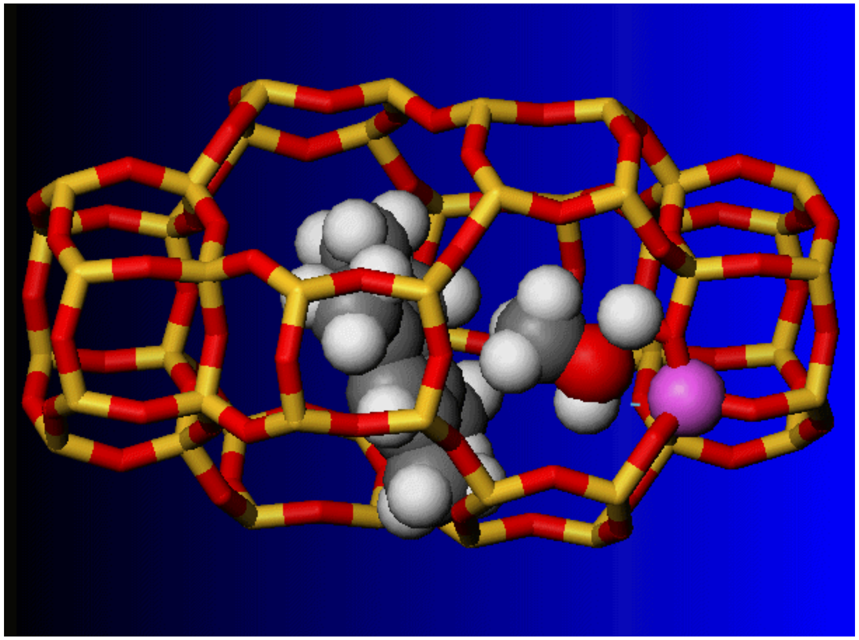
CATALYSIS – A small glimpse into an (industrially & vitally) important area

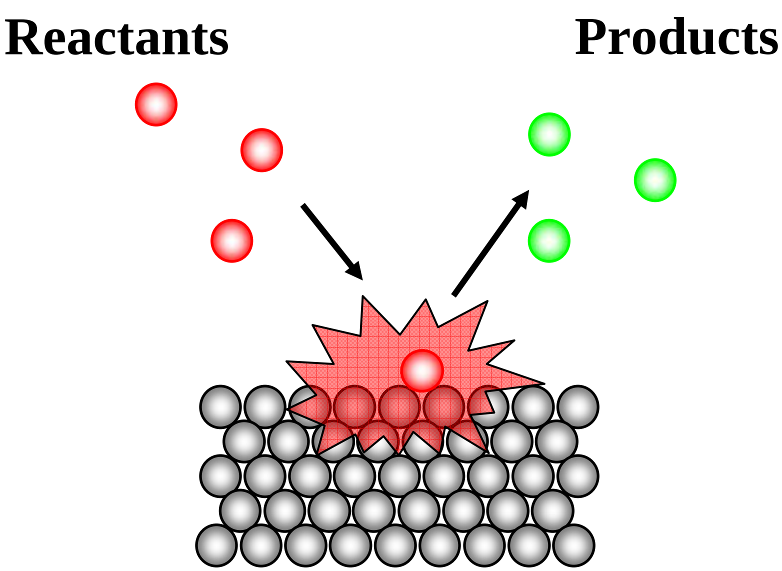


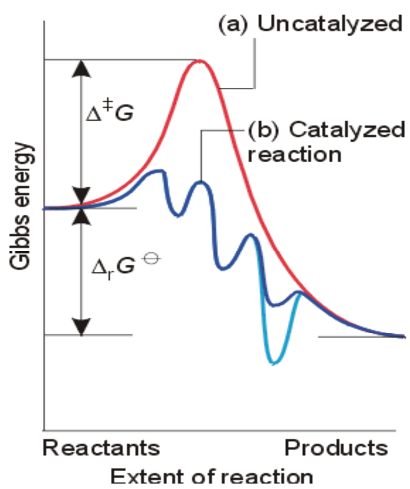
MEF1000 – 28.10.2004

Unni Olsbye

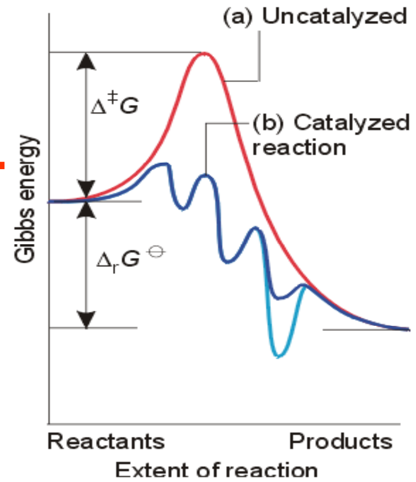
What is catalysis?

- “Chemical marriage brokers”





A catalysis example



H_2O_2 (l) –> H_2O (l) + O_2 (g) dE = 1,06 V

The reaction is thermodynamically feasible, but slow.

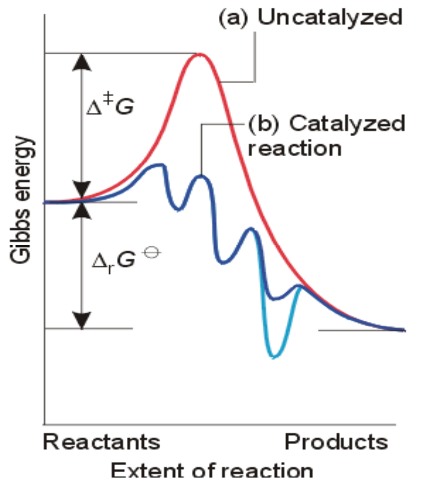
H_2O_2 (l) –> H_2O (l) + O_2 (g) dE = 1,06 V

What happened?

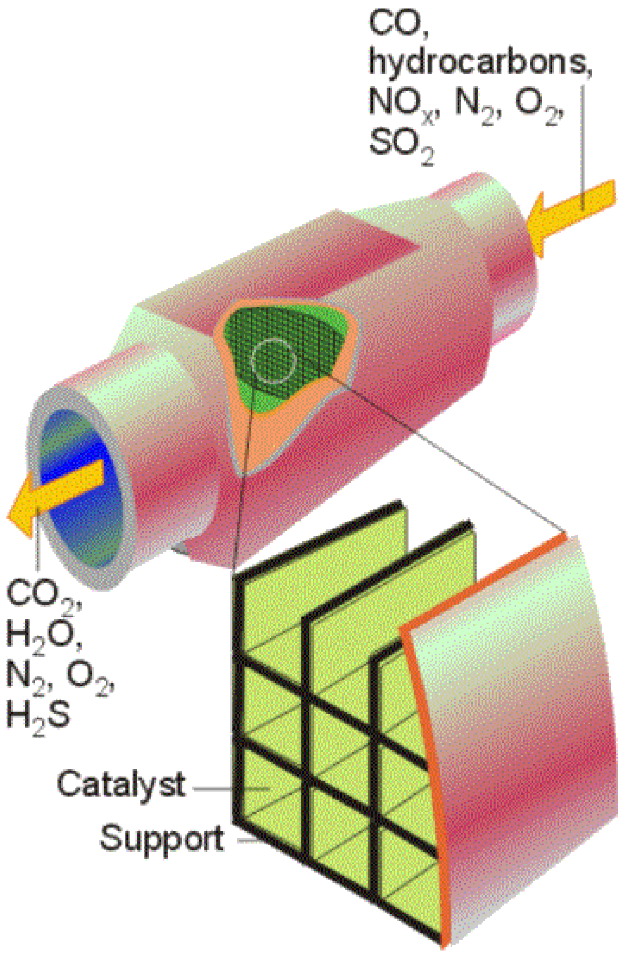
$H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O$	dE = 1,34 V
$2\,I^- \rightarrow I_2 + 2\,e^-$	dE = -0,53 V
	dE(tot) = 0,81 V
$H_2O_2 + \rightarrow O_2 + 2\,H^+ + 2\,e^-$	dE = -0,29 V
$I_2 + 2\,e^- \rightarrow 2\,I^-$	dE = 0,53 V
	dE(tot) = 0,24 V

- I^- is a catalyst for the reaction:
- It participates in the reaction without being consumed (=definition of a catalyst)

A catalyst increases the speed (and selectivity) of a reaction by changing the reaction path. BUT:
It does not change the thermodynamics of reaction



Where do we find catalysts?



In a car:

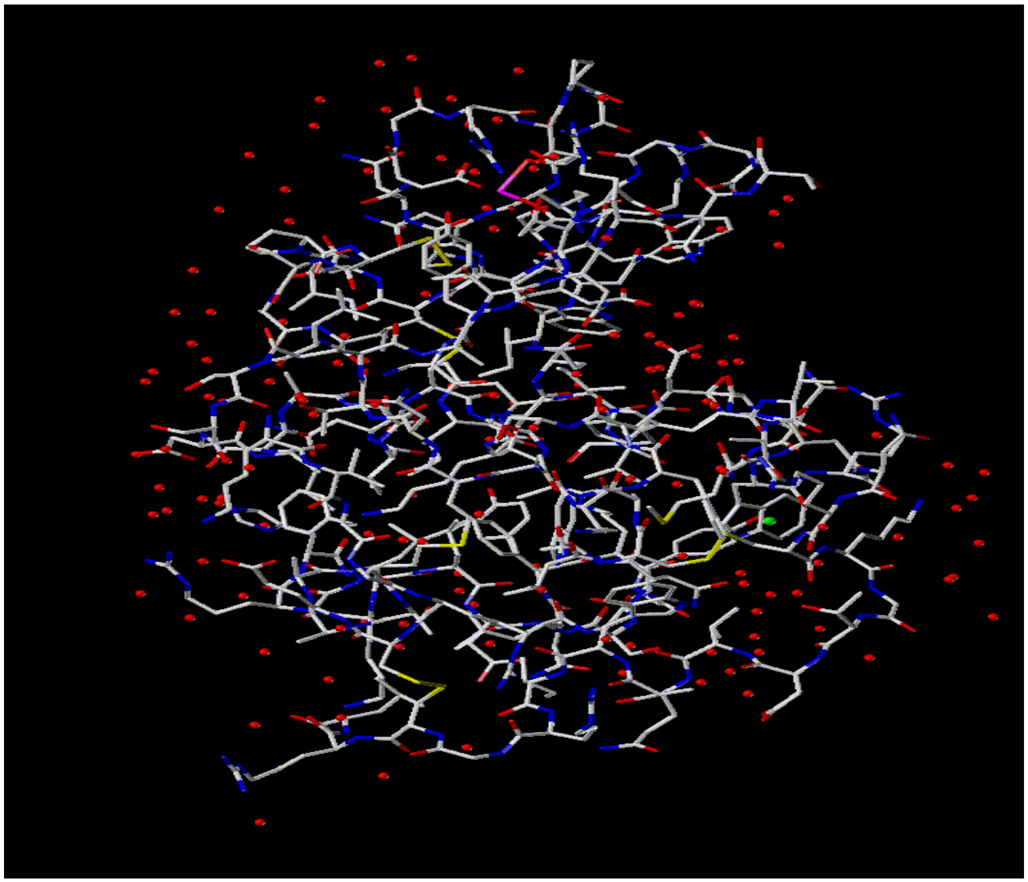
When gasoline is burned in the car engine, there is formation of nitrous oxides ($N_2 + O_2 \rightarrow 2\ NO$) and carbon monoxide (CO), and some unconverted gasoline leaves the engine.

Therefore, the exhaust is passed over a catalyst which transforms NO to air (N_2 + O_2) and oxidises CO and unconverted gasoline to CO_2 and water (steam).

Without a catalyst:

The mixture of NO_x, CO and gasoline forms smog (= smoke + fog). Smog gives dim air which may lead to health problems. The pollution also leads to acid rain. A car catalyst is shown to the left.

Where do we find catalysts?



In our bodies:
We have lots of catalysts in our bodies. In living species a catalyst is called an enzyme. Enzymes are specific and selective, and thus a source of inspiration for all catalysis chemists.

Without a catalyst:
We would not exist.

The enzyme lysozyme is shown to the left. This enzyme fights bacterias by dismantling their cell walls.

Where do we find catalysts?

In oil refineries
Every minute, day and night, 10 000 tons of oil (=1000 tankers) passes over a catalyst which transforms it into e.g. gasoline, diesel, and oil for heating purposes.

Other industries
Pharmaceuticals are produced by a series of complicated chemical reactions. Many steps are catalysed.

An oil refinery is shown to the left.

Industrially important processes (1997)

Kjemisk produkt	**Rekkefølge***	**Katalytisk prosess**
Eten	1	Hydrokarbon cracking, heterogen
Svovelsyre	2	SO_2 oksidasjon, heterogen
Propen	3	Hydrokarbon cracking, heterogen
1,2-Dikloretan	4	$C_2H_4 + Cl_2$; heterogen
Kalsiumhydroksid $Ca(OH)_2$	5	Uten katalysator
Ammoniakk	6	$N_2 + H_2$; heterogen H_2 og energi fra CH_4
Urea	7	Fra NH_3 katalysert
Fosforsyre	8	Uten katalysator
Klor	9	Elektrolyse
Etylbenzen	10	Alkylering av benzen, homogen katalyse
$NaCO_3$	11	Uten katalysator
NaOH	12	Elekrolyse
Styren	13	Dehydrogenering av ethylbenzen, heterogen
HNO_3	14	$NH_3 + O_2$, heterogen
NH_4NO_3	15	Forløper katalytisk
HCl	16	Forløper katalytisk
Akrylonitril	17	$HCN + C_2H_2$, homogen katalyse
$(NH_4)_2SO_4$	18	Forløper katalytisk
K_2O	19	Uten katalysator
TiO_2	20	Uten katalysator

*) Fra Chemical and Engineering news, June 29 (1998)

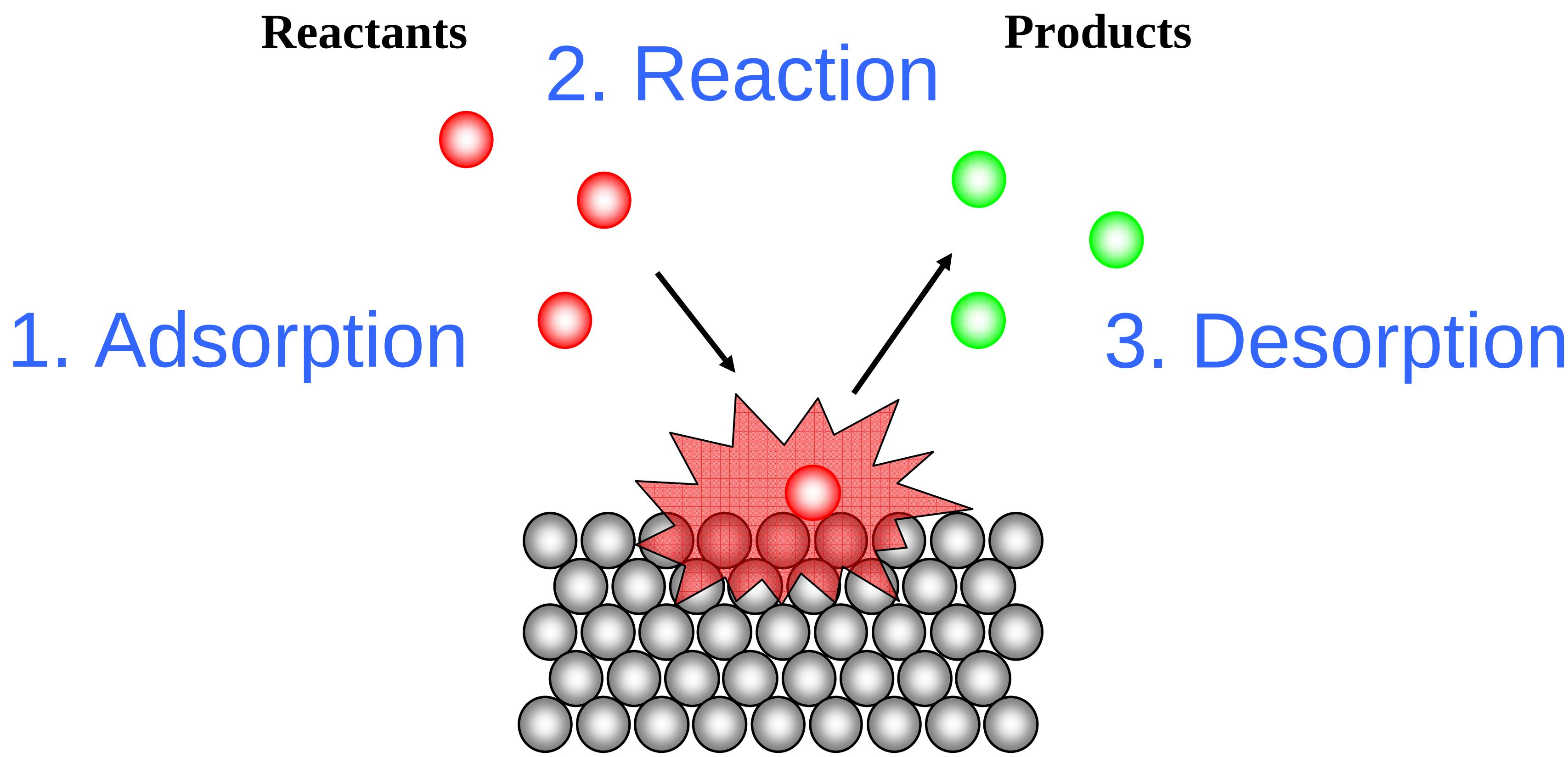
Homogeneous vs. Heterogeneous catalysis

- Homogeneous catalysis
  - The catalyst, reactants and products are all in one phase, normally the liquid phase. The reactions proceed over a metal complex and are often highly selective, but separation of the products and the catalyst is difficult.

- Heterogeneous catalysis
  - The catalyst is in one phase, normally solid, while the reactants and products are in another phase. Separation of catalyst and products is easy, but the reaction is often less selective, because the catalyst material is not homogeneous.

Most industrial processes are based on heterogeneous catalysts, and the rest of this lecture will be devoted to heterogeneous catalysis.

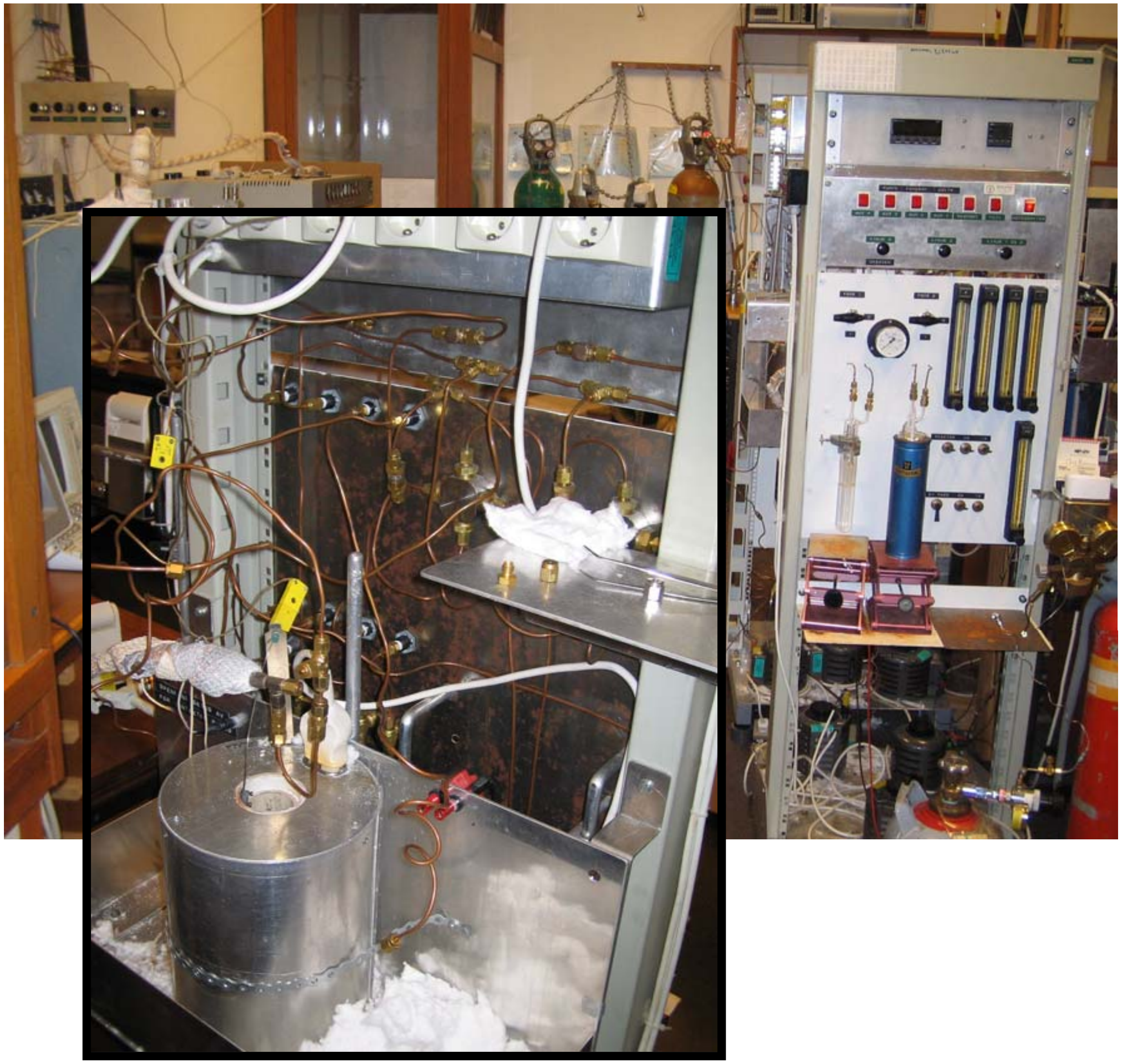
Steps in a heterogeneously catalysed reaction



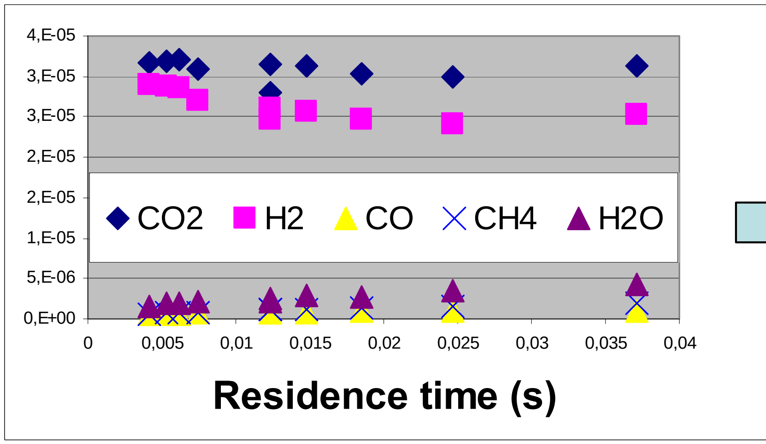
How to study a catalytic reaction?

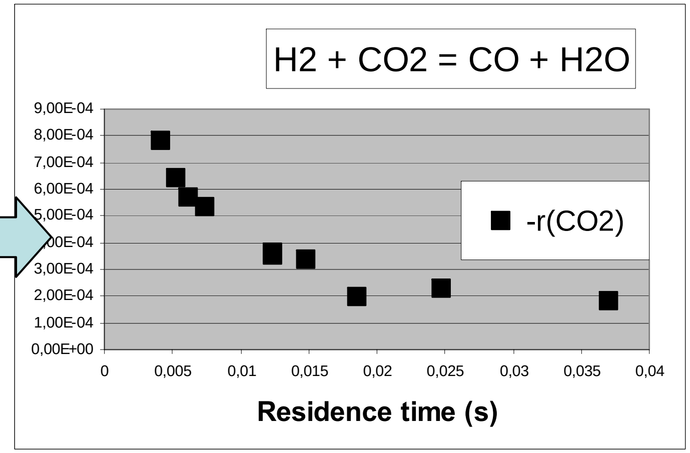
- Catalytic testing
- Mechanistic studies
  - Isotopic labelling
  - Spectroscopy
- Adsorption calorimetry
- Theoretical modelling

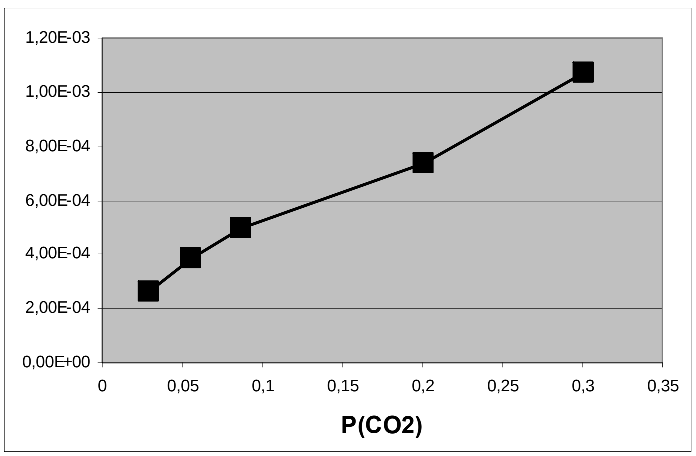
Catalytic testing

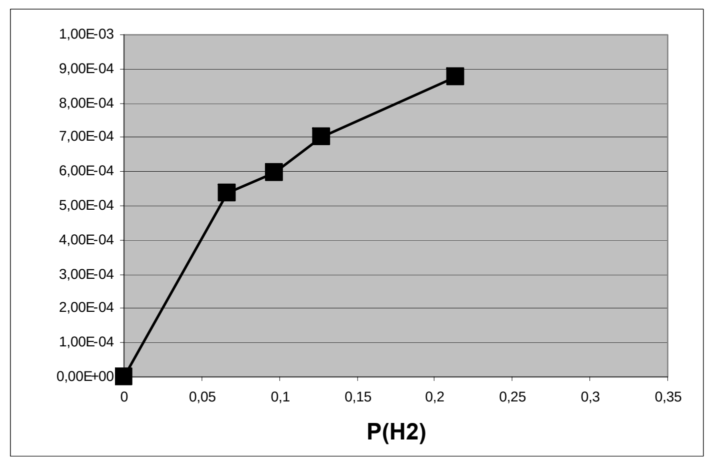


Catalytic testing (II)





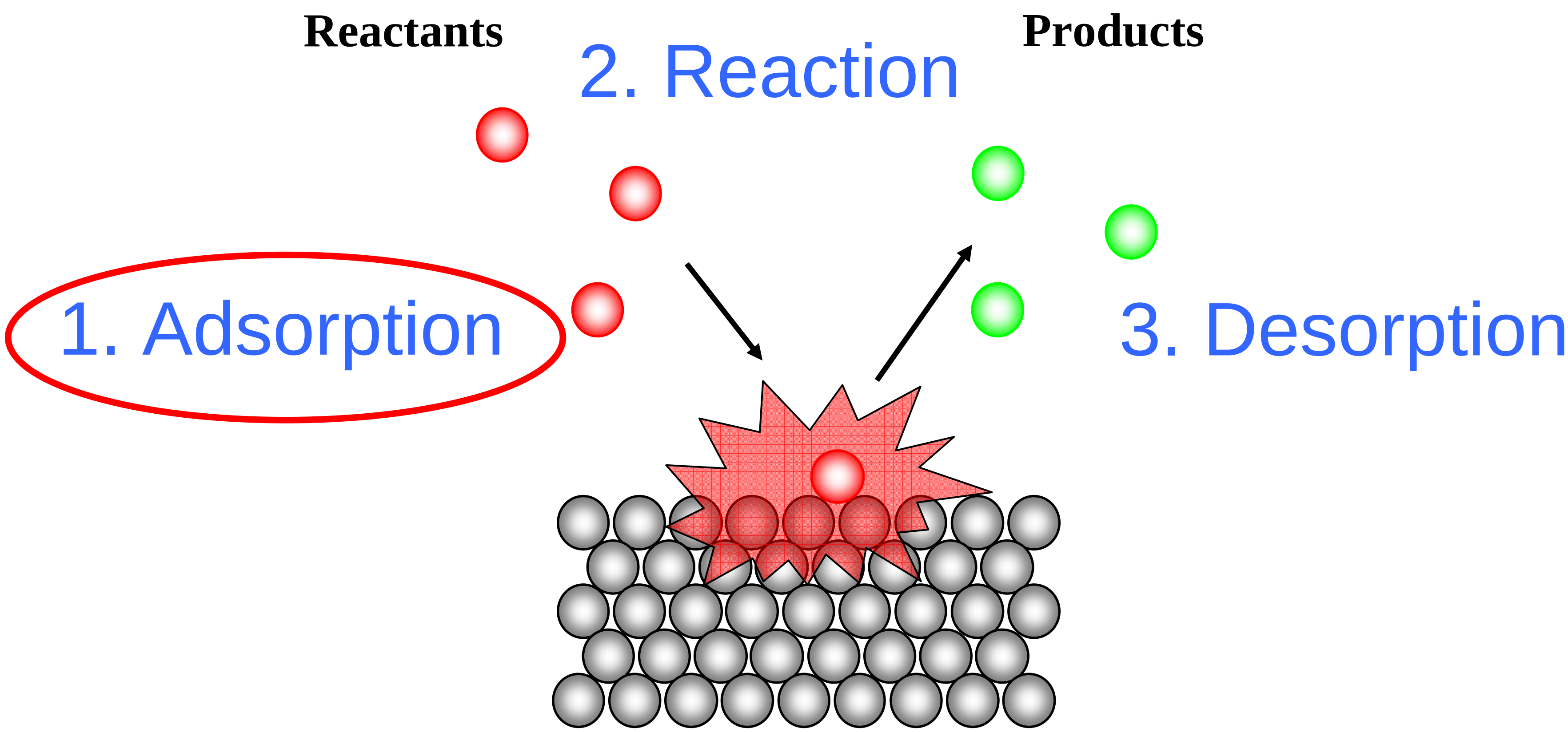




The catalyst is gradually covered by reaction species;

products ..and reactants

Steps in a heterogeneously catalysed reaction



Adsorption energies

Adsorption energy:

$\Delta G = \Delta H - T \Delta S$

$\Delta S < 0 \Rightarrow \Delta H < 0$

Adsorption is (nearly) always an exothermic process

The heat of adsorption, ΔH, may be measured by adsorption microcalorimetry

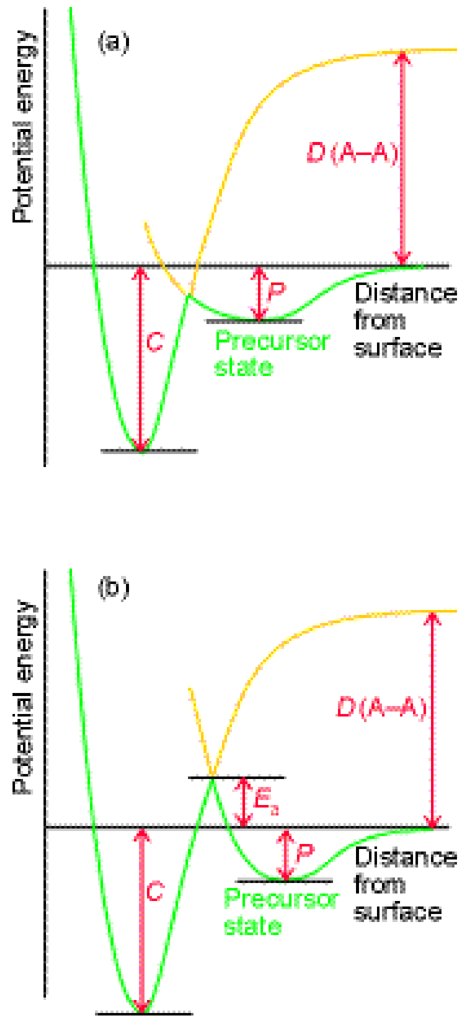


Illustration: Atkins VI, Figure 28.29

Adsorption calorimetry

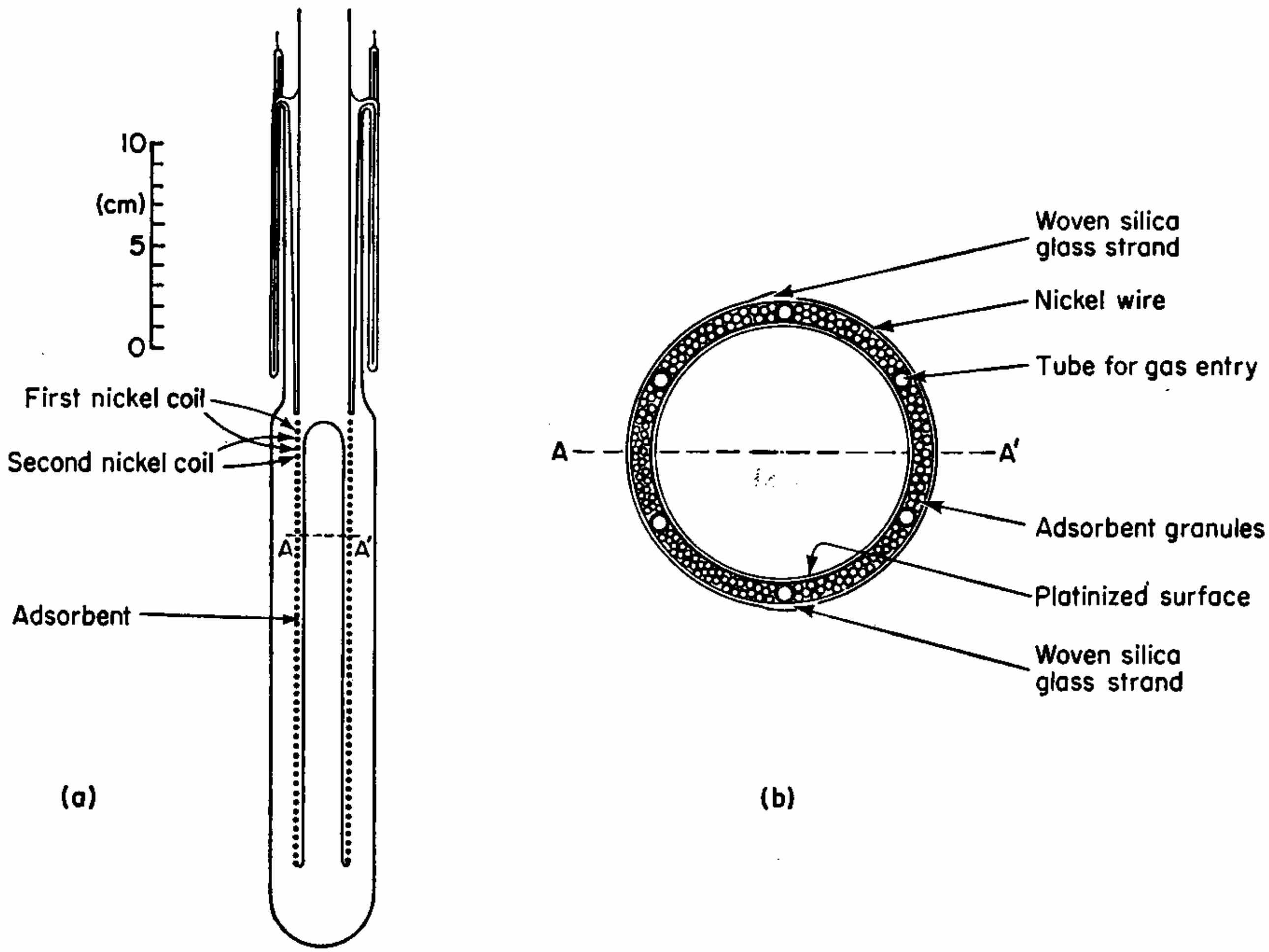
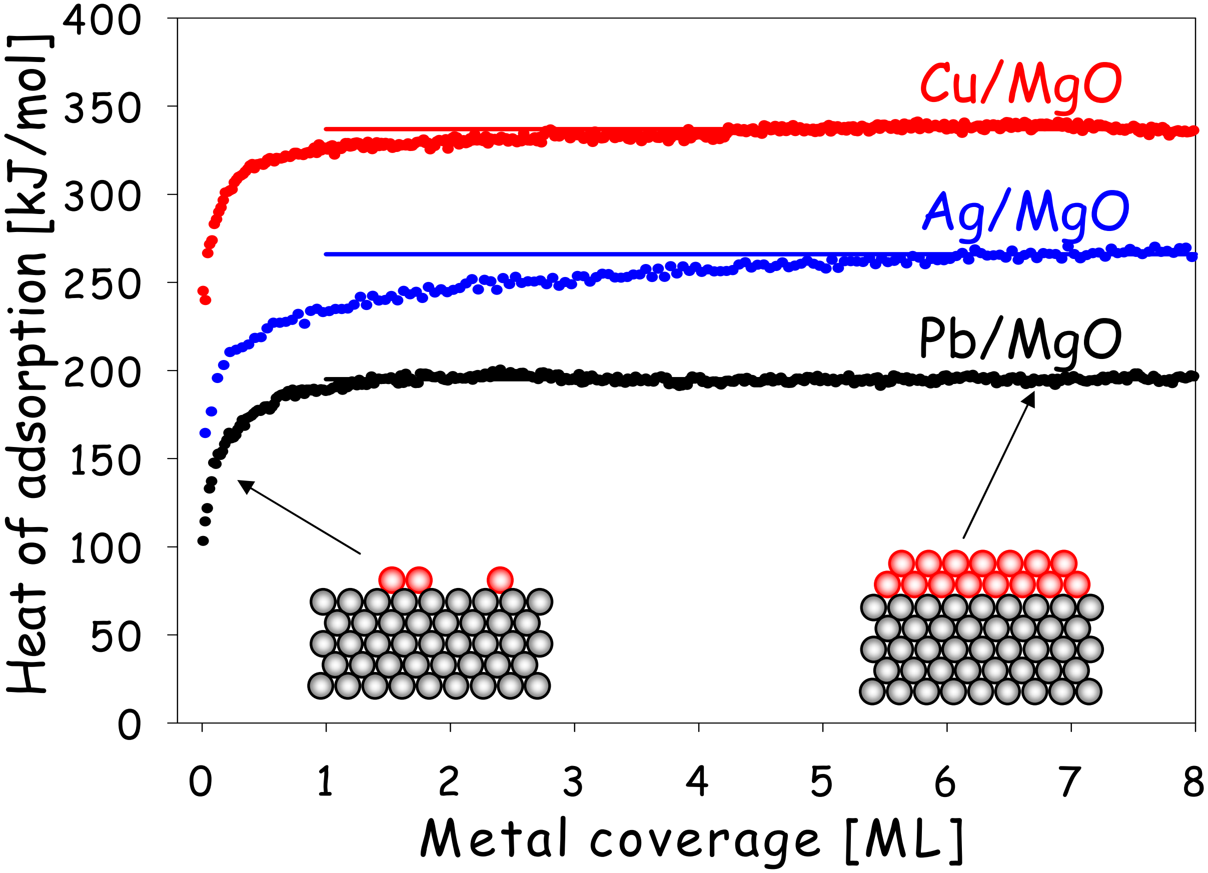
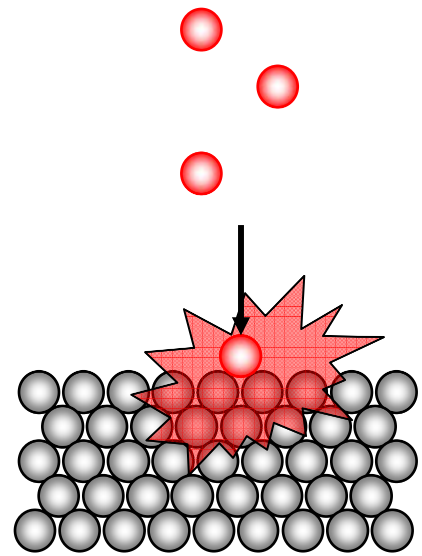


FIG. 12. (a) Diagram of the calorimeter used by Stone and co-workers [*211*] for measuring heats of adsorption on granulated catalysts. (b) Enlarged cross-section of central portion AA'.

Delanney: Characterisation of heterogeneous catalysts

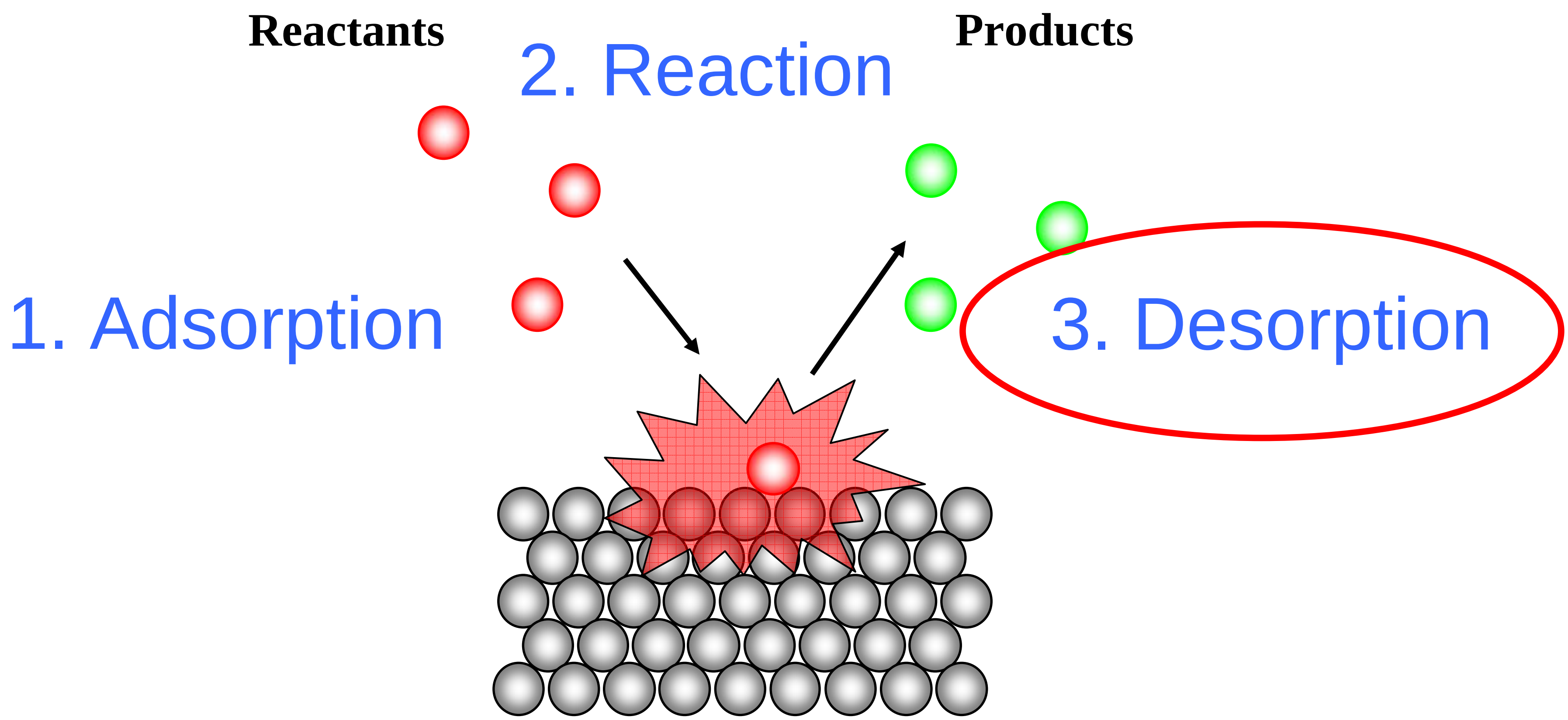
Single crystal microcalorimetry





Larsen, Starr, Campbell, Chem.Thermodyn. **33**, 333 (2001)
Brown, Kose, King, Chem. Rev. **98**, 797 (1998).

Steps in a heterogeneously catalysed reaction



Temperature-programmed methods

Heating of an adsorbent-adsorbate system typically gives rise to the following desorption spectrum:

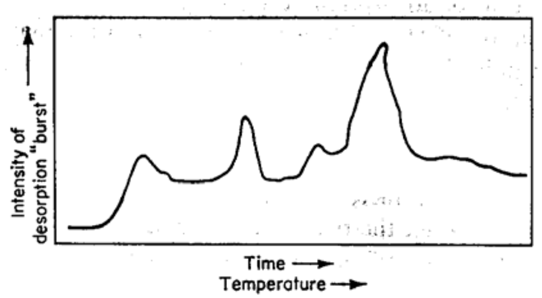
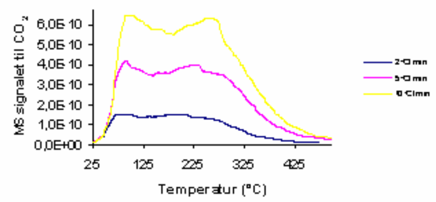
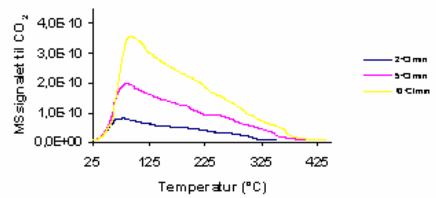


FIG. 14. Illustration of a typical desorption spectrum.

Thomas & Thomas 1st ed. (1967)



Desorption of CO_2 from HT at three different heating rates.



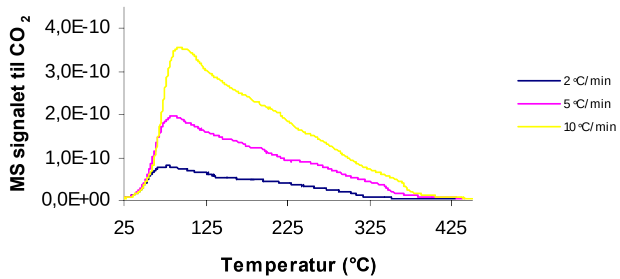
Desorption of CO_2 from Pt/HT at three different heating rates.

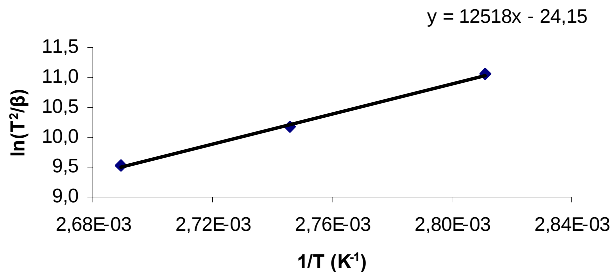
Jasmina Hafizovic, UiO (2004)

The different peaks correspond to adsorption sites with different bond energy to the adsorbate.

Temperature-programmed desorption

Example





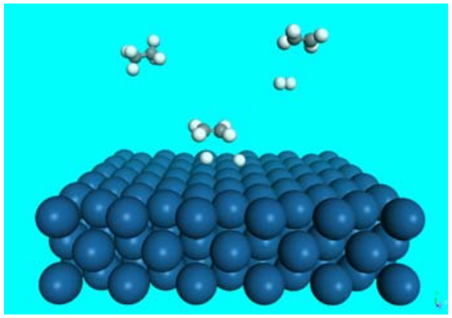
The activation energy for desorption is calculated from the slope of the plot above.

Sample	E_d (kJ/mol)
HT	104
Pt/HT_a	80
Pt/HT_b	106
Pt/HT_c	87
Pt/HT_d	94

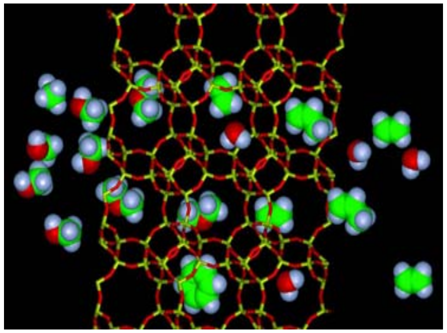
Illustrations: Jasmina Hafizovic, UiO

Two main classes of heterogeneous catalysts

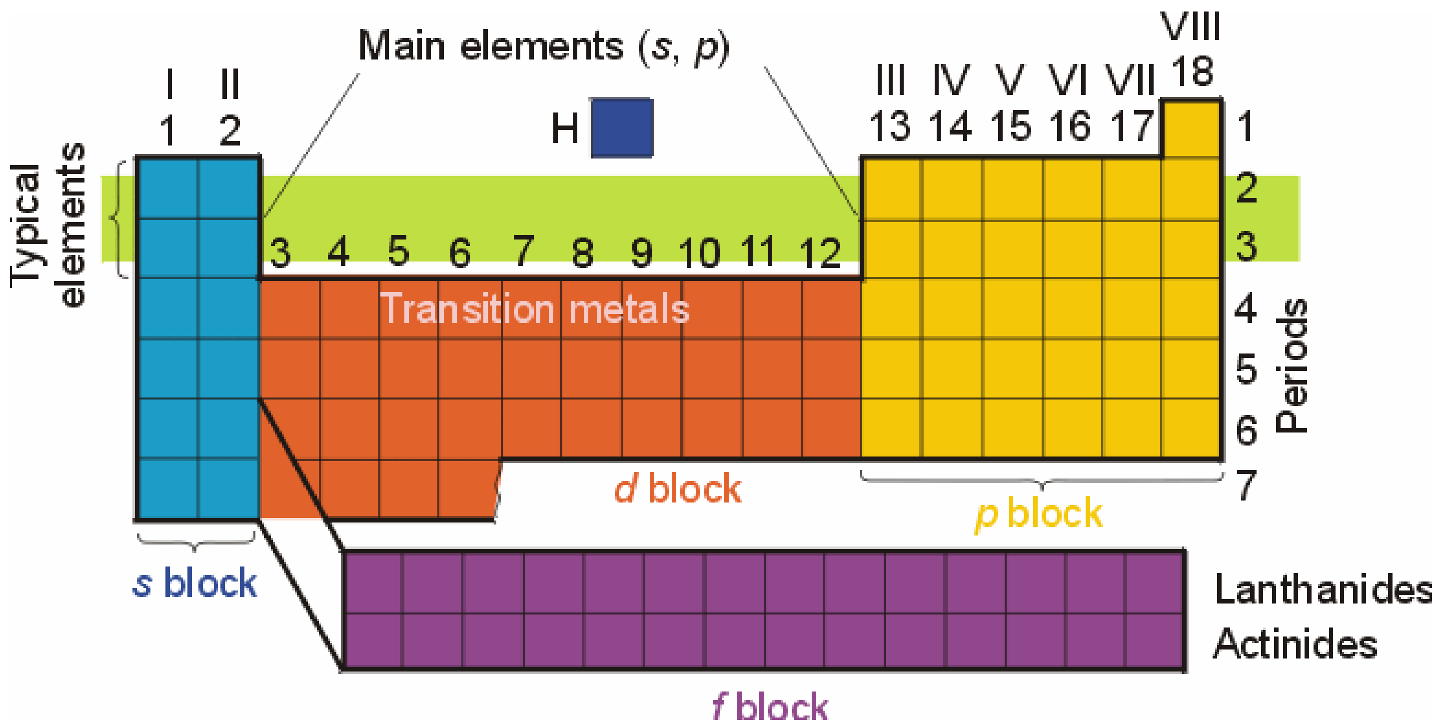
- ”Red-ox” catalysts (electron transfer)
  - Metal
  - Metal/Support



- ”Acid-base” catalysts (proton transfer)
  - Phosphorous acid/support
  - Zeolites



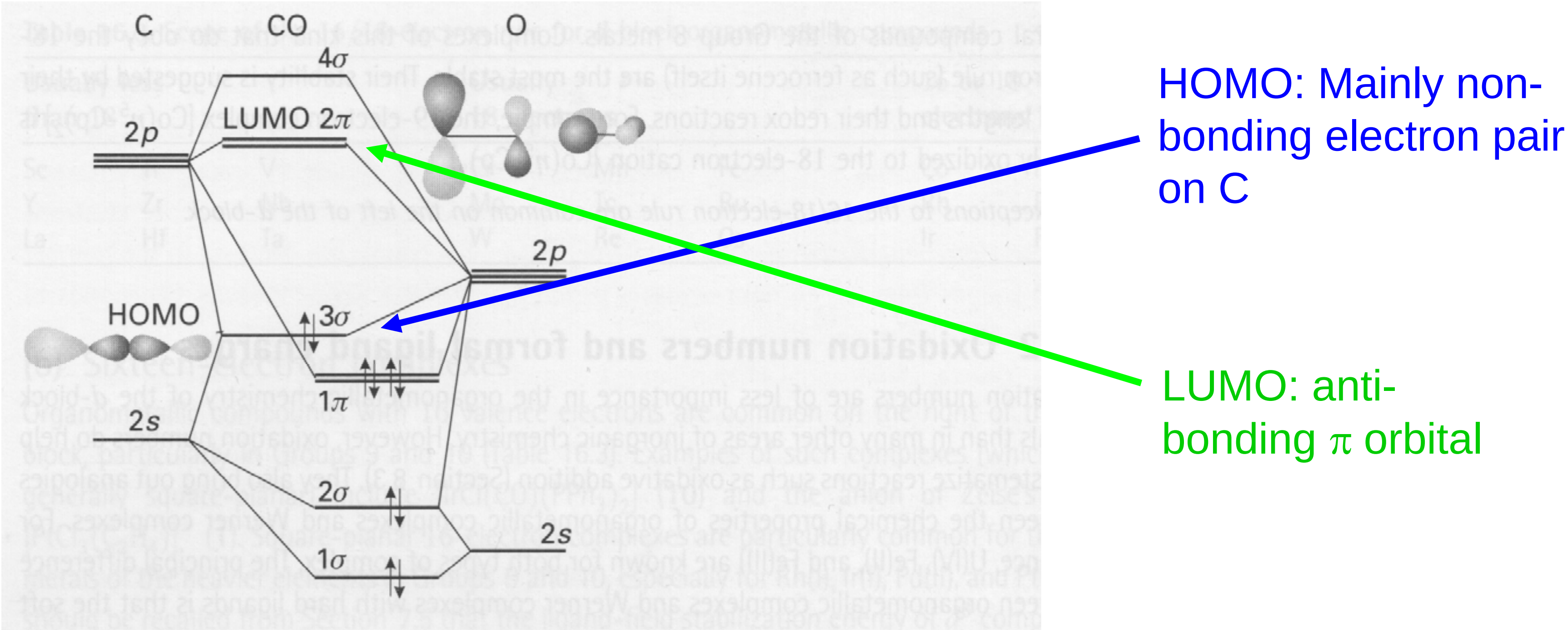
Metal catalysed reactions



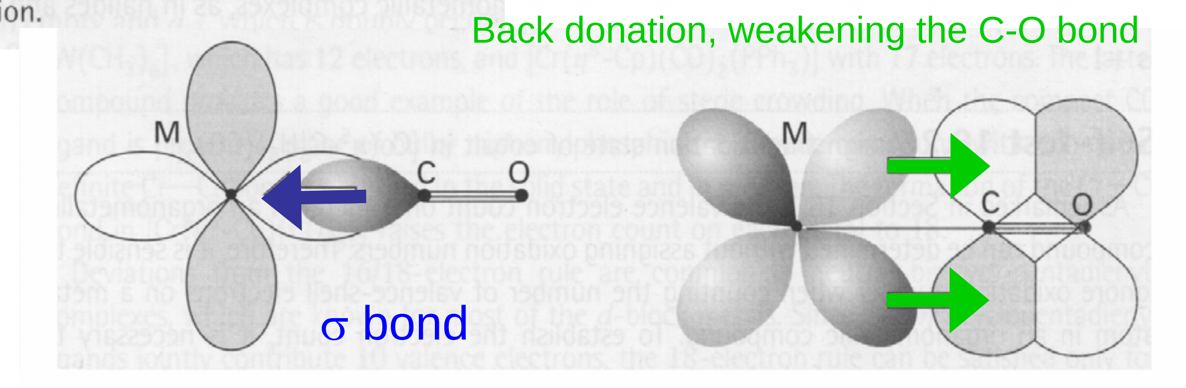
Transition metals = d electron donors

Metal catalysed reactions

CO adsorption

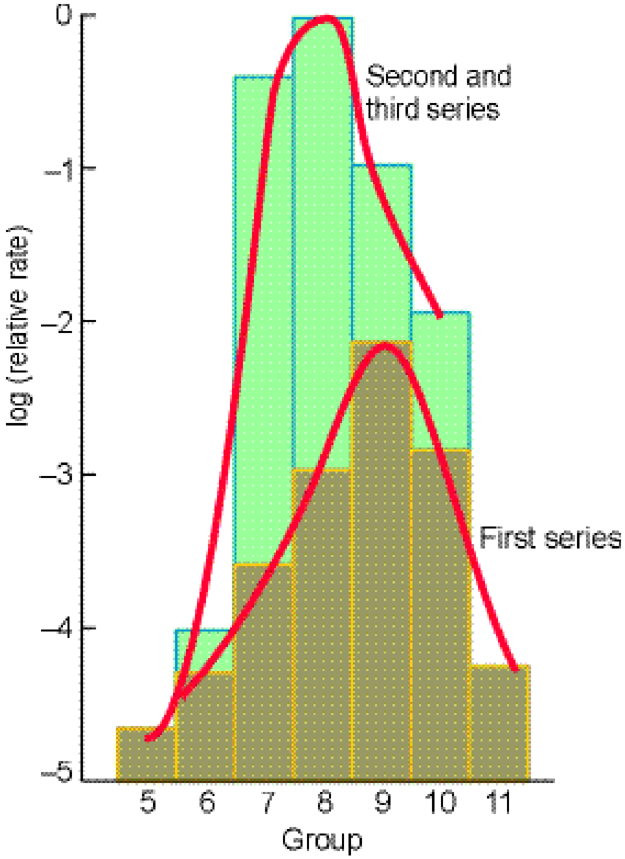


16.1 The molecular orbital energy level diagram for CO. The filled 3σ and vacant 2π orbitals are important in metal complex formation.



Shriver and Atkins, Inorganic Chemistry (1999)

Volcano plots



Catalytic activity of d metals

Moving from Group 5 towards Group 11 metals, the transition metals become increasingly noble.

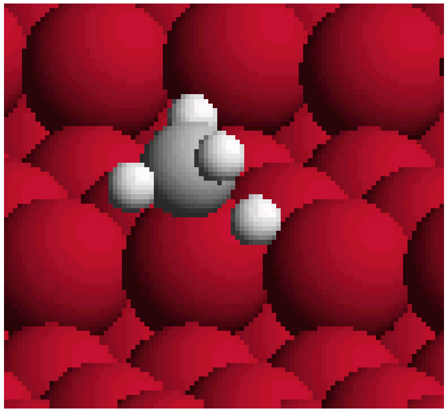
Thus, the reaction rates go from desorption-limited towards adsorption-limited.

The optimal adsorption enthalpies are found in groups 7 to 9:

Fe	Co	Ni
Ru	Rh	Pd
Os	Ir	Pt

Quantum-chemical modelling

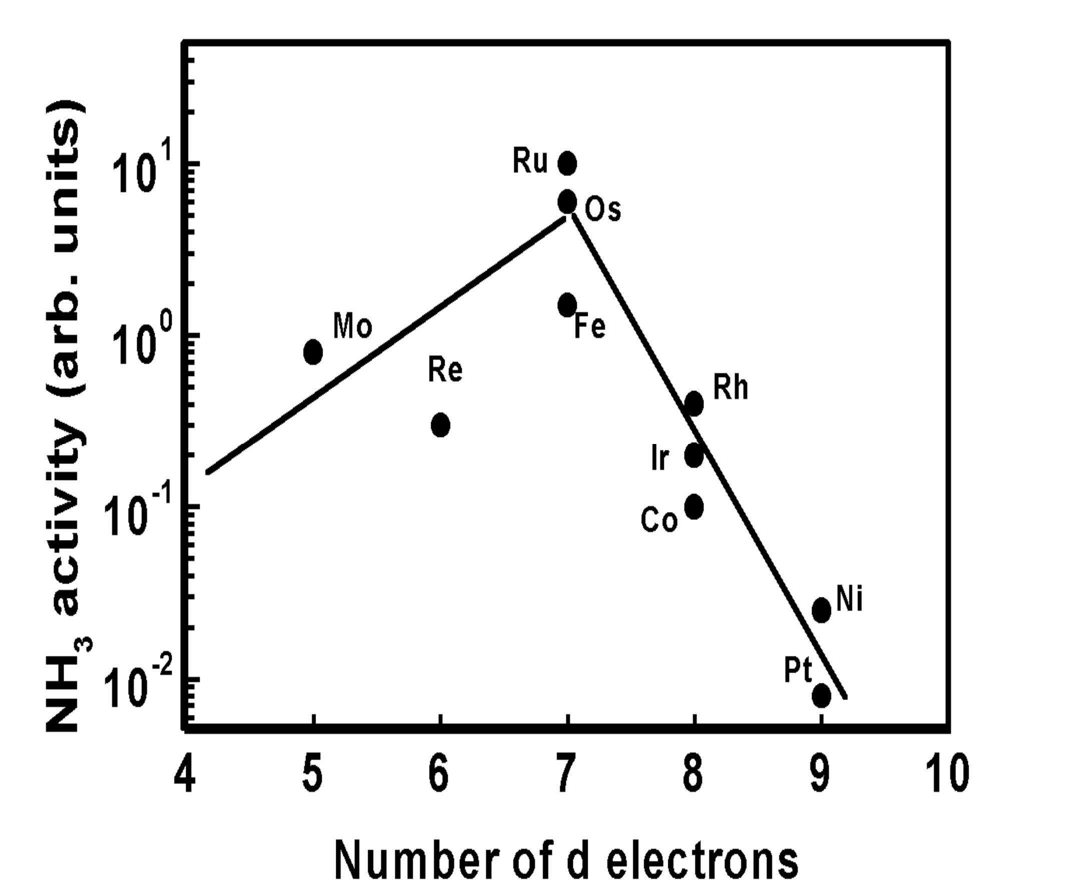
Transition state for CH_4
dissociation on Ni(211)



Bengaard, Rostrup-Nielsen, Nørskov

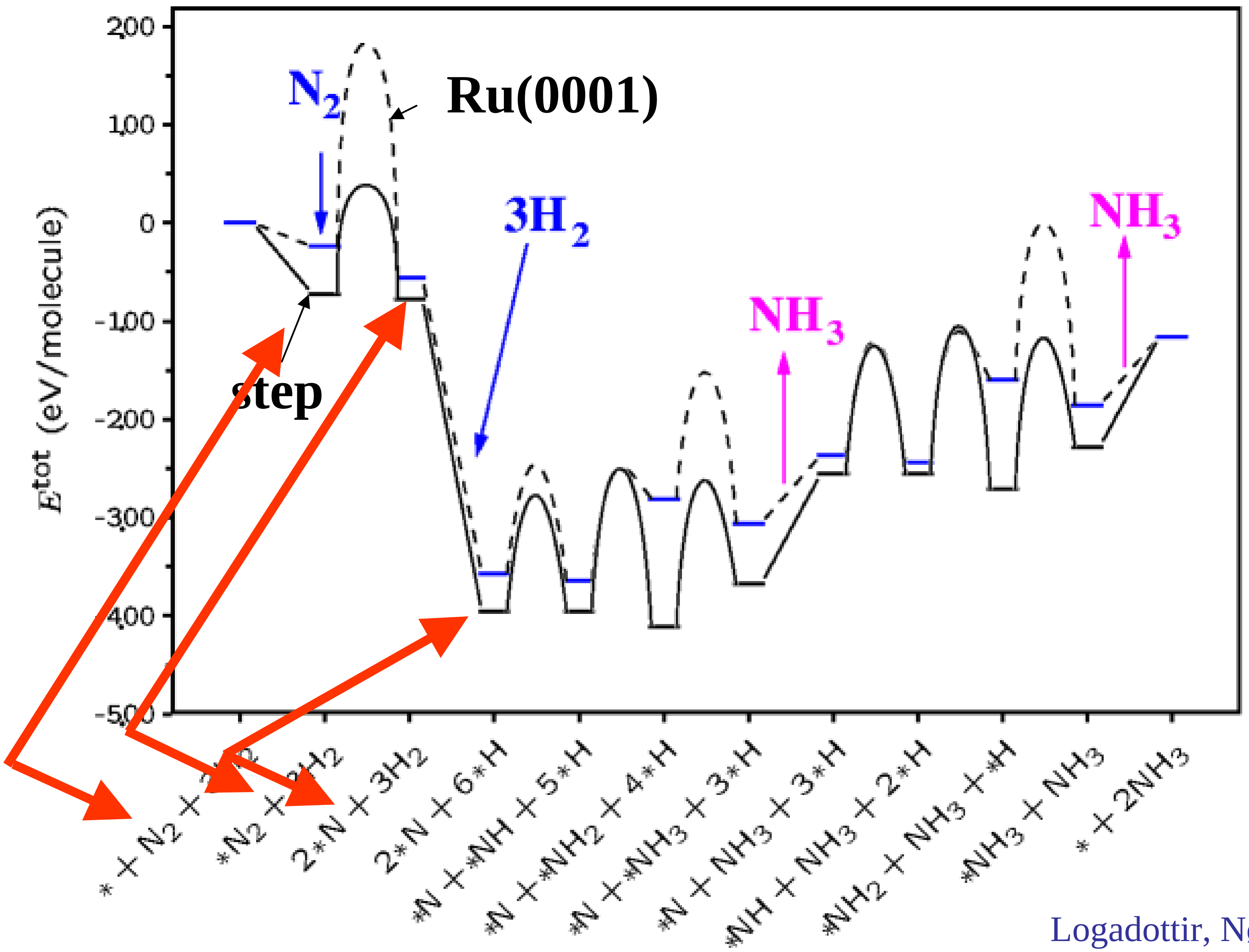
Ammonia synthesis

$N_2 + 3H_2 \rightarrow 2NH_3$



Ozaki and Aika, *Catalysis* **1** (Anderson and Boudart, Ed.)

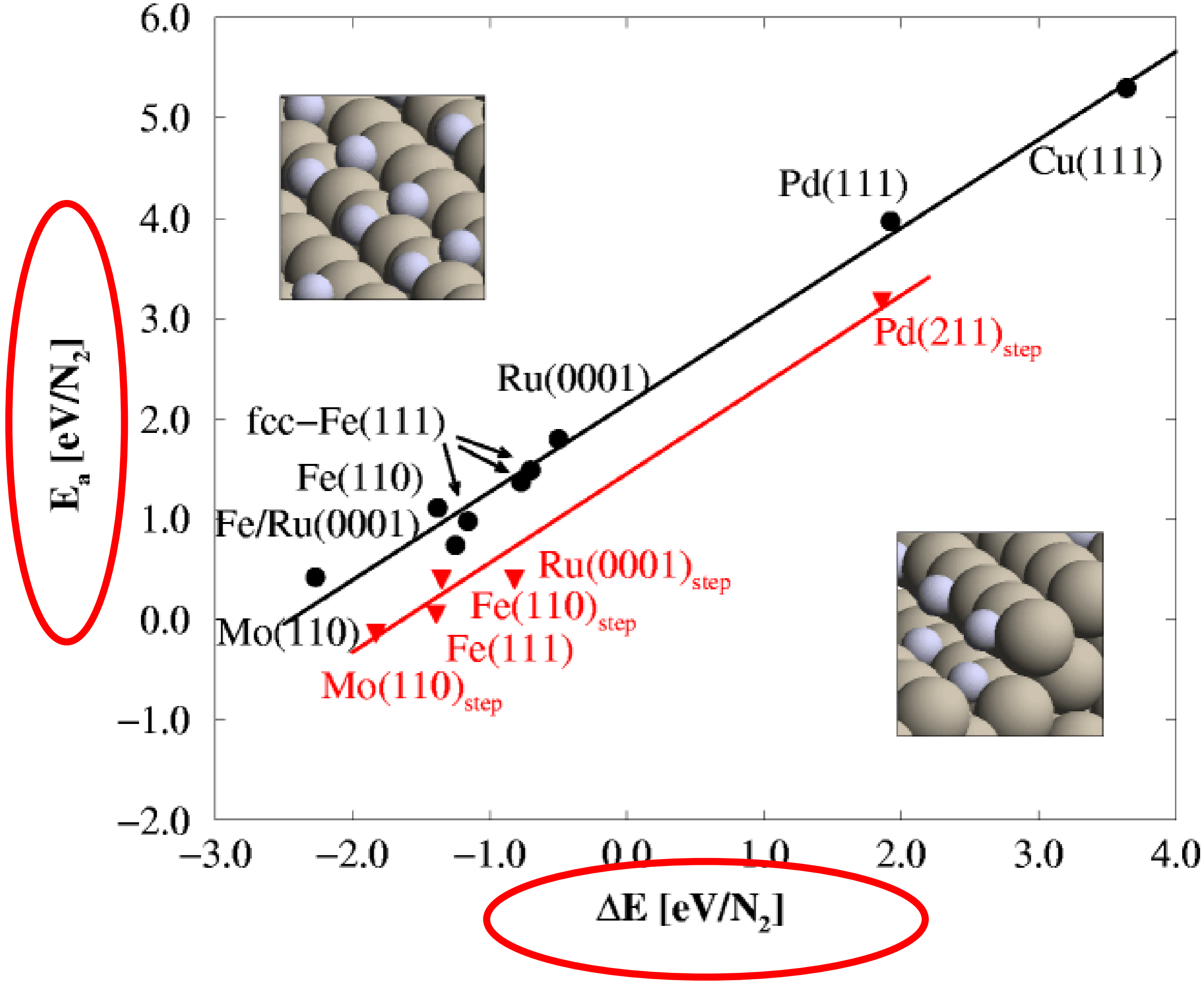
Ammonia synthesis over Ru



Logadottir, Nørskov

The Brønsted-Evans-Polanyi relation

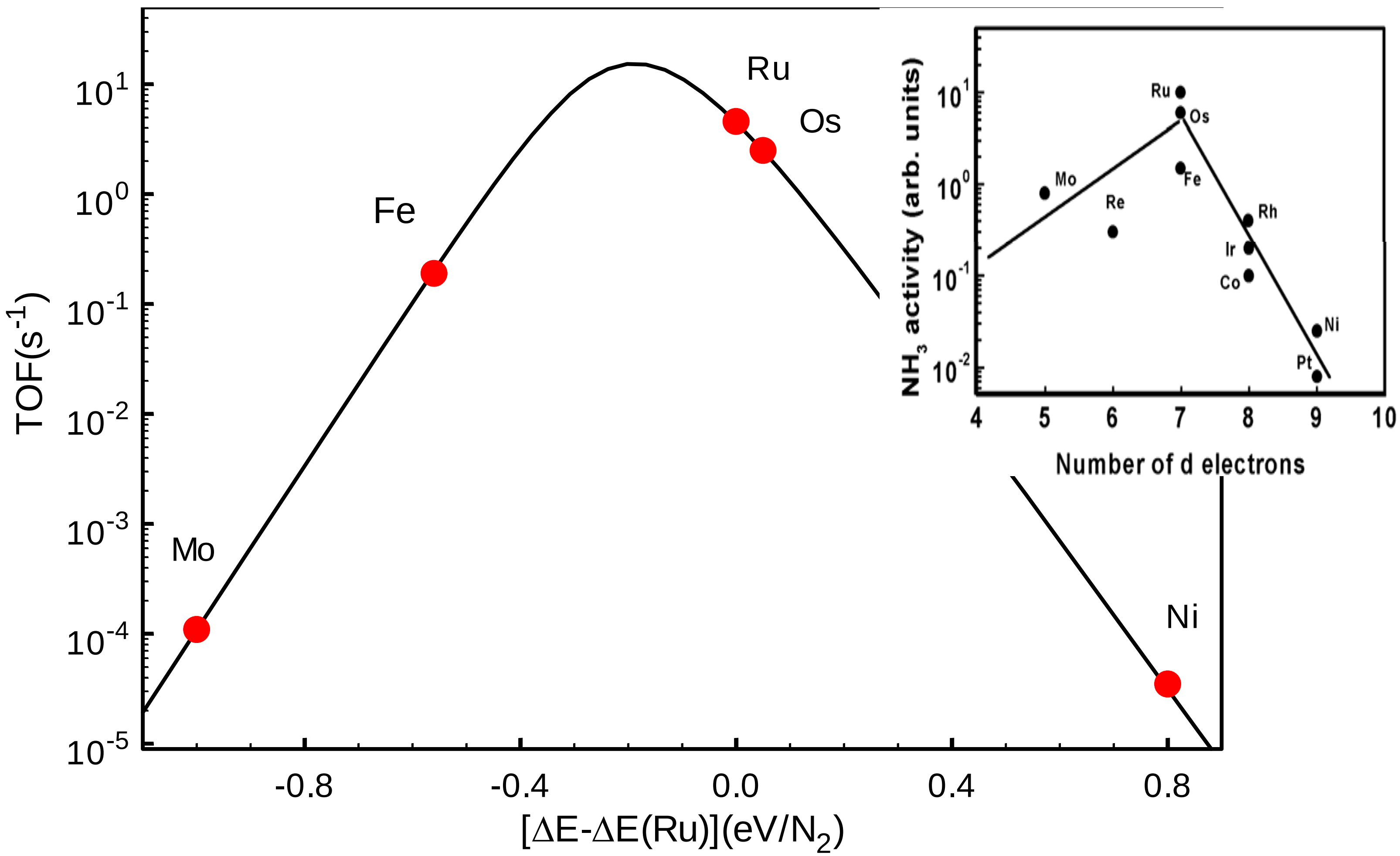
$E_a = \alpha * \Delta E + \beta$



Logadottir, Rod, Nørskov, Hammer, Dahl, Jacobsen, J. Catal. **197**, 229 (2001)

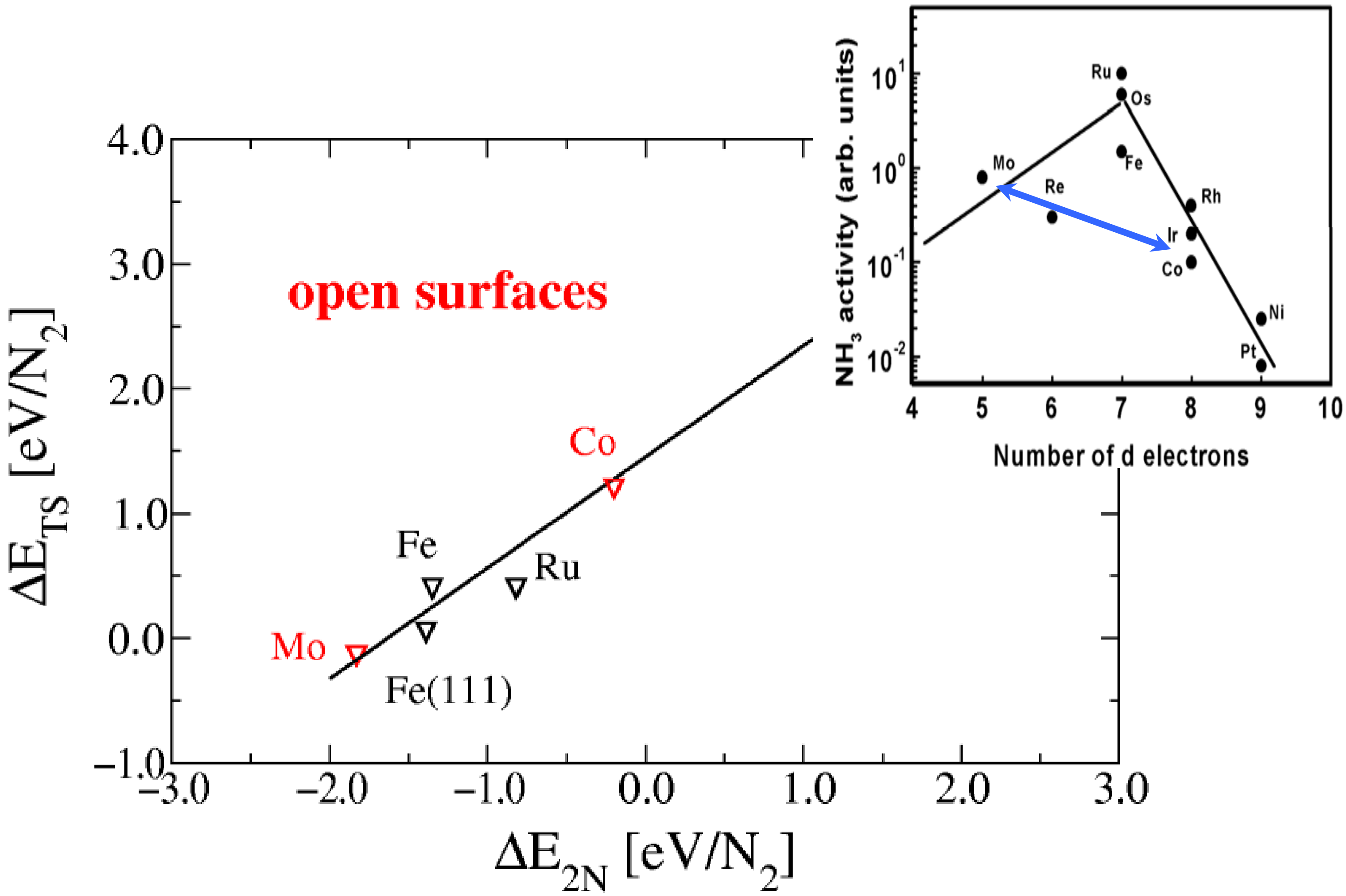
Calculated ammonia synthesis rates

400 C, 50 bar, H_2:N_2=3:1, 5% NH_3



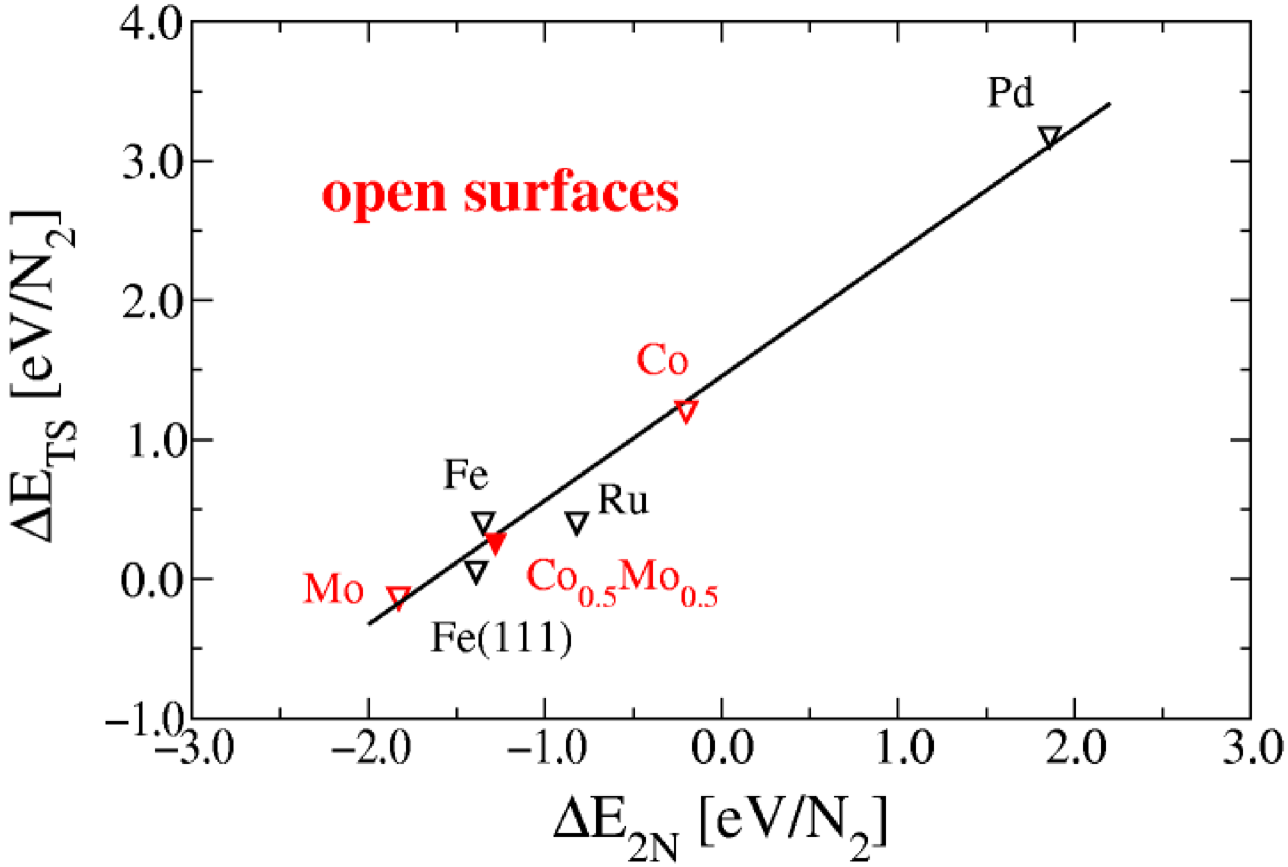
Logadottir, Rod, Nørskov, Hammer, Dahl, Jacobsen, J. Catal. **197**, 229 (2001)

Interpolation in the periodic table



Jacobsen, Dahl, Clausen, Bahn, Logadottir, Nørskov, JACS **123** (2001) 8404.

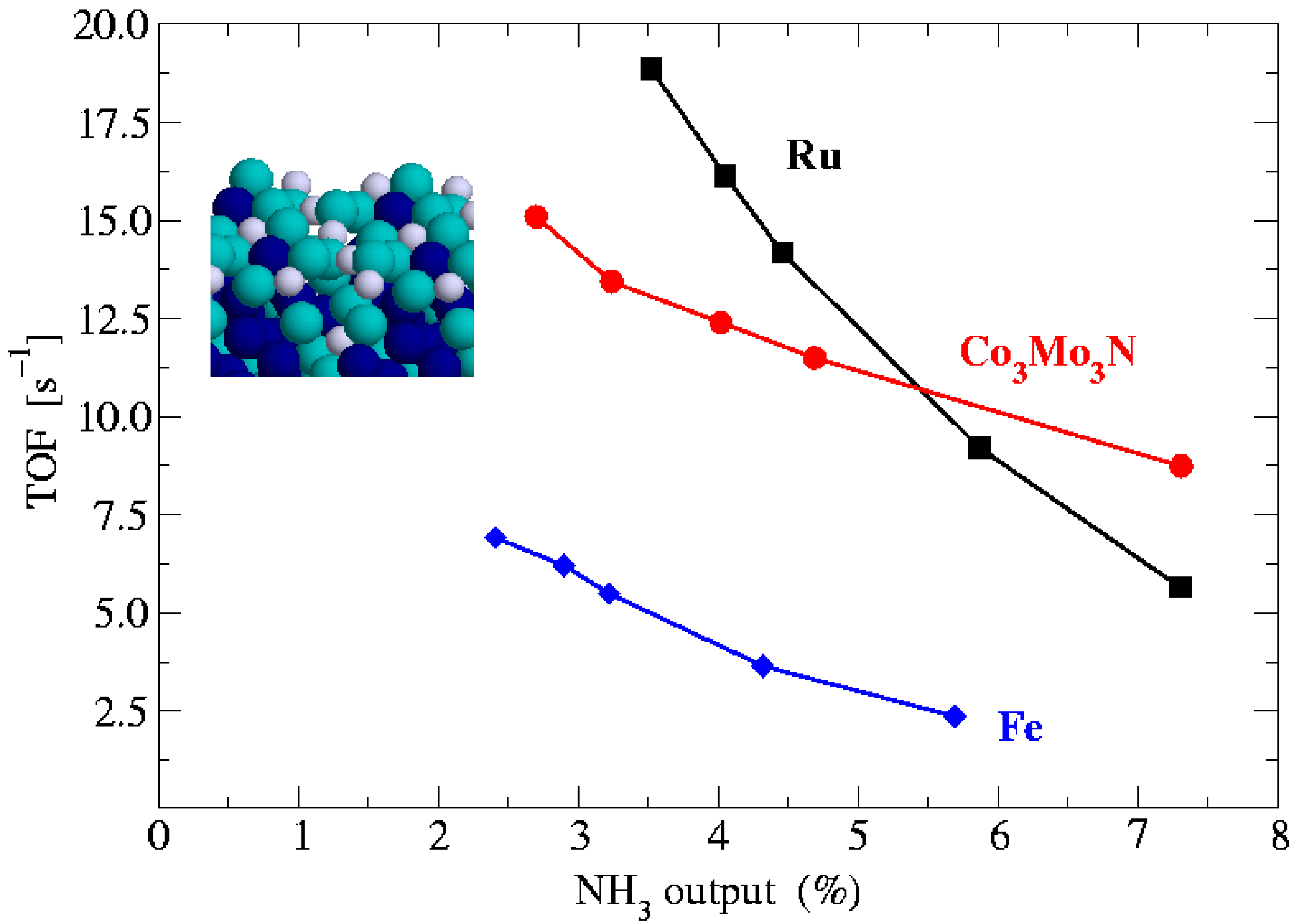
Interpolation in the periodic table



Jacobsen, Dahl, Clausen, Bahn, Logadottir, Nørskov, JACS **123** (2001) 8404.

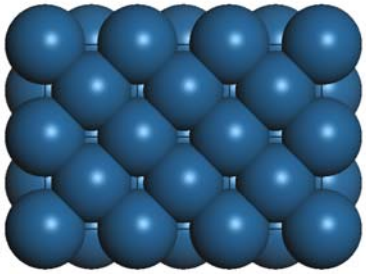
Measured ammonia synthesis rates

400 C, 50 bar, H_2:N_2=3:1

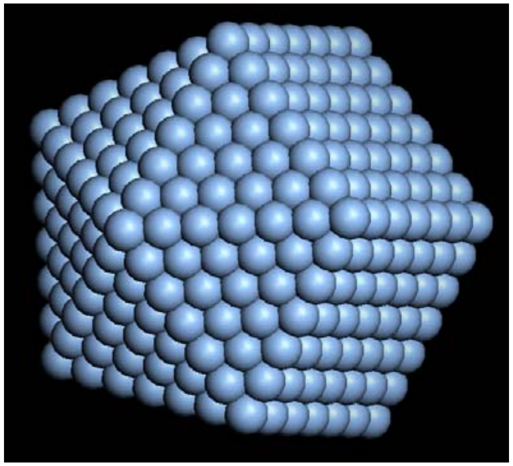


Jacobsen, Dahl, Clausen, Bahn, Logadottir, Nørskov, JACS **123** (2001) 8404.

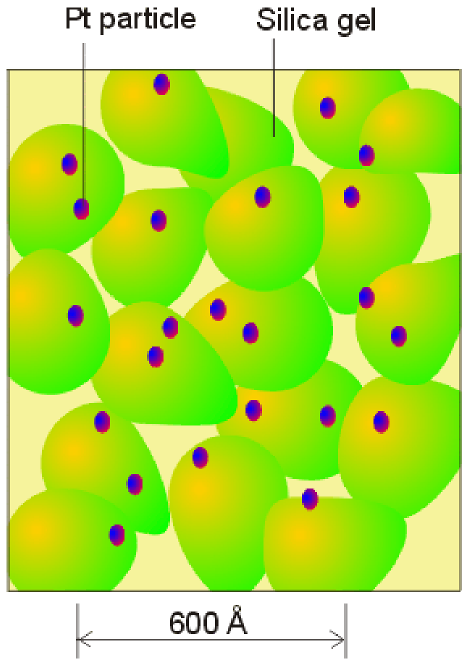
Supported metal catalysts



Ideal model of Pt 6-unit cells.
All exposed phases are [001]-phases.



Calculated shape of Ag nanoparticle



The active metal is most often dispersed on a metal oxide support.

Reconstruction of metal particles under reaction atmosphere

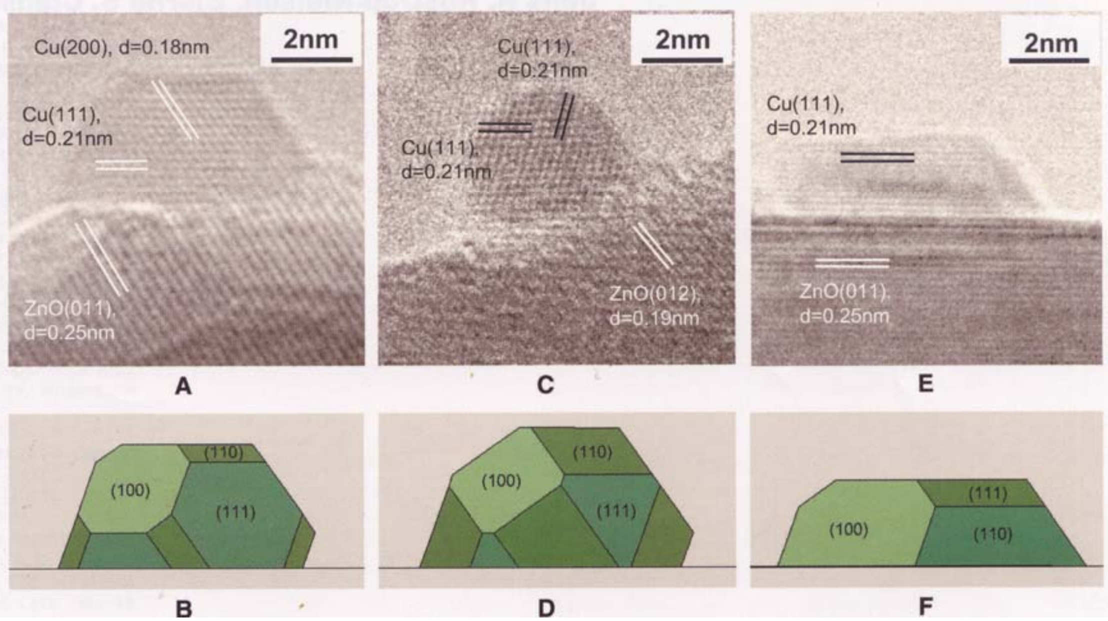


Fig. 1. In situ TEM images (**A**, **C**, and **E**) of a Cu/ZnO catalyst in various gas environments together with the corresponding Wulff constructions of the Cu nanocrystals (**B**, **D**, and **F**). (A) The image was recorded at a pressure of 1.5 mbar of H_2 at 220°C. The electron beam is parallel to the [011] zone axis of copper. (C) Obtained in a gas mixture of H_2 and H_2O, H_2:H_2O = 3:1 at a total pressure of 1.5 mbar at 220°C. (E) Obtained in a gas mixture of H_2 (95%) and CO (5%) at a total pressure of 5 mbar at 220°C.

P.L.Hansen, J.B.Wagner, S. Helveg, J.R. Rostrup-Nielsen, B.S. Clausen, H. Topsøe Science 295 (2002) 2053

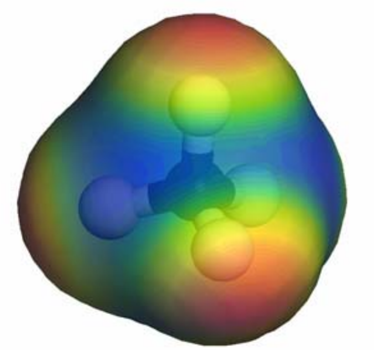
Catalysis at UiO

Homogeneous and heterogeneous catalysis groups

The catalysis group - Research focus

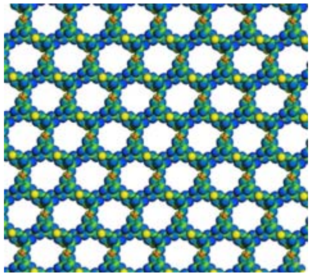
The focused problem:

utilization of natural gas

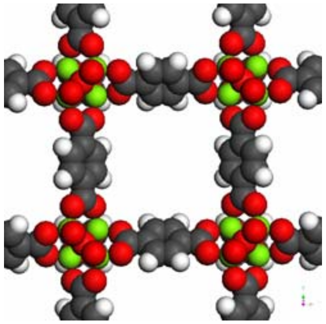


The research is materials based:

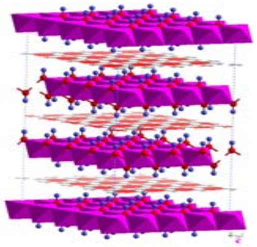
Zeotypes



MOF



Metal/Hydrotalcite



Detailed understanding of the reaction mechanism is used as a guideline for developing new active catalytic materials.