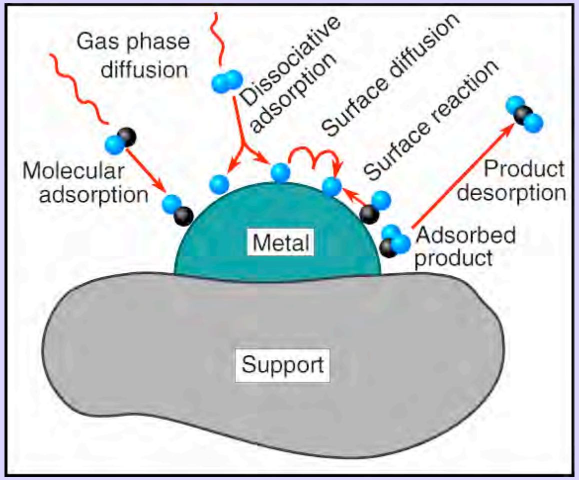
Catalytic synthesis of ammonia

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

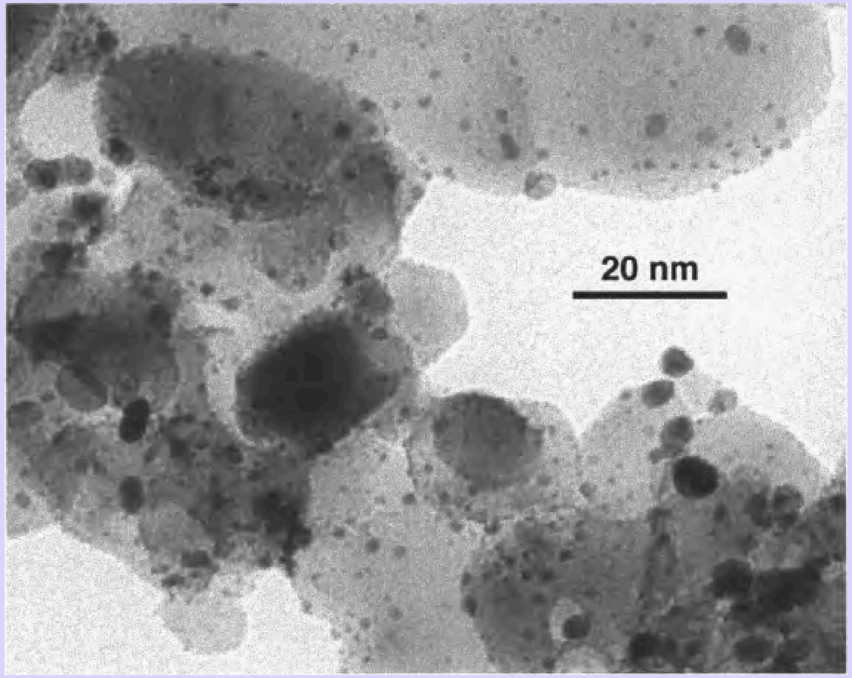
(Haber-Bosch process)

Heterogeneous catalysis

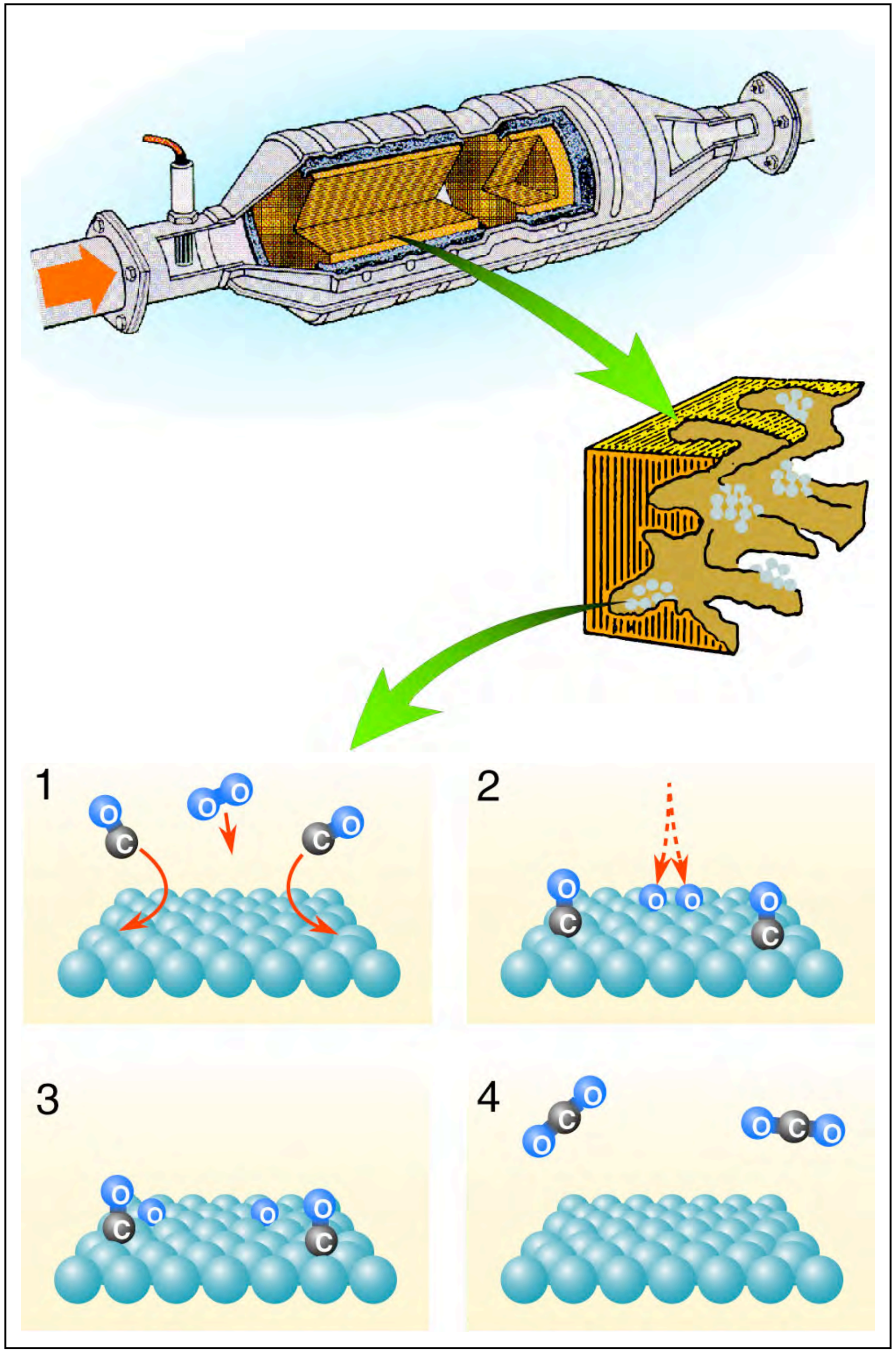




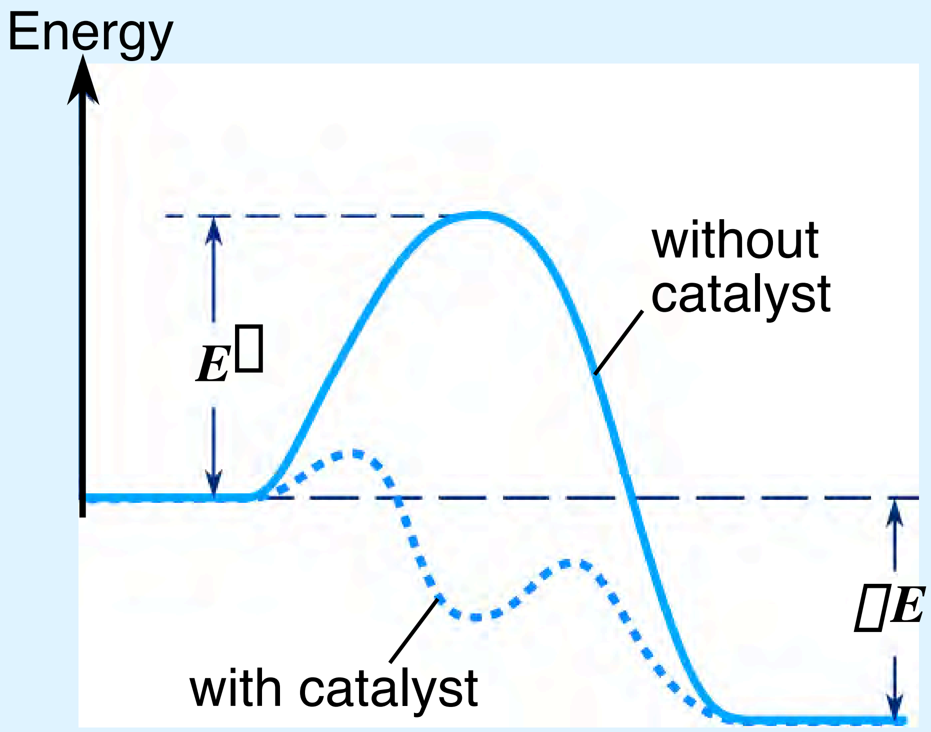
Gas phase diffusion
Dissociative adsorption
Surface diffusion
Surface reaction
Molecular adsorption
Product desorption
Adsorbed product
Metal
Support

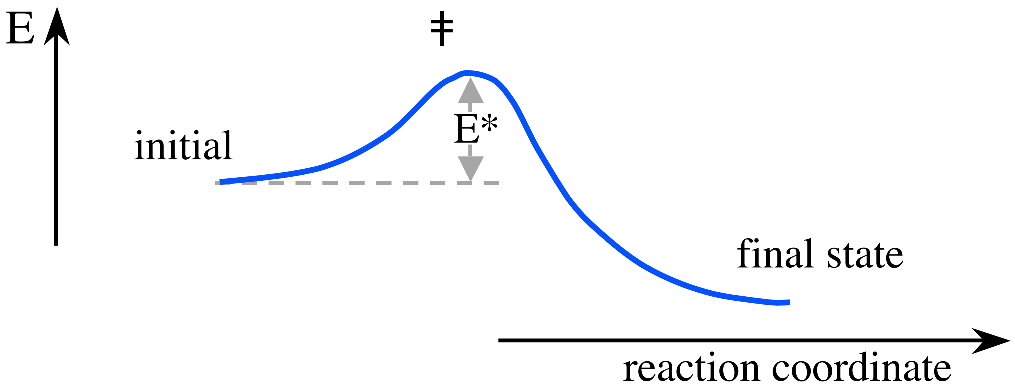


20 nm


1
2
3
4

Progress of a chemical reaction

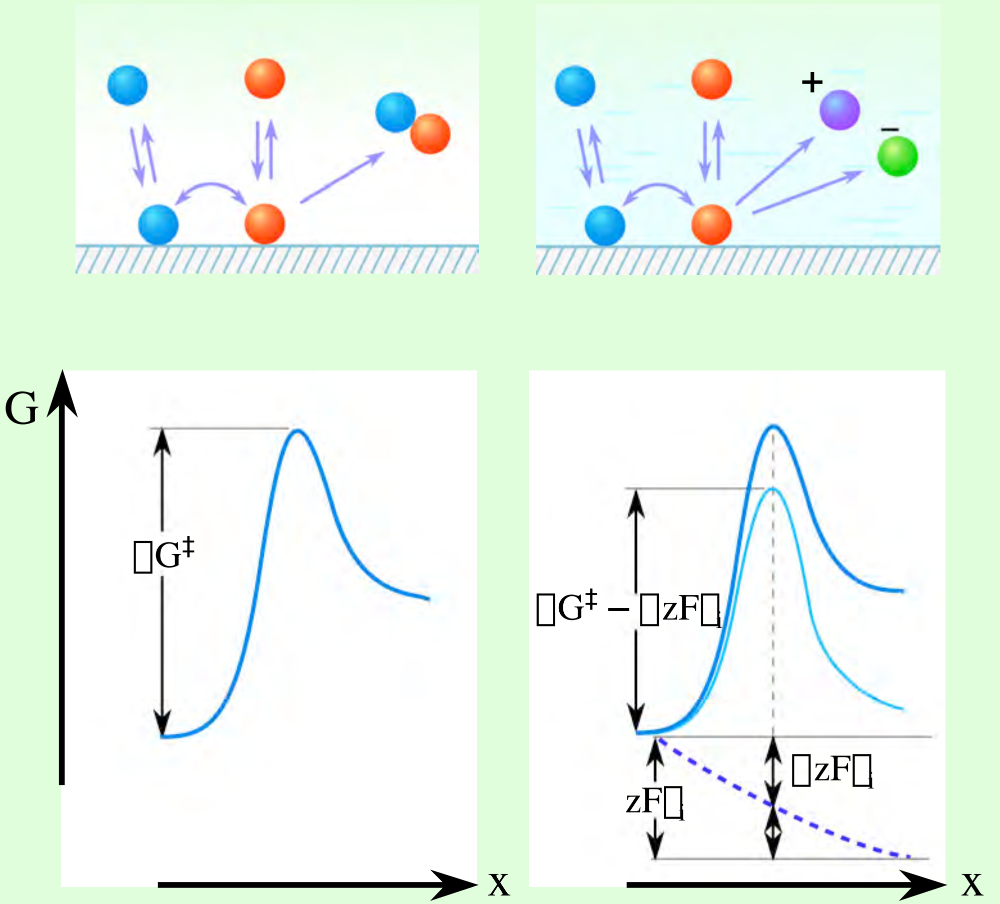




Transition state theory

$$k_r = \frac{k_B T}{h} e^{\Delta S^{\ddagger}/R} \cdot e^{-E^{*}/RT}$$

Heterogeneous catalysis | Electrocatalysis

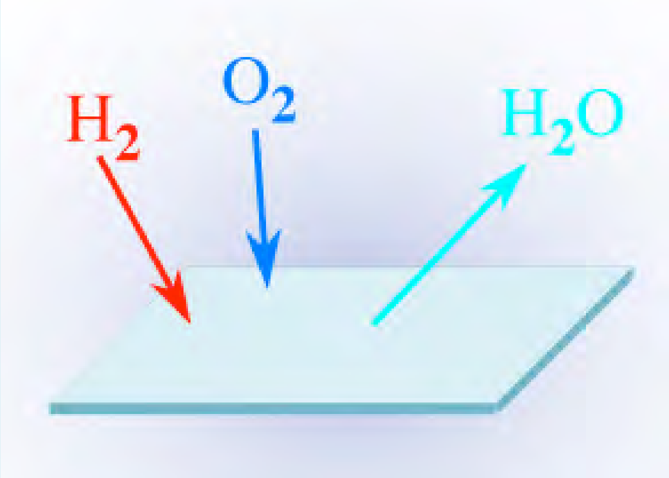


$$r_+ \propto \exp\left[-\frac{\Delta G^\ddagger}{RT}\right]$$

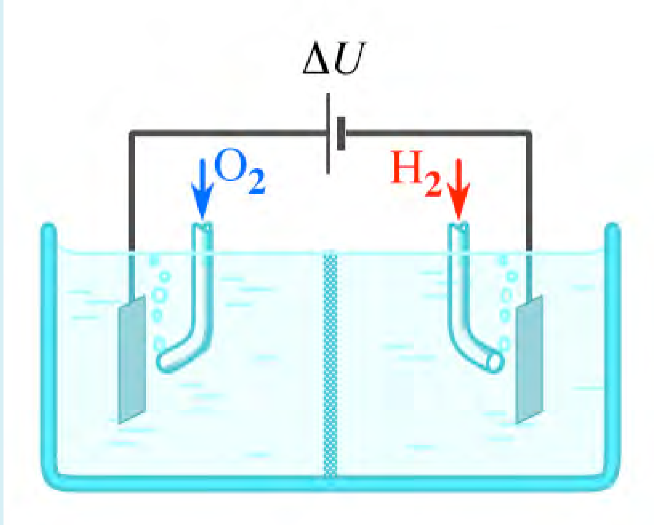
$$r_+ \propto j_+ \propto \exp\left[-\frac{\Delta G^\ddagger - \alpha zF\eta}{RT}\right]$$

$2\,H_2 + O_2 \rightarrow 2\,H_2O$ / Pt

Heterogeneous catalysis



Electrocatalysis

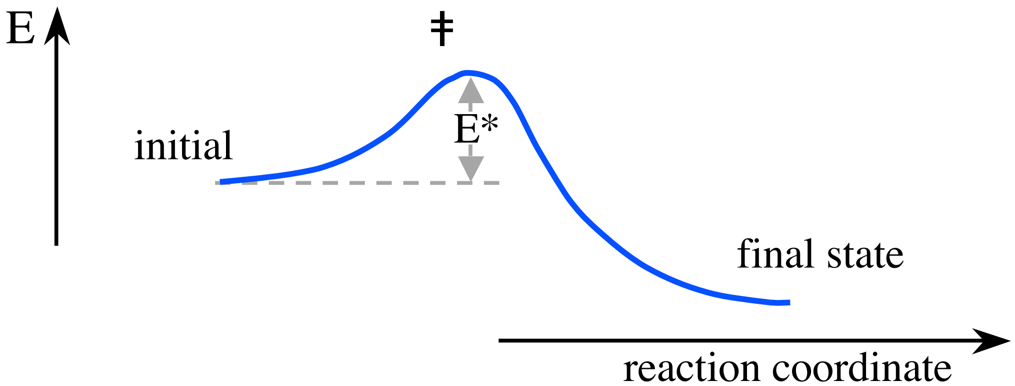


$O_2 + 4\,H^+_{aq} + 4\,e^- \rightleftharpoons 2\,H_2O$	$H_2 \rightleftharpoons 2\,H^+_{aq} + 2\,e^-$

$$U_1^0 = 1.23\ \mathrm{V} \qquad U_2^0 = 0\ \mathrm{V}$$

$$\Delta U = U_1 - U_2$$

$$\Delta G^0 = -nF\Delta U$$

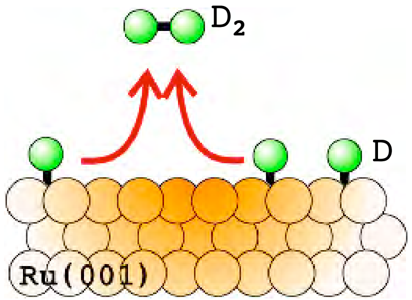


Transition state theory

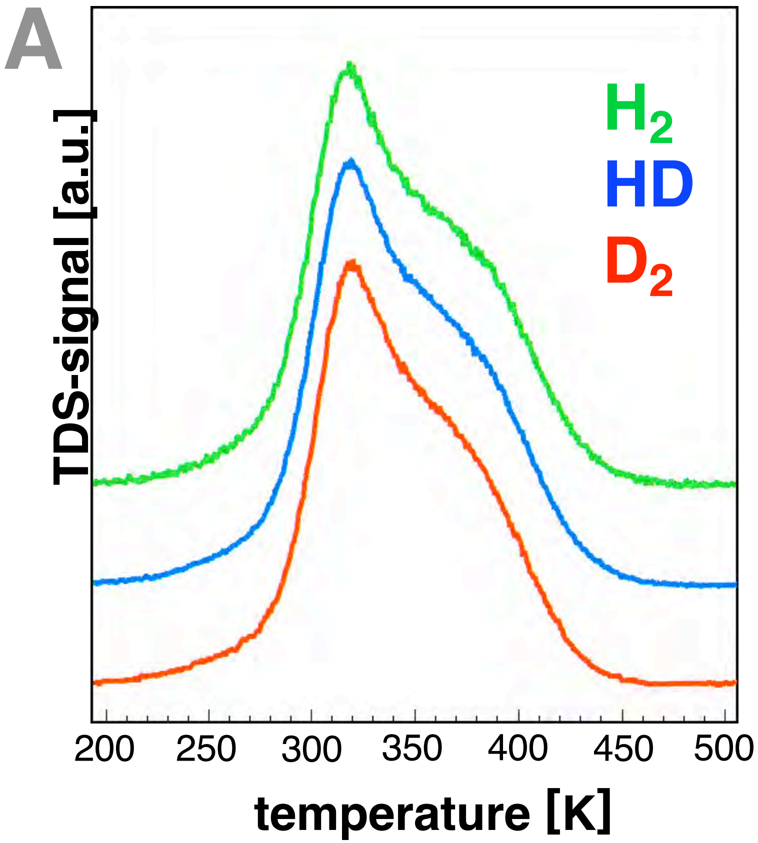
$$k_r = \frac{k_B T}{h} e^{\Delta S^{\ddagger}/R} \cdot e^{-E^{*}/RT}$$

time scale >> relaxation times for energy exchange between adsorbate and heat bath of solid (= phonons + electrons)

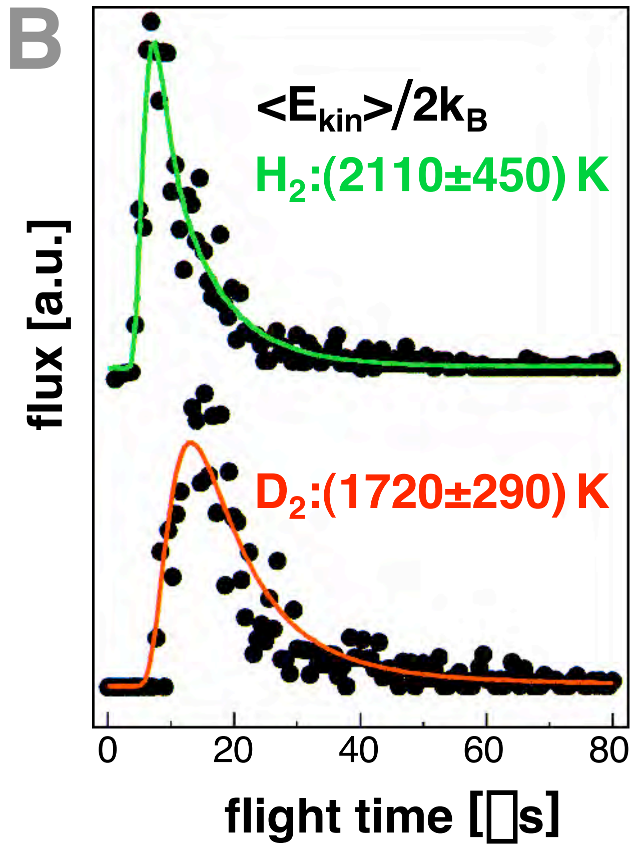
Associative desorption of hydrogen from Ru(0001)

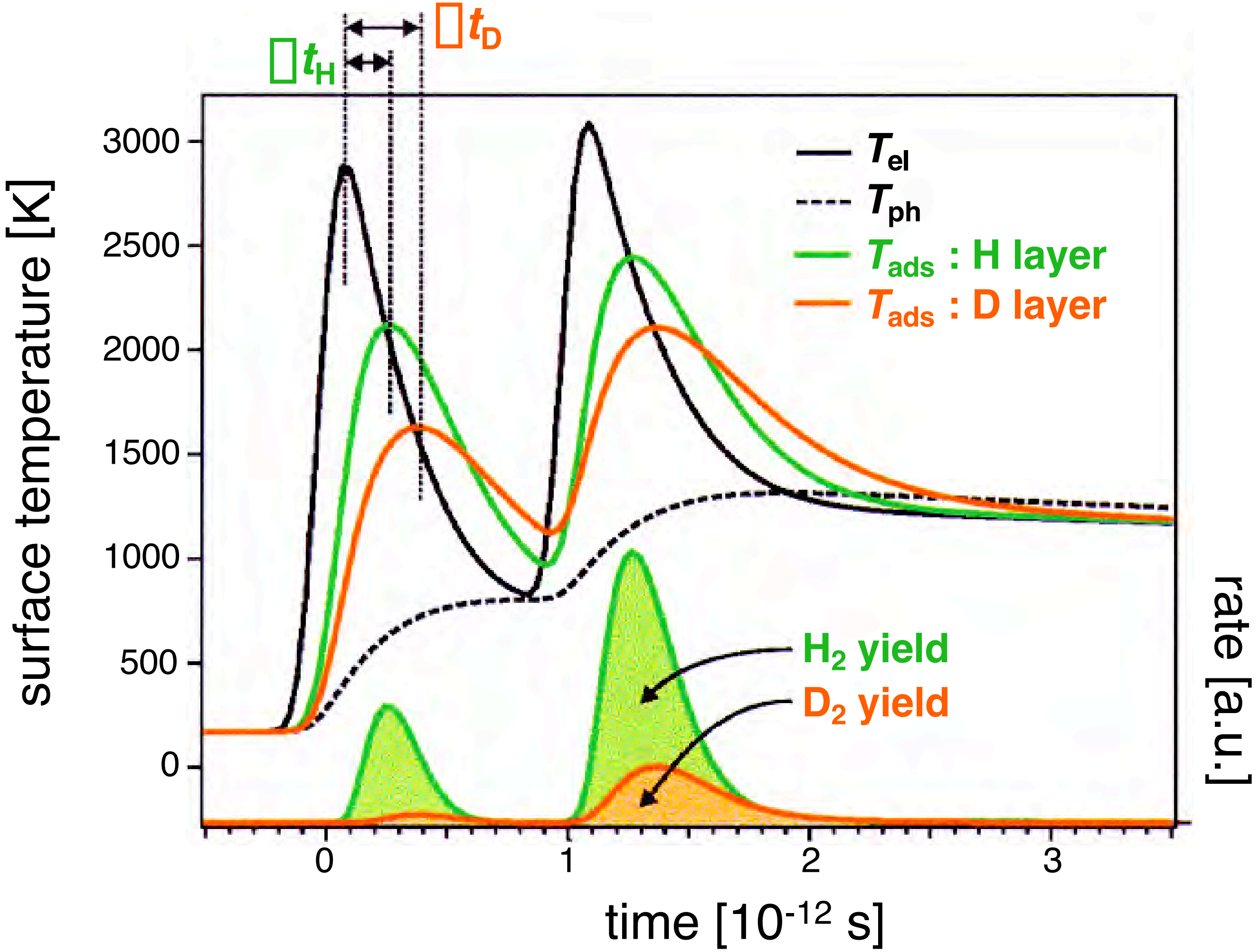


Thermal desorption spectroscopy (TDS)

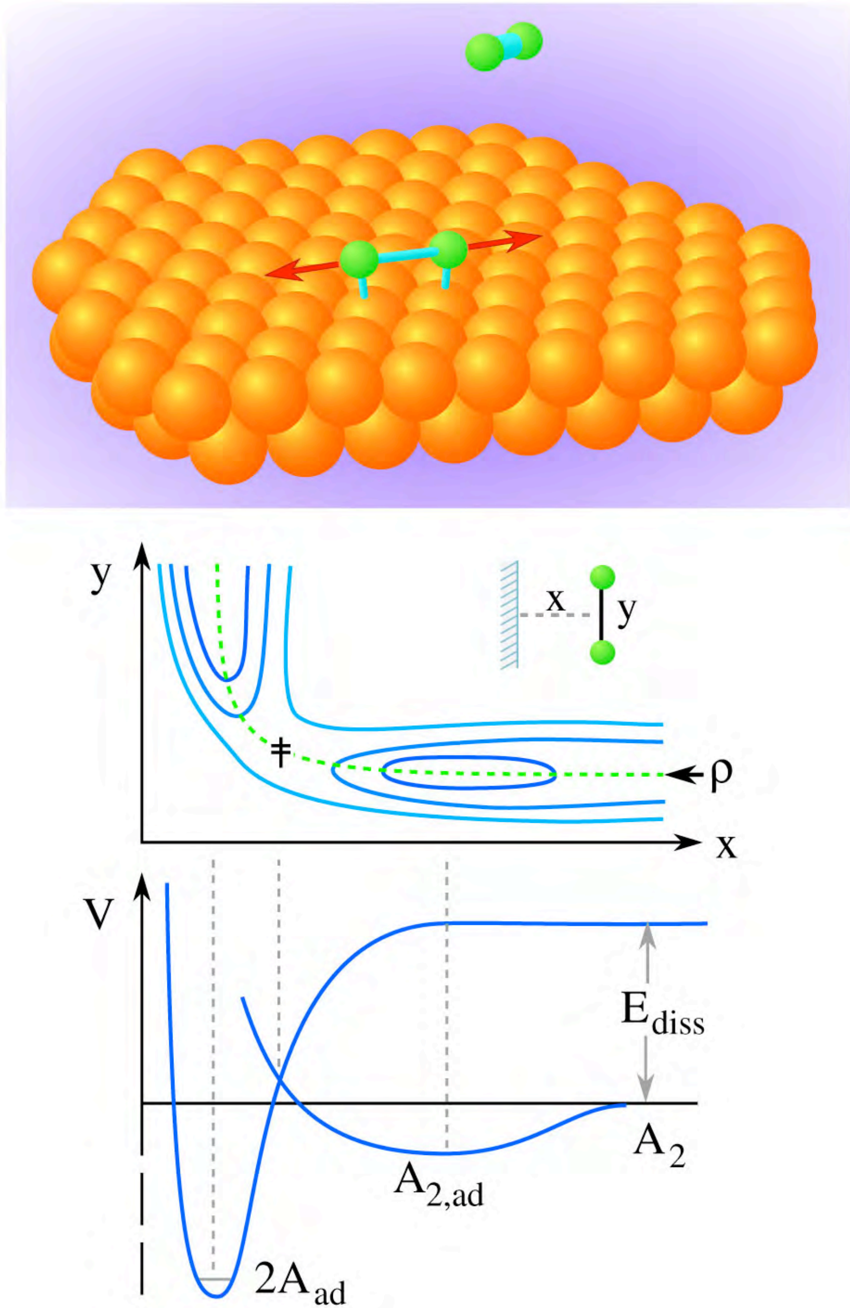


fs-laser induced ToF spectra



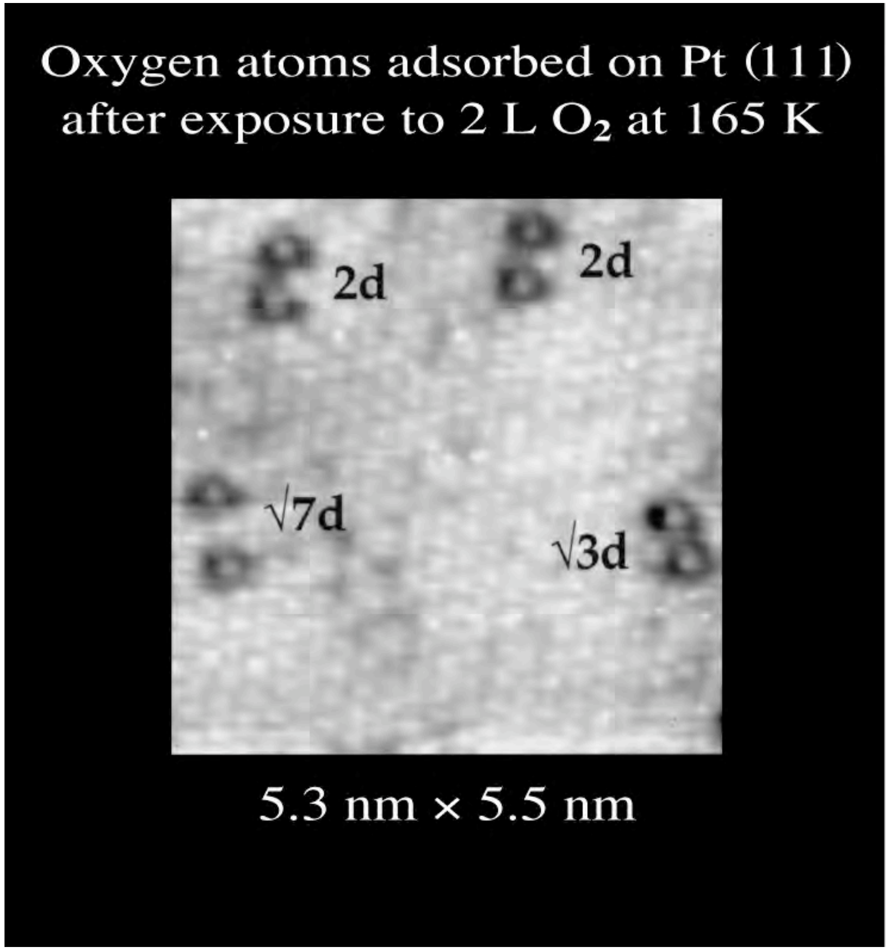


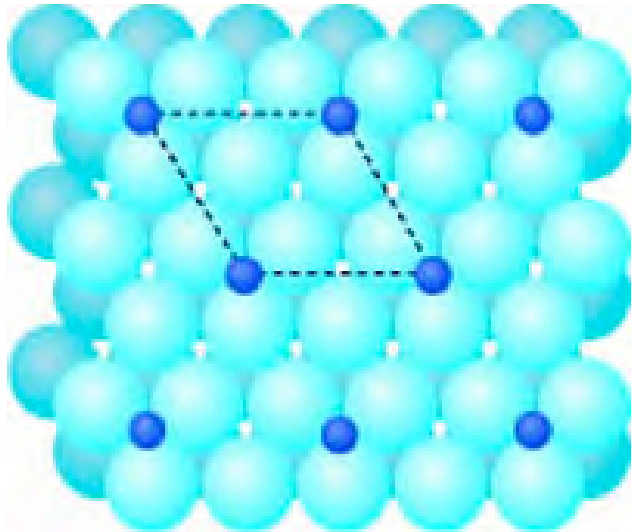
D. Denzler, C. Frischkorn, C. Hess, M. Wolf, G. Ertl,
Phys.Rev.Lett. **91** (2003), 226102; J.Phys.Chem. B **108** (2004), 14503



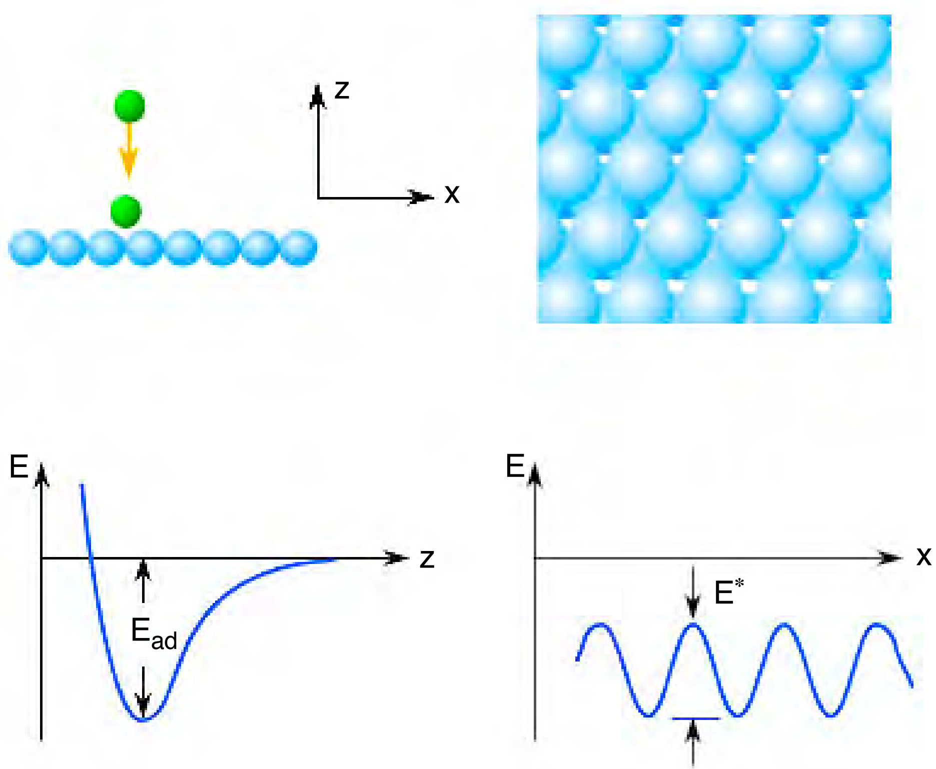
y
x
y
‡
ρ
x
V
E_{diss}
A_2
$A_{2,ad}$
$2A_{ad}$

O / Pt(111)





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

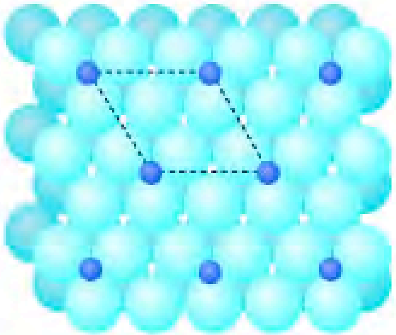


$$\square_{surf} = \square_0 \cdot e^{E_{ad}/RT} \qquad \square_{site} = \square_0 \square e^{E^*/RT}$$

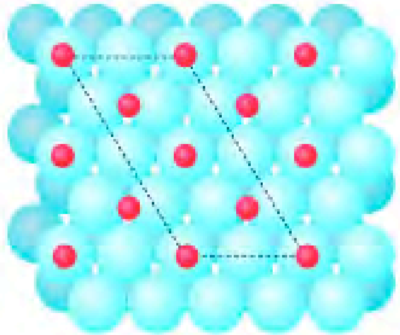
O/Ru (0001)

T = 300 K

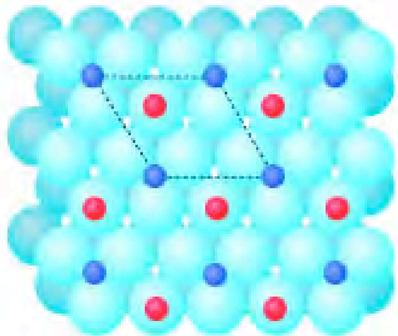
Pt (111)



2x2 – O

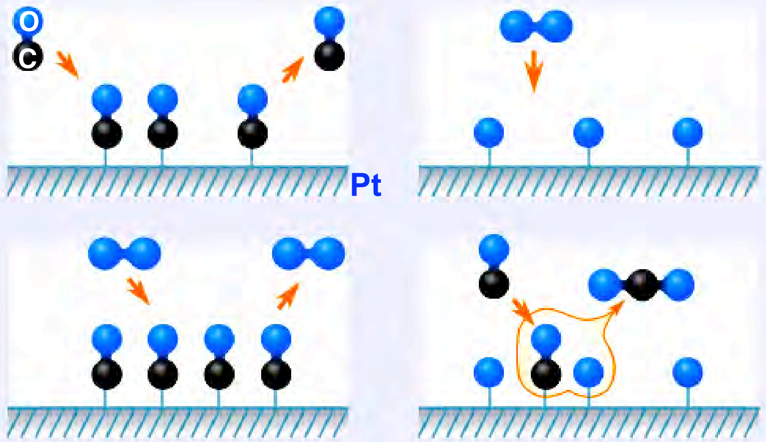


c(4x2) – CO



2x2 – O + CO

Catalytic oxidation of CO

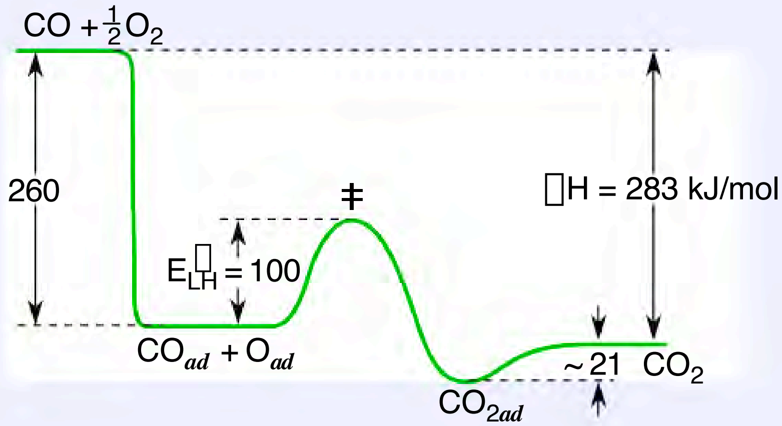


$$2CO + O_2 \longrightarrow 2CO_2$$

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

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

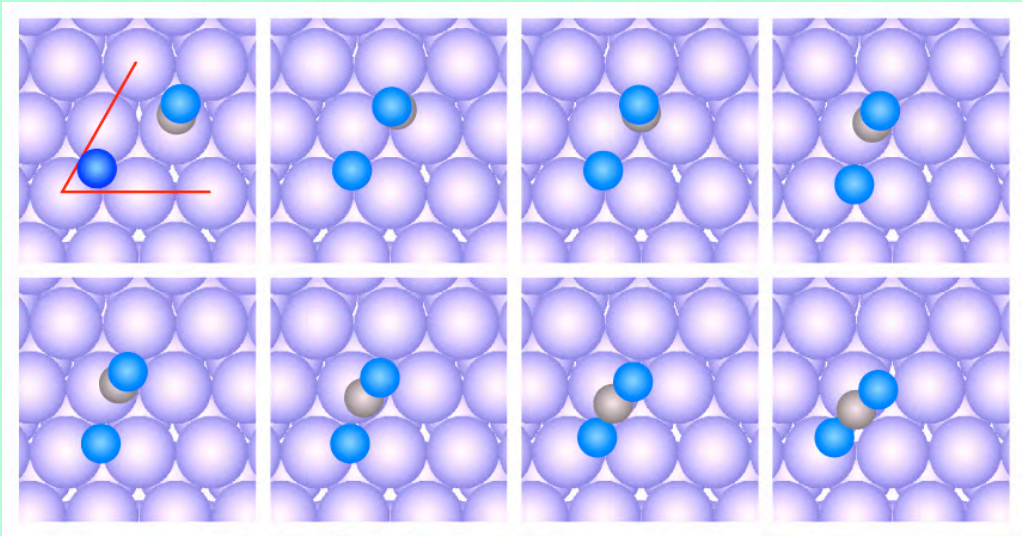
$$O_{ad} + CO_{ad} \rightarrow CO_2 + 2*$$

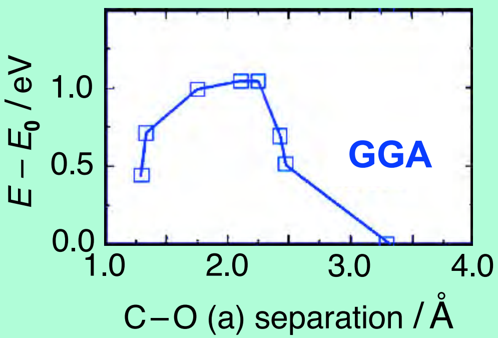


(Pt at low coverages)

$O_{ad} + CO_{ad} \rightarrow CO_2 / Pt(111)$

Density Functional Theory Study





A. Alavi, P. Hu, T. Deutsch, P.L. Silvestrelli, J. Hutter, *Phys. Rev. Lett.* **80** (1998), 3650

$2H_2 + O_2 \rightarrow 2H_2O$ / Pt

Mechanism (?) :

(1)	$O_2 + \square \rightarrow 2\,O_{ad}$	
(2)	$H_2 + \square \rightarrow 2\,H_{ad}$	
(3)	$O_{ad} + H_{ad} \rightarrow OH_{ad}$	
(4)	$OH_{ad} + H_{ad} \rightarrow H_2O_{ad}$	
(5)	$H_2O_{ad} \rightarrow H_2O_g + \square$	($T \geq 170$ K)

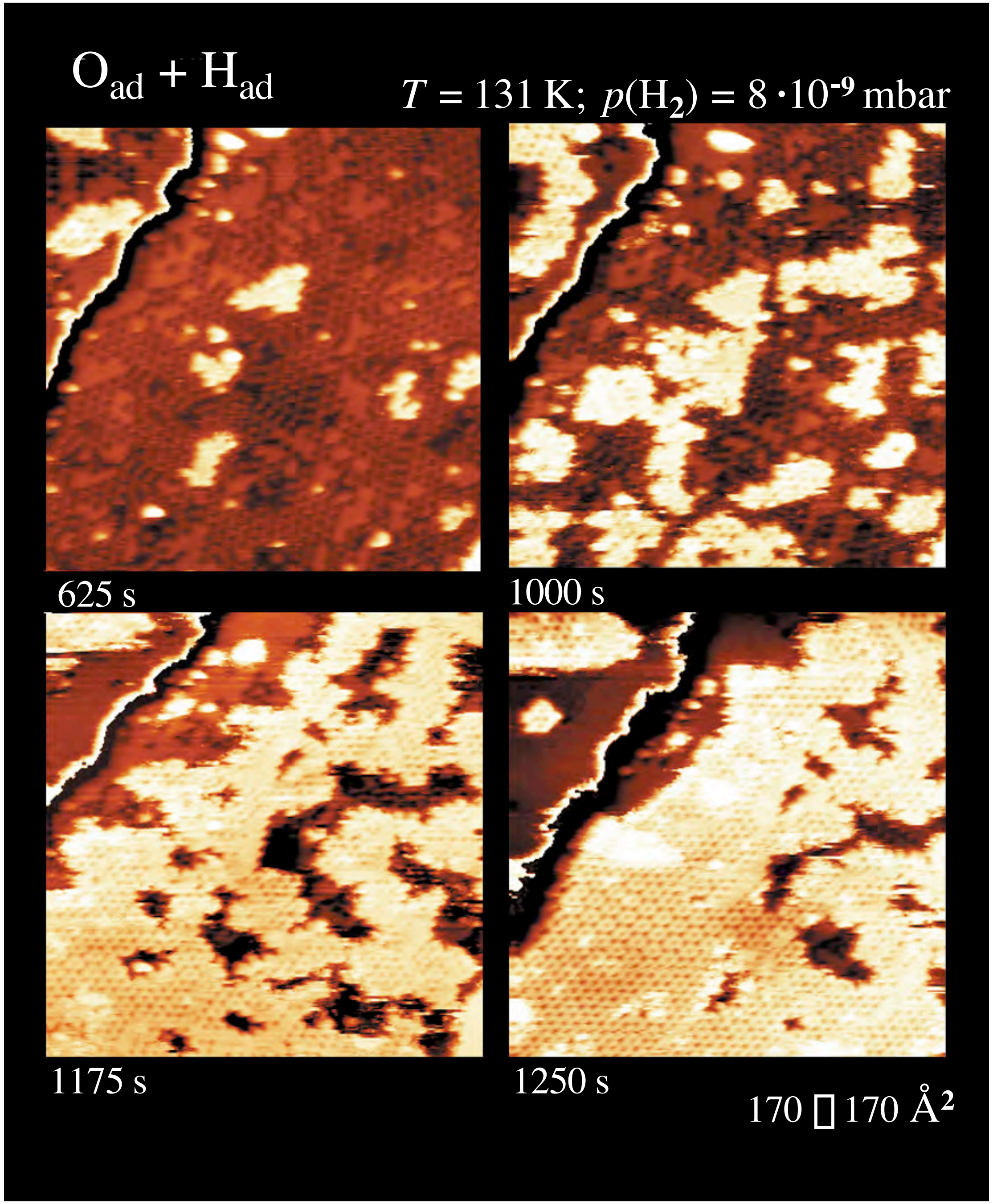
But :

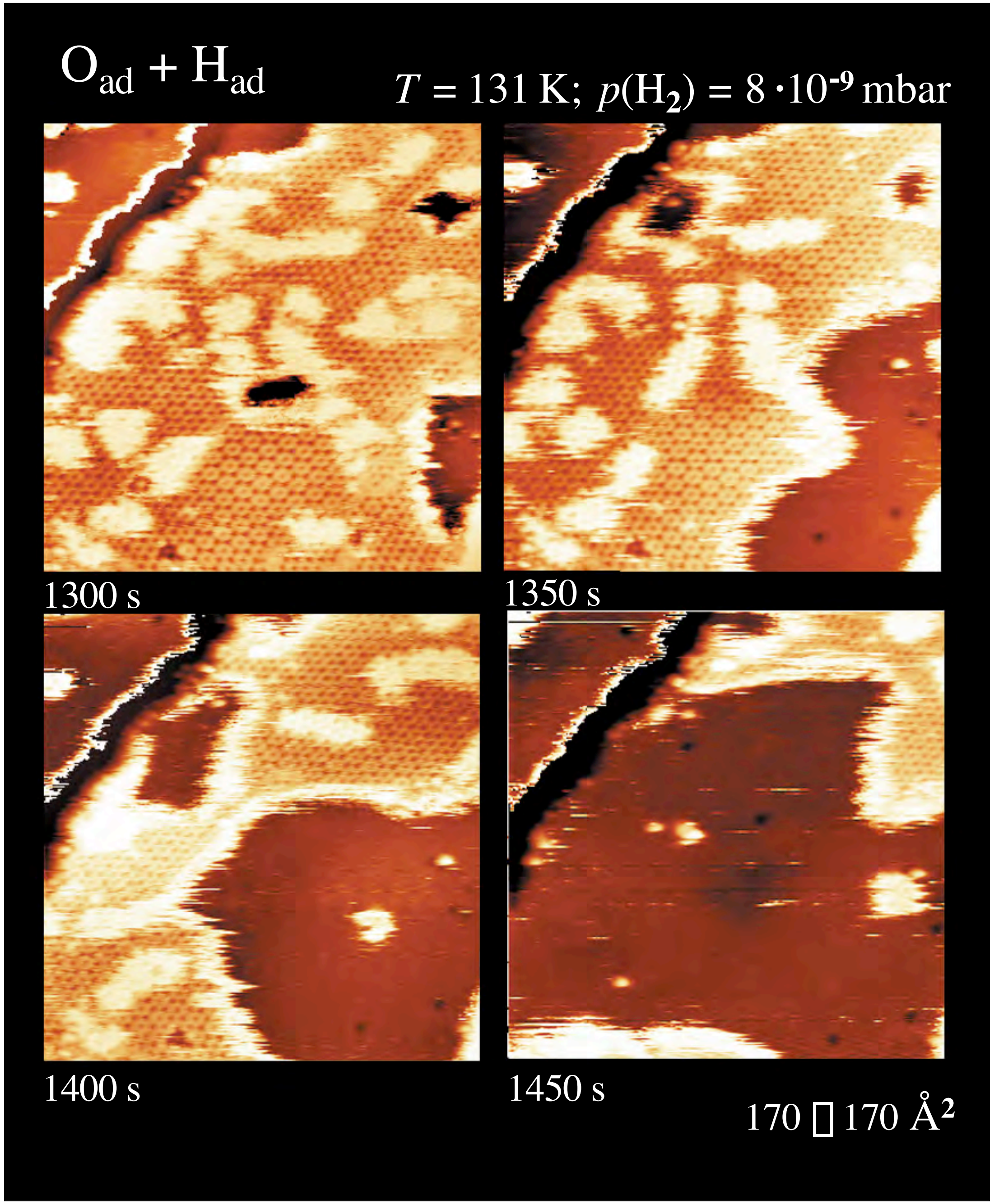
	$T < 170$ K Induction period	$T > 230$ K No induction period
*E** :	~ 12 kJ/mol	> 50 kJ/mol

Important :

(6) $H_2O_{ad} + O_{ad} \rightarrow 2\,OH_{ad}$

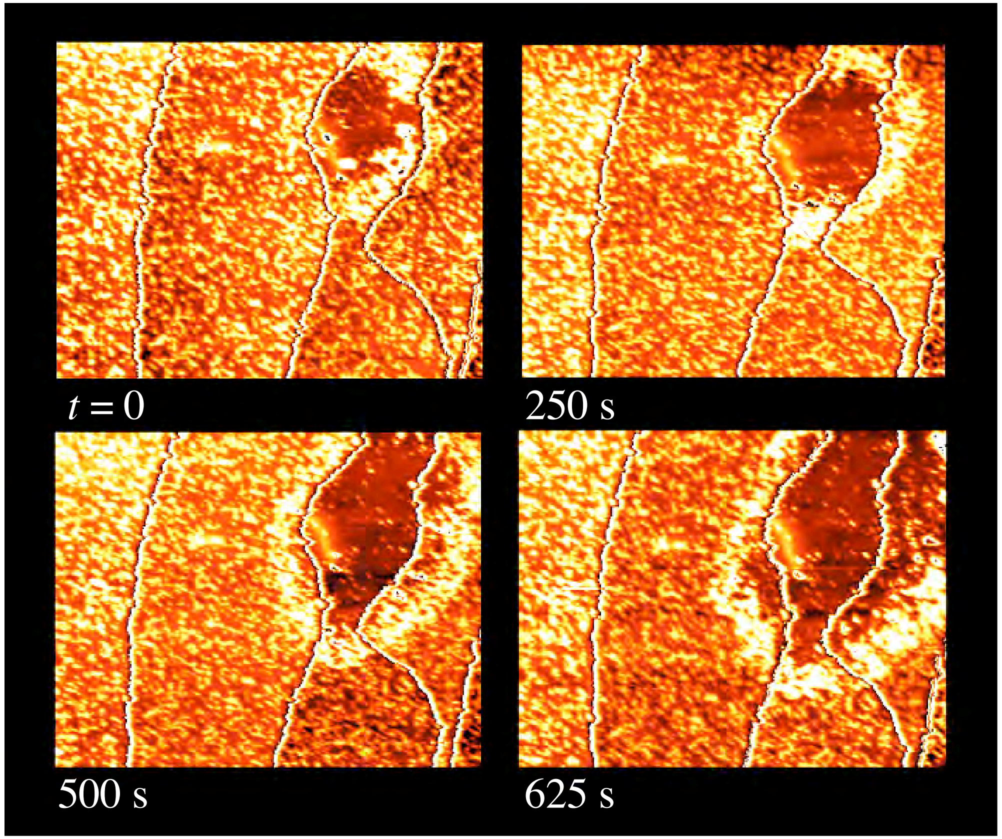
S. Völkening, K. Bedürftig, K. Jacobi, J. Wintterlin and G. Ertl, *Phys. Rev. Lett.* **83** (1999), 2672.

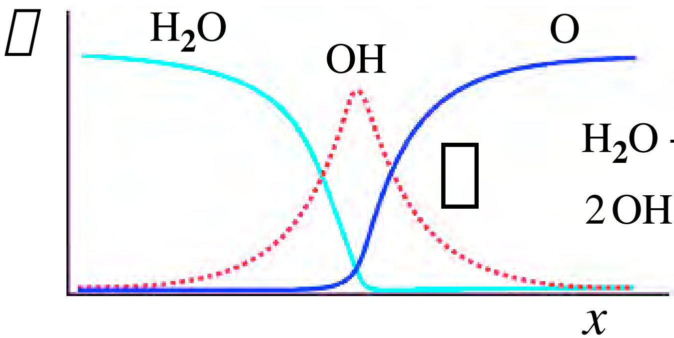

O ad + H ad
T = 131 K; p(H2) = 8 ·10-9 mbar
625 s
1000 s
1175 s
1250 s
170 170 Å2


$O_{ad} + H_{ad}$
T = 131 K; $p(H_2) = 8 \cdot 10^{-9}$ mbar
1300 s
1350 s
1400 s
1450 s
170 □ 170 $Å^2$

OH-fronts

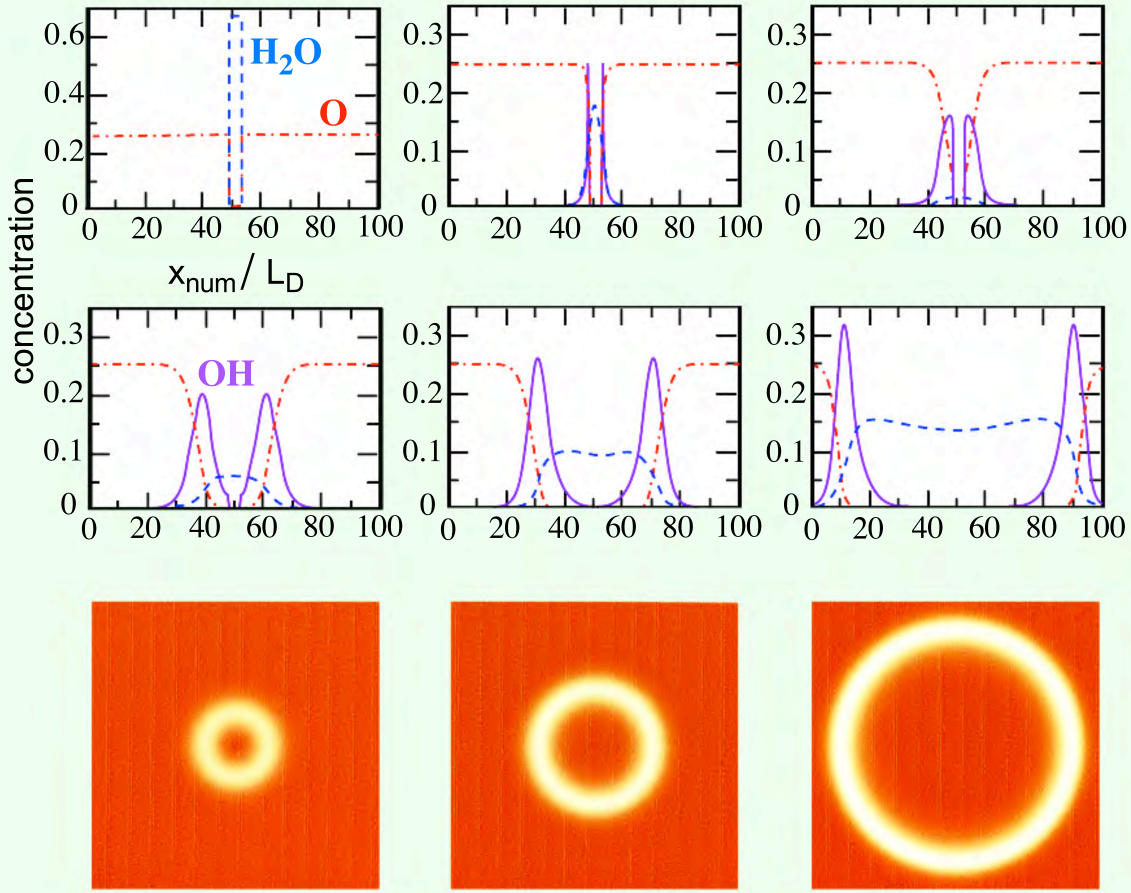
T = 111 K; $p(H_2) = 8 \cdot 10^{-9}$ mbar; 2100×1760 Å^2





$$H_2O + O \rightarrow 2\,OH$$

$$2\,OH + 2\,H \rightarrow 2\,H_2O$$



C. Sachs, M. Hildebrand, S. Völkening,
J. Wintterlin, and G. Ertl, Science ***293*** *(2001), 1635;*
J. Chem. Phys. ***116*** *(2002), 5759*

Spatio-temporal self-organization

Temporal and spatial variation of state variables (surface concentrations)

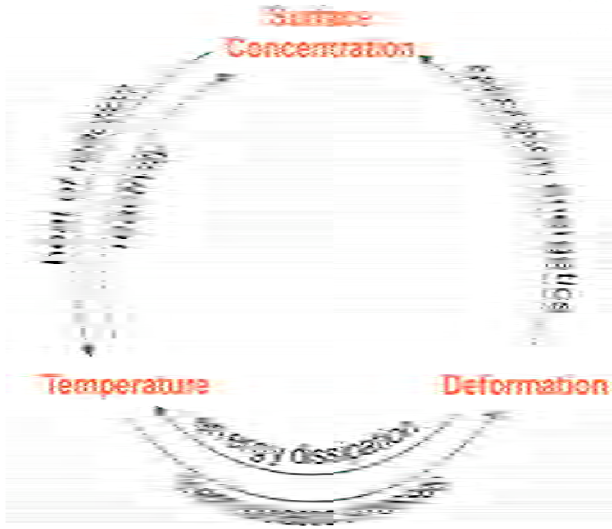
Coupling between different parts of the surface via

- **Diffusion**
- **Heat conductance**
- **Variation of partial pressures**
- **Electric field**

Reaction-diffusion systems

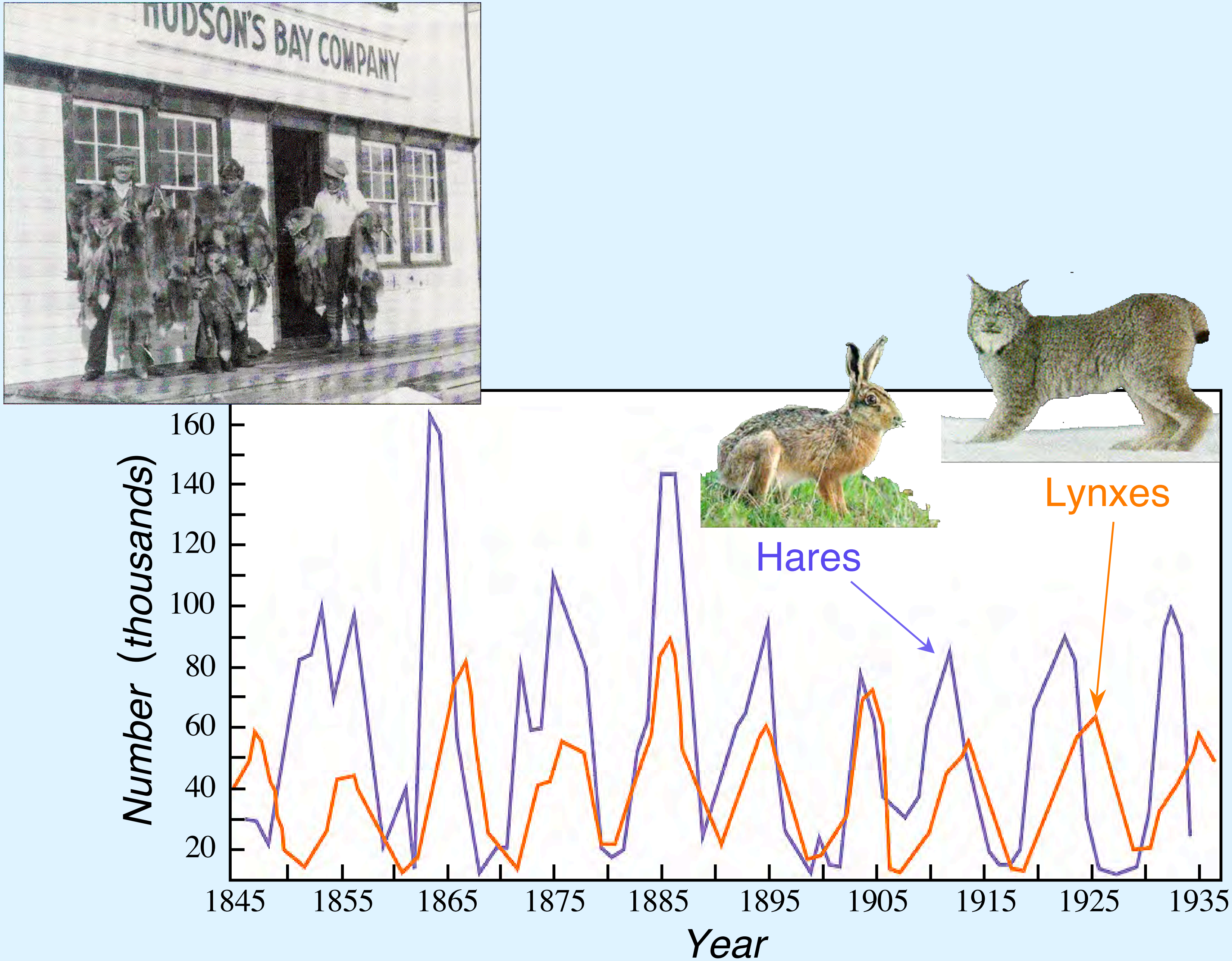
$$\frac{\partial x_i}{\partial t} = F_i(x_j, p_k) + D_i \nabla^2 x_i$$

Heartbeats of ultra thin catalyst



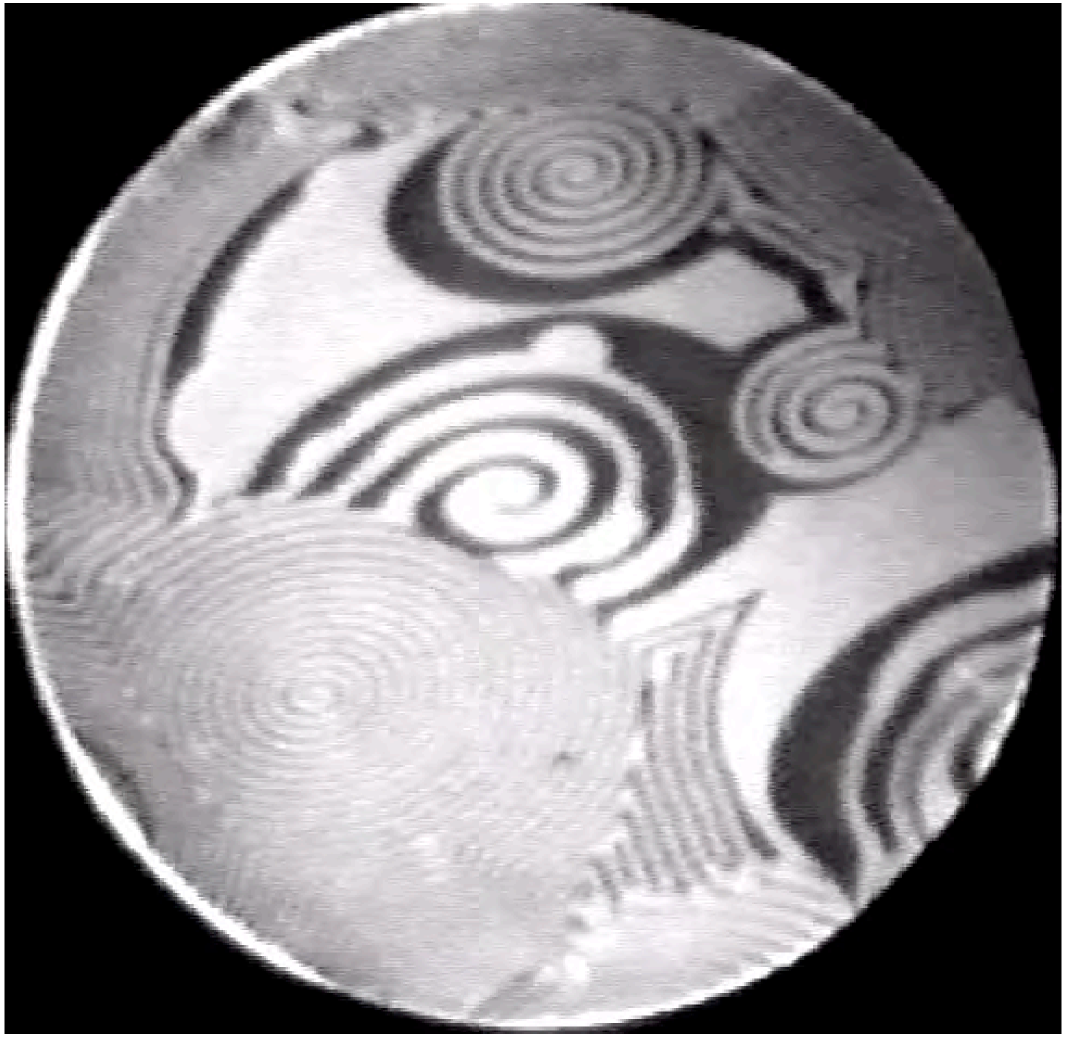
F. Cirak, J.E. Cisternas, A.M. Cuitino,
G. Ertl, P.Holmes, I. Kevrekidis, M.Ortiz,
H.H. Rotermund, M.Schunack, J. Wolff,
Science **300** (2003), 1932

Ultra thin (200 nm thick) Pt(110) catalyst during CO oxidation, 5 mm sample diameter, T□□28 K, p_{O2} = 1 x 10^{-2} mbar, p_{CO} = 1.85 x 10^{-3} mbar



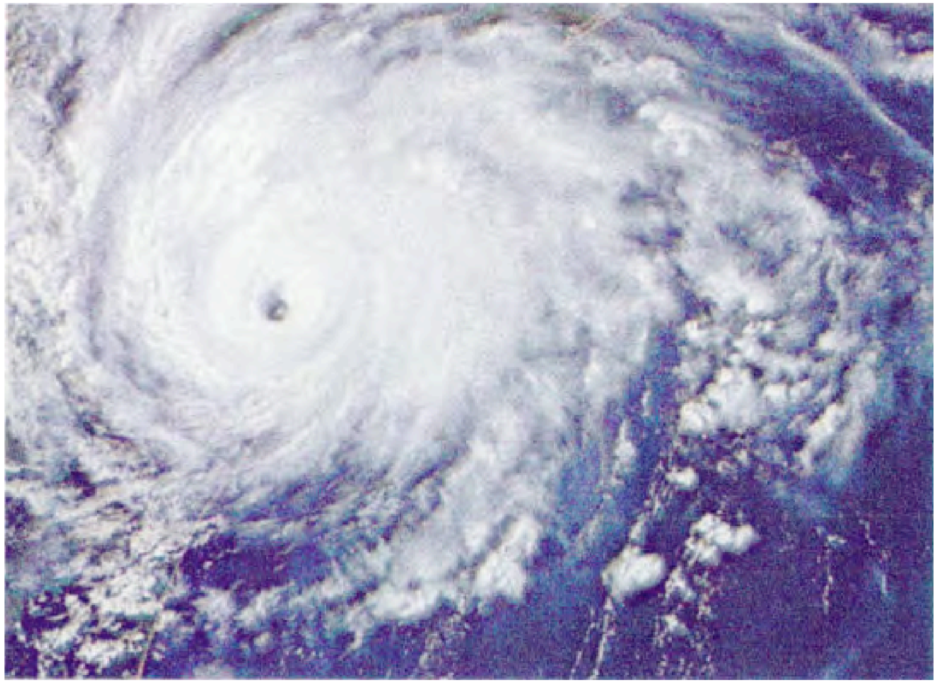
HUDSON'S BAY COMPANY
Number (thousands)
160
140
120
100
80
60
40
20
1845
1855
1865
1875
1885
1895
1905
1915
1925
1935
Year
Hares
Lynxes

Spiral waves during CO-oxidation on Pt(110)



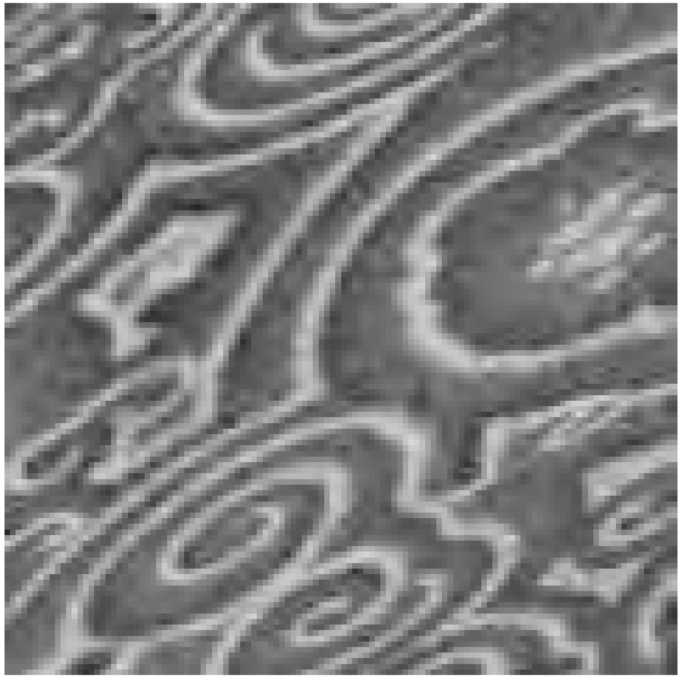
PEEM images with 500 μm diameter,
steady-state conditions: $p_{O_2} = 4 \times 10^{-4}$ mbar, $p_{CO} = 4.3 \times 10^{-5}$ mbar, $T = 448$ K

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



Hurricane Bret over the coast of Texas,
August 1999 (photo: NASA, GOES)

Chemical turbulence

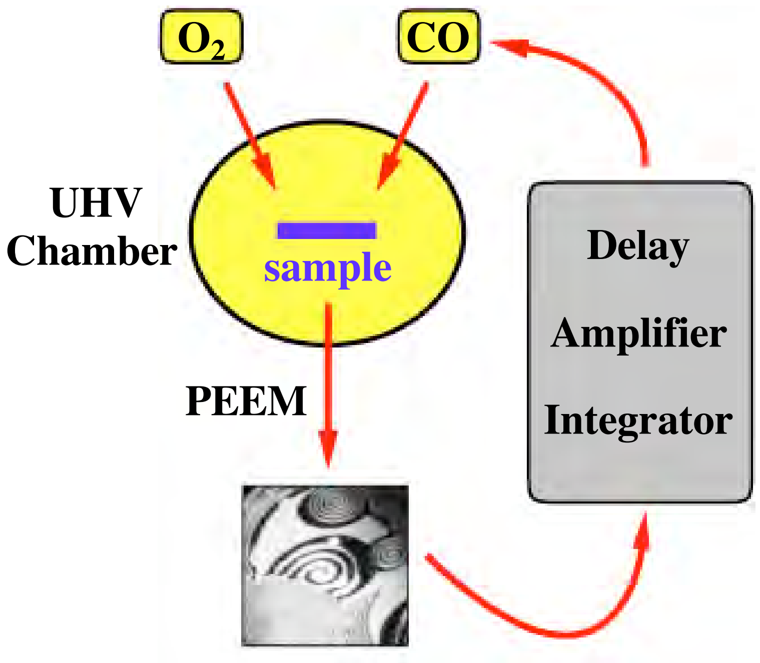


Photoemission electron microscope (PEEM) imaging. Dark regions are predominantly oxygen covered, bright regions are mainly CO covered.

Real time, image size 360 x 360 μm

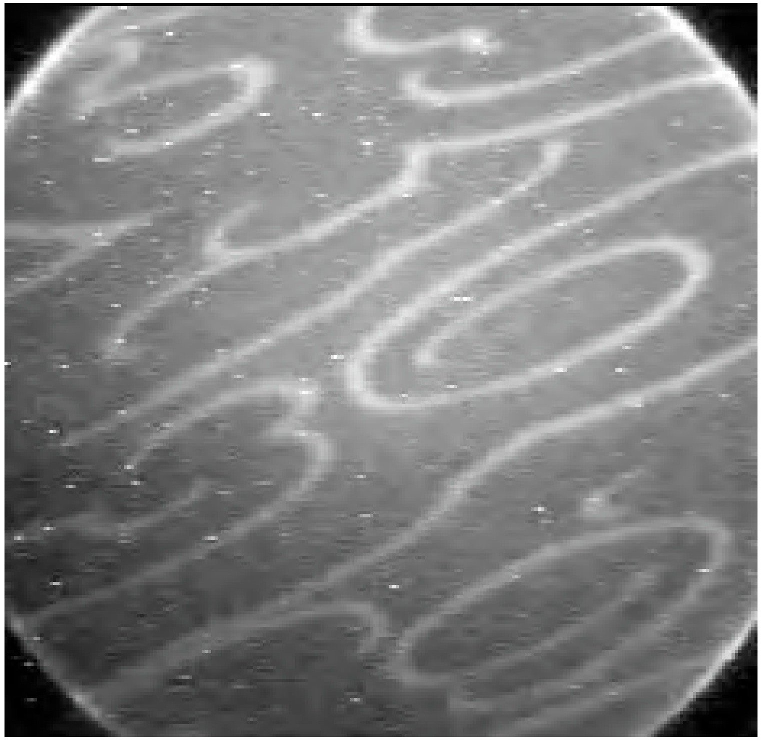
Temperature T = 548 K, oxygen partial pressure p_{o2} = 4 x 10^{-4} mbar, CO partial pressure p_{co} = 1.2 x10^{-4} mbar.

Global delayed feedback



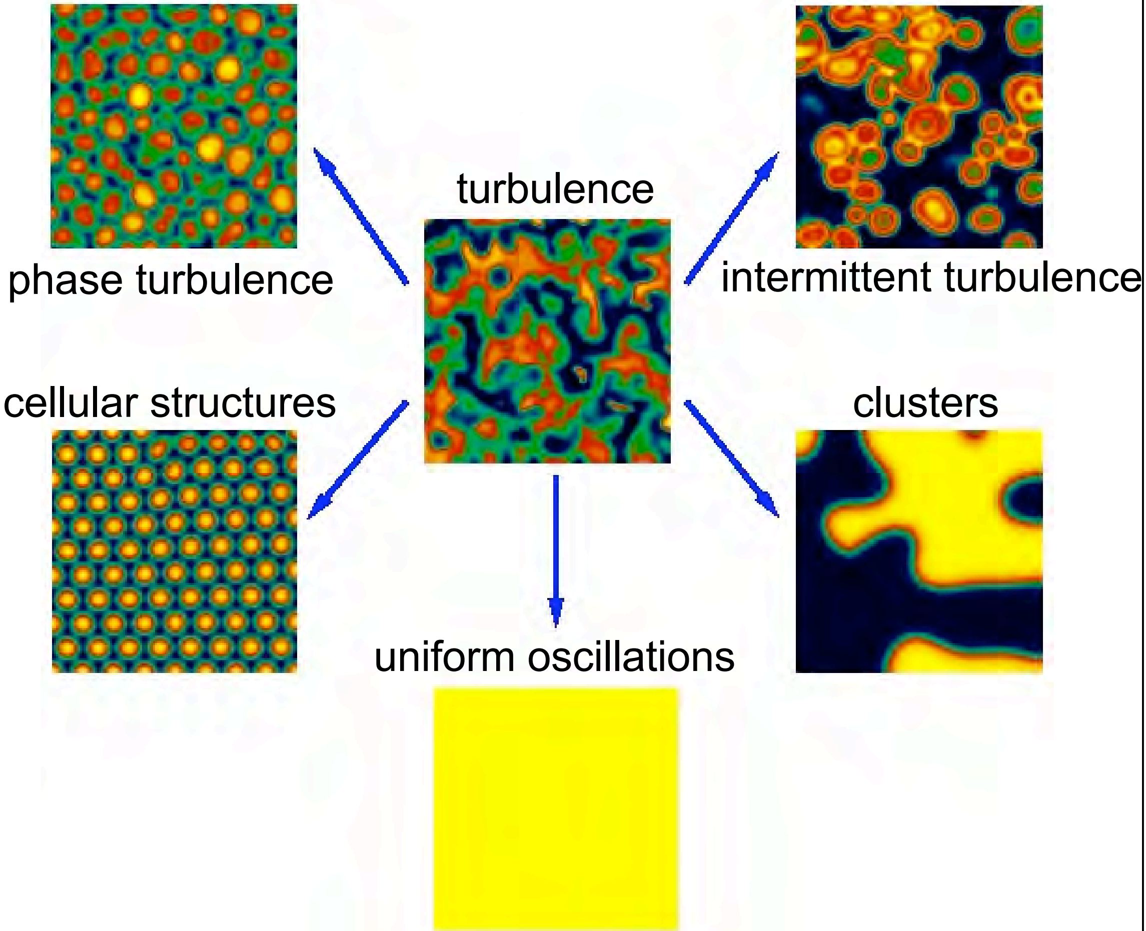
M. Kim, M. Bertram, M. Pollmann, A. von Oertzen;
A.S. Mikhailov, H.H. Rotermund, and G. Ertl,
Science **292** (2001), 1357

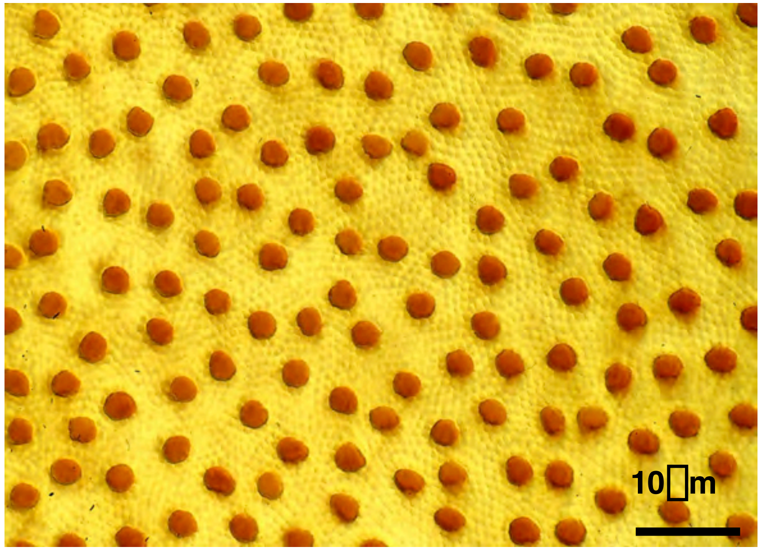
CO oxidation reaction on Pt(110)



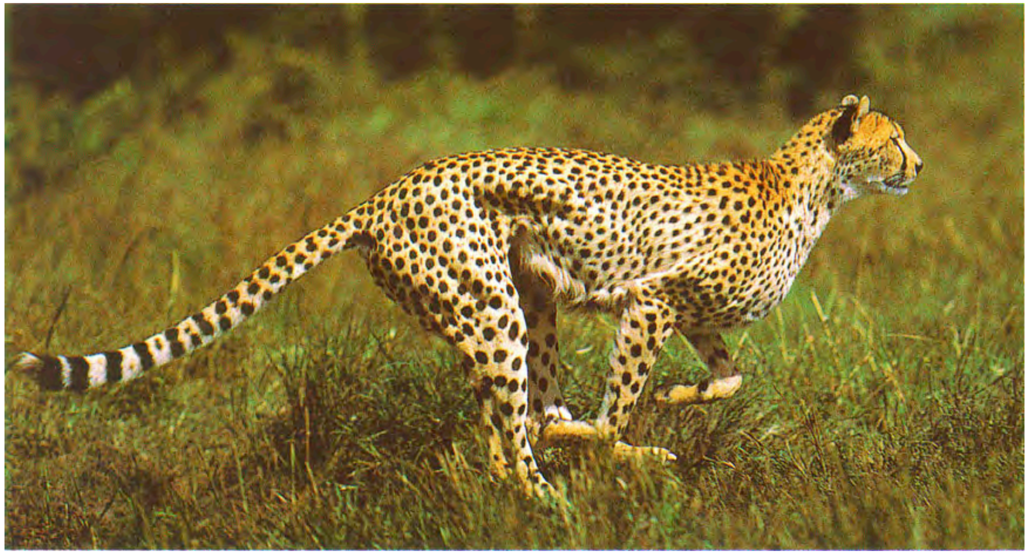
- Suppression of spiral-wave turbulence and development of intermittent turbulence with cascades of reproducing bubbles

CO oxidation on Pt(110) with delayed global feedback





Retina



Heterogeneous catalysis : Dynamics of surface reactions