2012

Making Bread from Air: The World's Most Important Chemical Synthesis

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The World's Most Important Chemical Synthesis

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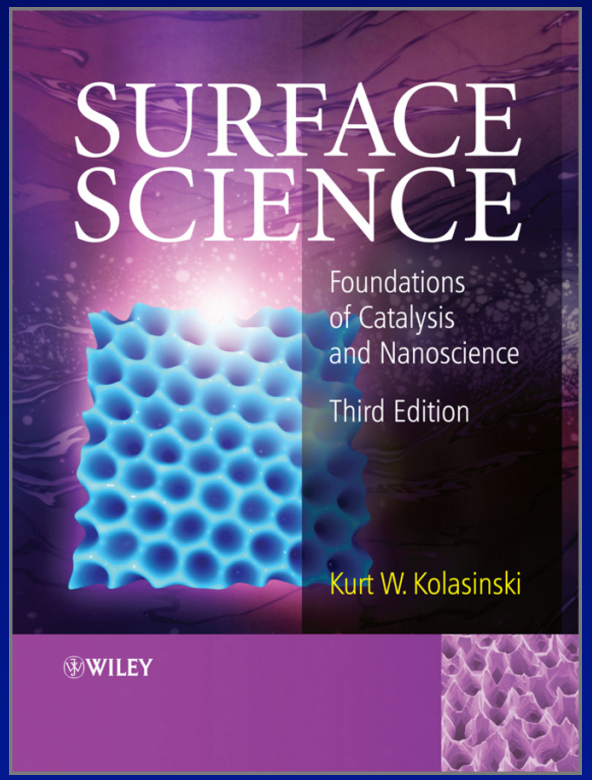
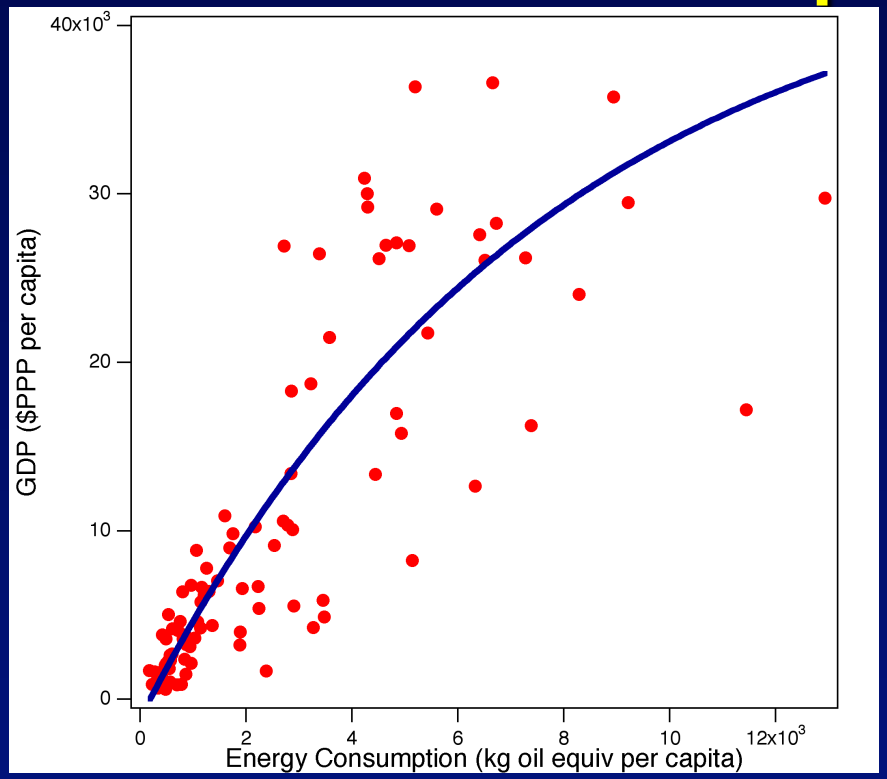


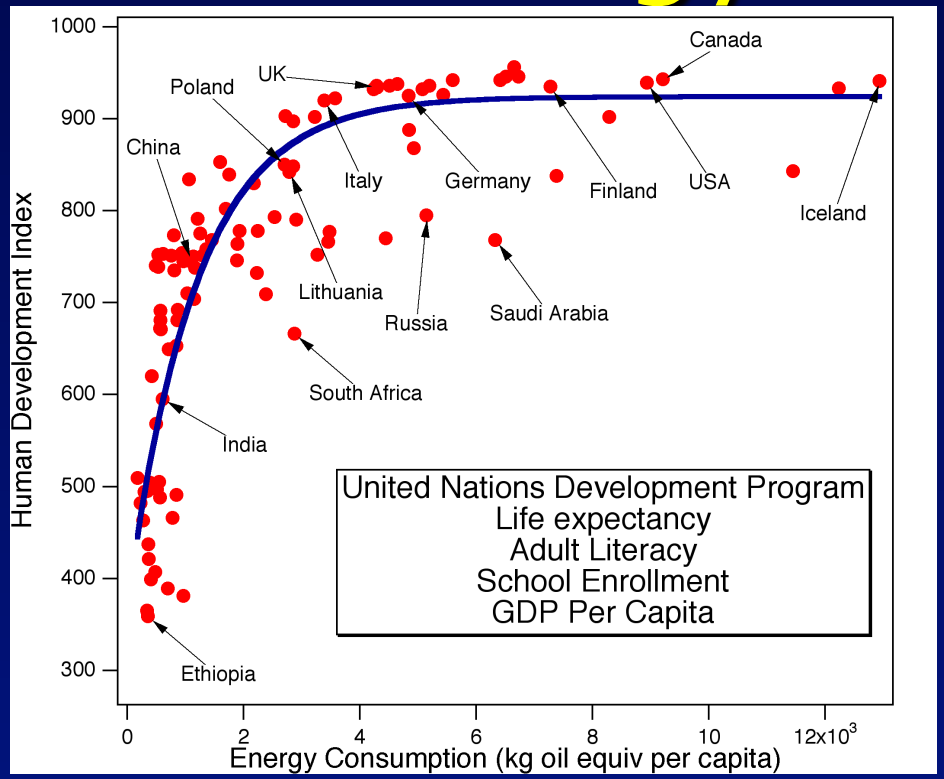
Too Precious to be Expensive

- Energy
- Water
- Ammonia

- What does surface chemistry have to offer?

Human Impact of Energy





- Strong correlation between HDI & energy consumption
- To elevate Developing World to status of Poland requires equivalent of 148 Mbbl/day of oil
- Current production = 84 Mbbl/day
  - Kolasinski, *Curr. Opin. Solid State Mater. Sci.* **2006**, *10*, 129

Ammonia Synthesis

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

- Why so important
- Can it really be that difficult?
- Can it really be that interesting?

Ammonia = Fixed Nitrogen

- Animals need protein (a nitrogen containing molecule)
- Most plants lousy at incorporating nitrogen (need fertilizer)
- Humans now fix more nitrogen than all natural sources combined
- >1% of world energy consumption
- Natural gas is the source of H_2

The Nobel Prize in Chemistry 1918

Fritz Haber

Kaiser-Wilhelm-Institut

Berlin, Germany

"for the synthesis of ammonia from its elements"

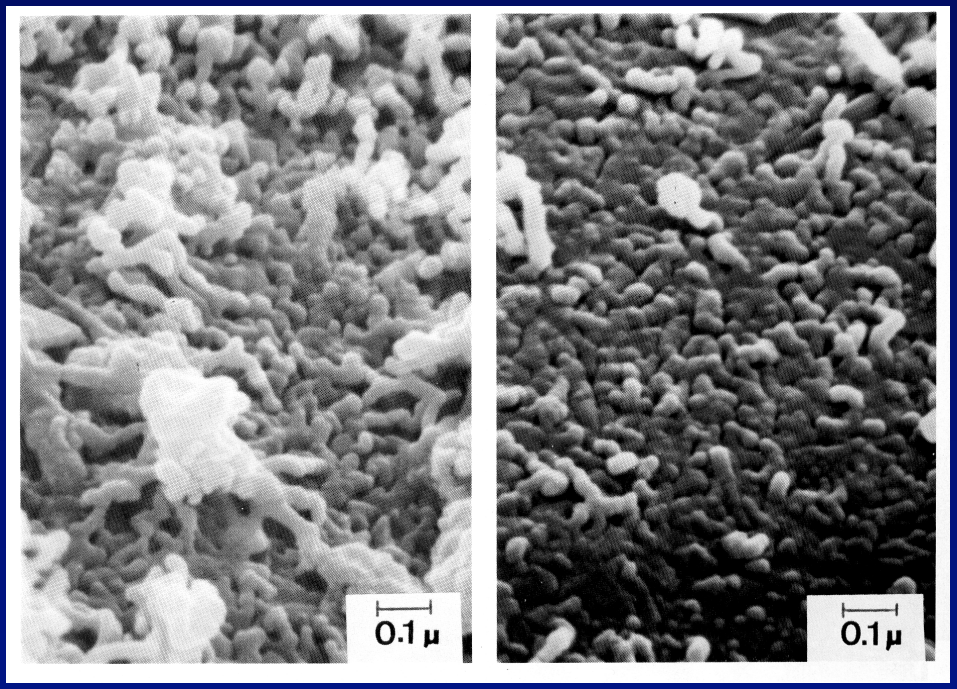
Enriching the Earth, Vaclav Smil, MIT Press (2001)


KAISER WILHELM
INSTITUT FÜR
PHYSIKALISCHE CHEMIE
UND ELEKTROCHEMIE

The Surface Chemical Bond

- Haber is among the first to develop an understanding of how bonds form on surface
- He develops ideas on how to modify and control the chemistry on solid surfaces

Heterogeneous Catalysis



- The ammonia synthesis catalyst as revealed by high-resolution scanning electron microscopy

  G. Ertl, D. Prigge, R. Schloegl, M. Weiss, *J. Catal.*, **79** (1983) 359.
- 200–300 atm, 670–770 K
- 120 MMt annual production
- 1% of world's energy consumption just to run this reaction

The Nobel Prize in Chemistry 1931

Carl Bosch

University of Heidelberg, Germany

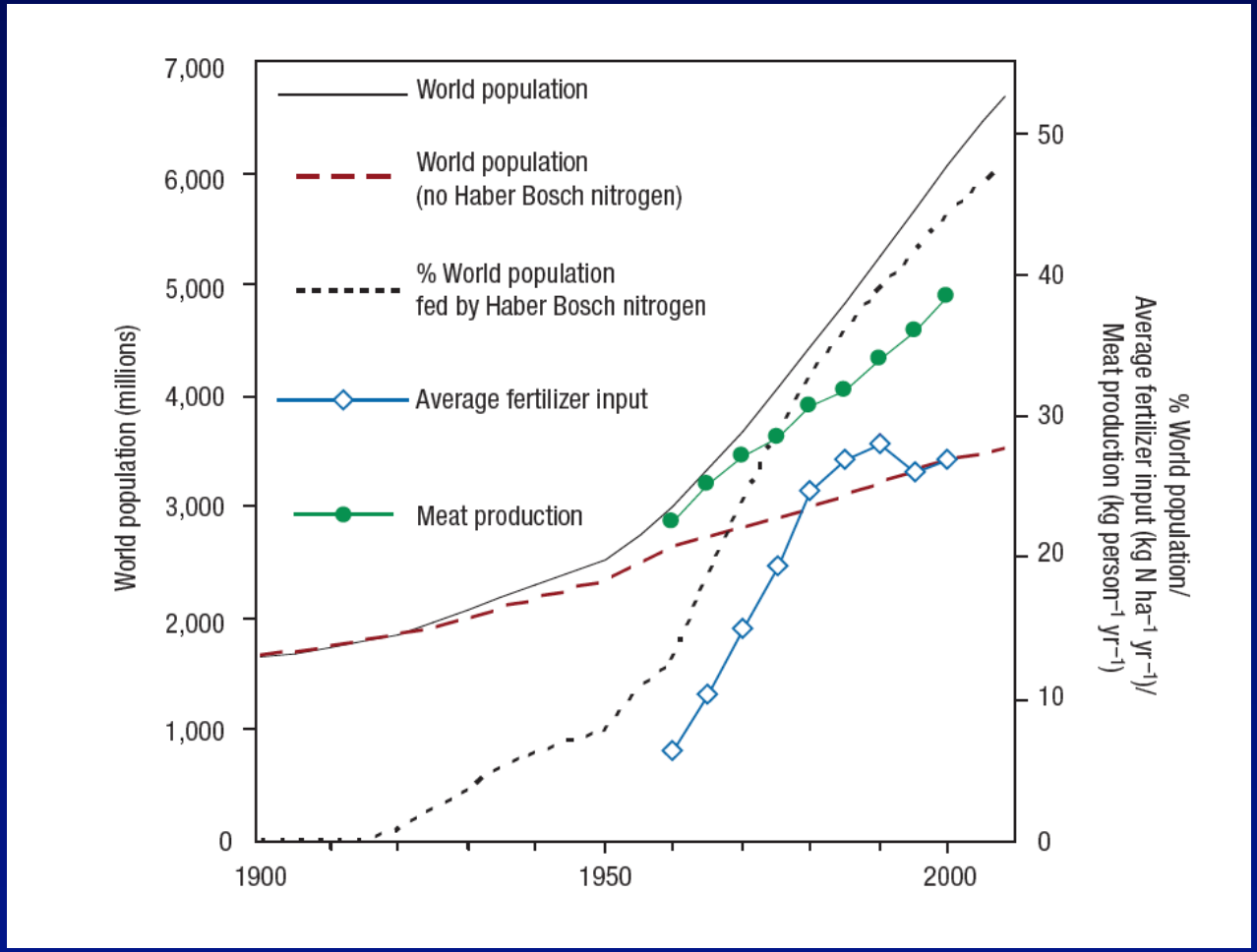
"in recognition of their contributions to the invention and development of chemical high pressure methods"

1965

World population surpasses 3.3 billion

- Modern agriculture dependent on ammonia based fertilizer
- This cannot be replaced by dung
- If ammonia production were shut down, **3.2 billion people** could not be supported by agriculture
- NH_3 requires fossil fuels both for H_2 and for the energy to run the chemical reaction

NH_3 Synthesis is, arguably, the single most important industrial chemical reaction



Erisman, Sutton, Galloway, Klimont & Winiwarter, Nature Geoscience 1 (2008) 636

The Nobel Prize in Chemistry 2007

Gerhard Ertl

Fritz-Haber-Institut

Berlin, Germany

"for his studies of chemical processes on solid surfaces"

G. Ertl, Angew. Chem., Int. Ed. Engl. 47 (2008) 3524

Surface Reaction Dynamics

- CO oxidation to form CO_2 on platinum

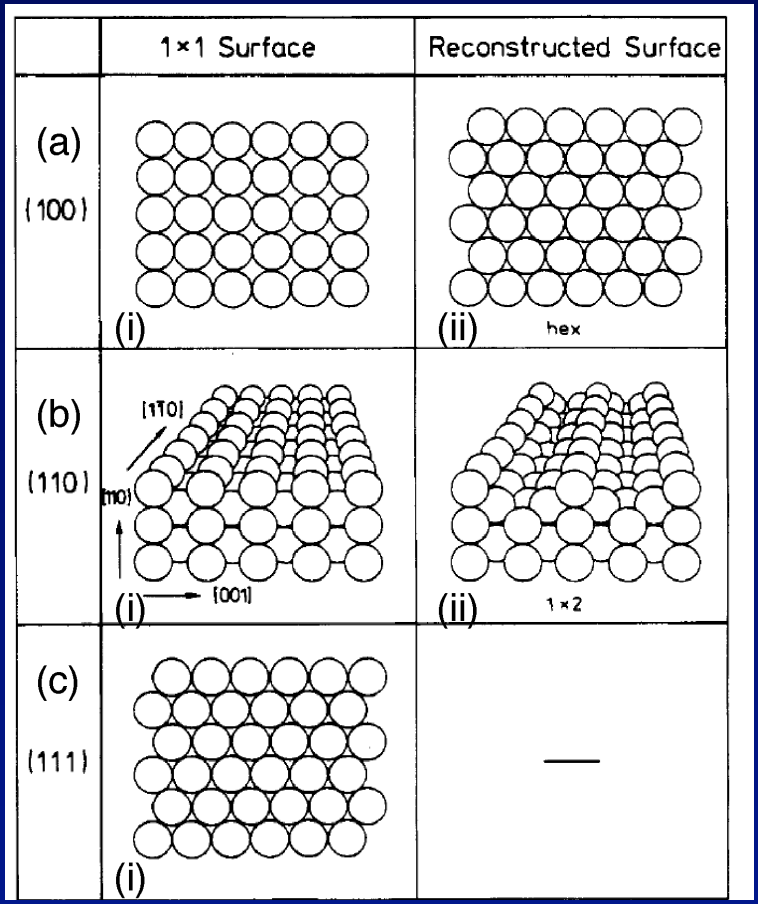
$$CO + * \rightarrow CO*$$

$$O_2 + 2* \rightarrow 2O*$$

$$O* + CO* \rightarrow CO_2$$

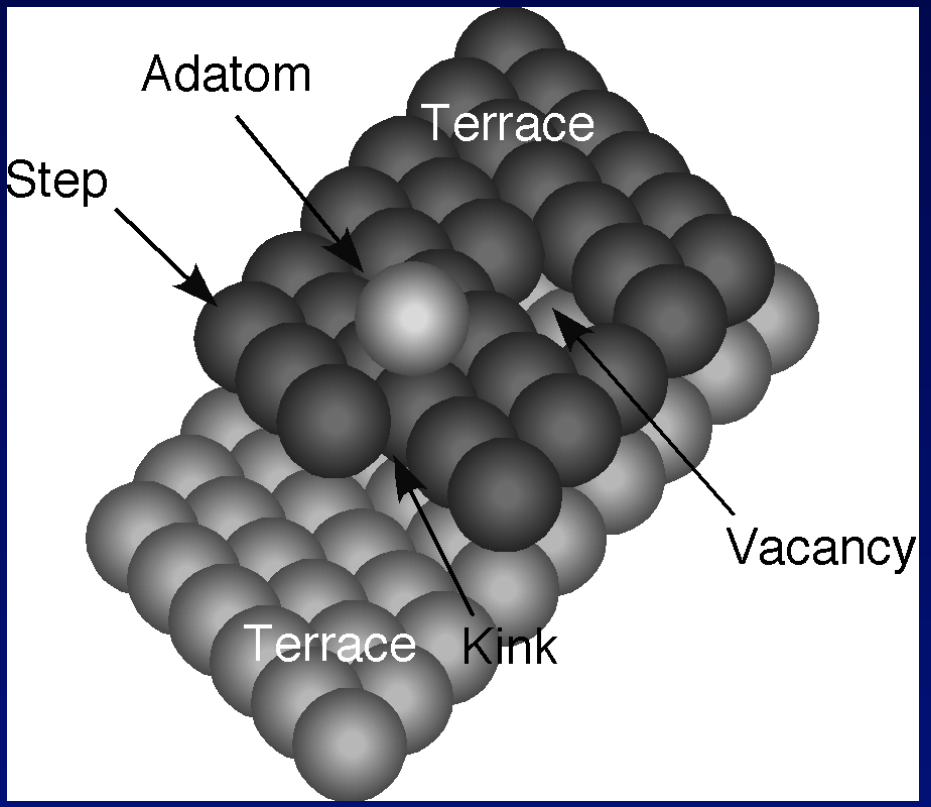
Imbihl & Ertl, *Chem. Rev.*, **95** (1995) 697
Wolff, Papathanasiou, Kevrekidis, Rotermund & Ertl, Science 294 (2001) 134
Ertl, *Reactions at Solid Surfaces*. (Wiley, Hoboken, NJ, 2009)

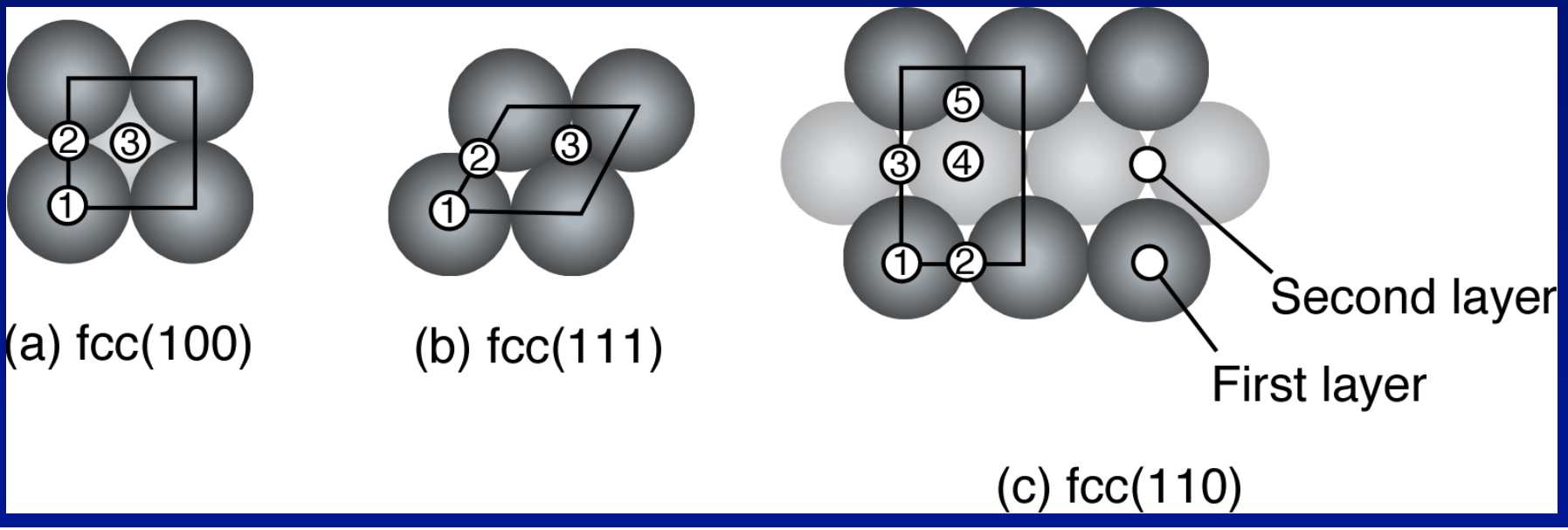
Surface Structure



- Reconstructed and non-reconstructed surfaces for the three low-index planes of Pt. Reproduced from R. Imbihl and G. Ertl, Chem. Rev. **95** (1995) 697.

Adsorbate Structure





Ammonia Synthesis

$H_2(g) + 2* \rightarrow 2H*$

$N_2(g) + * \rightarrow N_2*$

$N_2* + * \rightarrow 2N*$ (RDS)

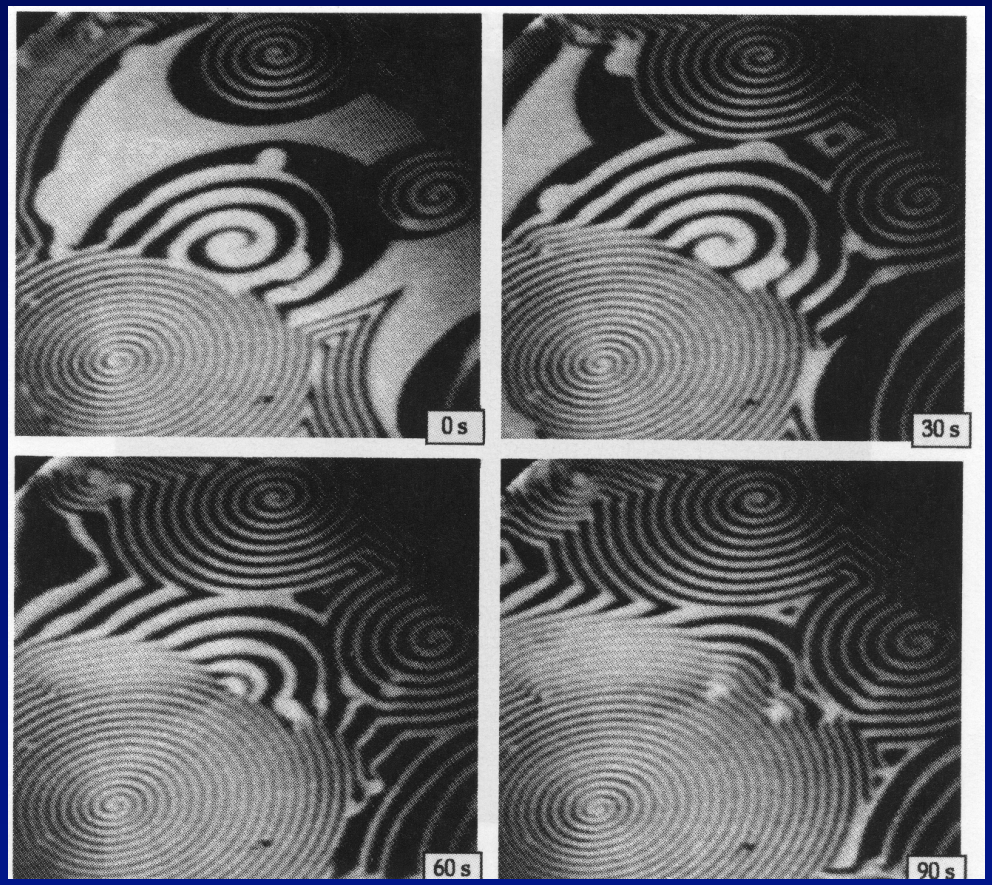
$N* + H* \rightarrow NH* + *$

$NH* + H* \rightarrow NH_2* + *$

$NH_2* + H* \rightarrow NH_3* + *$

$NH_3* \rightarrow NH_3(g) + *$

Surface Reaction Dynamics



- Spatiotemporal pattern formation in CO oxidation over Pt. Reproduced from R. Imbihl, G. Ertl, *Chem. Rev.*, **95** (1995) 697.

Solar Land Area Requirements

- U.S. Land Area: 9.1×10^{12} m^2 (incl. Alaska)
- Average Insolation: 200 W/m^2
- 2000 U.S. Primary Power Consumption: 99 Quads=3.3 TW
- 1999 U.S. Electricity Consumption = 0.4 TW
- Hence:
  3.3×10^{12} $W/(2 \times 10^2$ W/m^2 x 10% Efficiency) = 1.6×10^{11} m^2
  Requires 1.6×10^{11} m^2/ 9.1×10^{12} m^2 = 1.7% of Land

Nathan S Lewis, Caltech, http://nsl.caltech.edu

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Solar Land Area Requirements

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Challenges in Surface/Nano/ Materials Chemistry

- Solar! Solar!! Solar!!!
  - Nanocrystalline materials for light conversions
  - Charge transfer dynamics
  - Thin films of conducting organic polymers
  - Solar fuels
- Biorefinery
- Hydrogen production
- Hydrogen storage
- Fuel cells
- Interfaces
  - Catalysis
  - Electrode/Electrolyte
- Materials
  - Superconductors
  - Thermoelectrics
  - Smart windows
  - Batteries

Nonlinear Dynamics: Pattern Formation in Chemical Reactions

Wolff, Papathanasiou, Kevrekidis, Rotermund & Ertl, Science 294 (2001) 134
Ertl, *Reactions at Solid Surfaces*. (Wiley, Hoboken, NJ, 2009)