



Please read the papers of your group!  
Critical analysis is fine but ignoring the progress is wasteful

# The incomplete lecture

- Catalysis is a multi-scale phenomenon.
- Refers to scales and times.
- We discuss some physico-chemical foundations.
- We discuss material dynamics at a molecular level and place this in other temporal phenomena.
- We almost omit all meso-scopic and macroscopic phenomena related to chemical engineering and material synthesis.

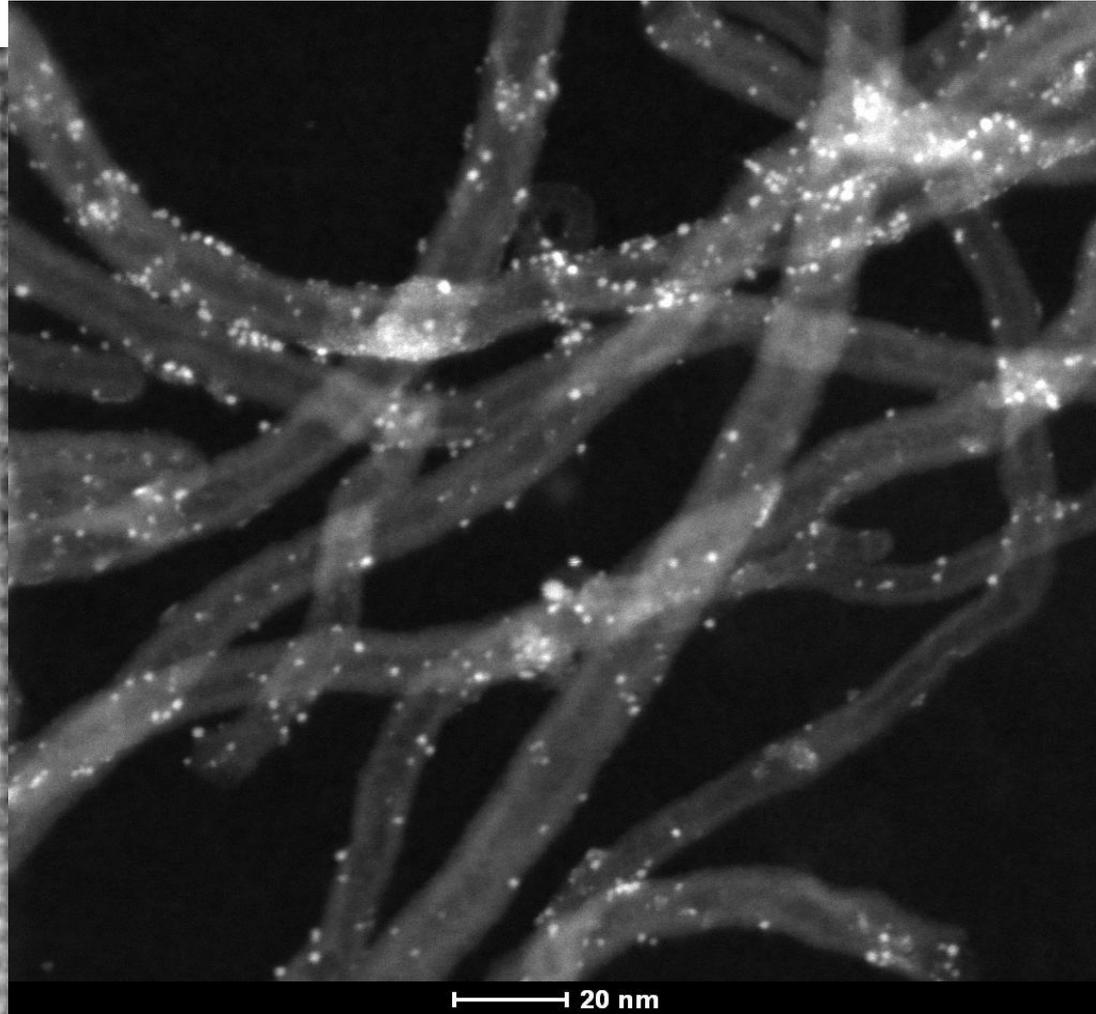
# Catalysis is still phenomenology or „black magic“: the complexity issue

- The mechanisms and active sites of some homogeneously catalysed reactions are known.
- In heterogeneous catalysis, the concept how the catalyst modifies the course of a chemical reaction is well established: adsorption and spatio-temporal separation.
- Proof-of-principle systems in heterogeneous catalysis have been studied to a great extent (ammonia synthesis, oxidation of CO).
- Many chemically only slightly more complex reactions are still far away from a fundamental understanding
  - validated sequence of elementary reaction steps
  - identification of the rate determining step: selectivity
  - nature of active site.

# The dirty dozen

- Catalysis is the change of a reaction rate.
- It is kinetics and not thermodynamics: the energy profile of a reaction can change, but not the beginning and the end of it.
- Catalysis requires a functional material called „catalyst“ .
- It functions without apparent consumption: it converts more moles of reactants than its own molarity.
- Conventional wisdom assumes reaction cycles as mechanism in which the active part of the catalyst is regenerated.
- We cannot determine a mechanism but only exclude options of a mode of operation.
- A mechanism is “Gedankenexperiment” with multiple unknowns.
- Kinetic measurements have nothing causal in common with a mechanism.
- The active part of the catalyst is called „active site“.
- Only a small number of potentially active atoms are really active at a unit time: the assumption that all accessible active atoms represent active sites is wrong.
- For this reason it is at the present time impossible to determine the activity of a catalyst: its efficiency in conversion per unit time (*tof*) or during its lifetime (*ton*).
- We use approximate scaling (conversion or rate per surface or mass)

# The standard model



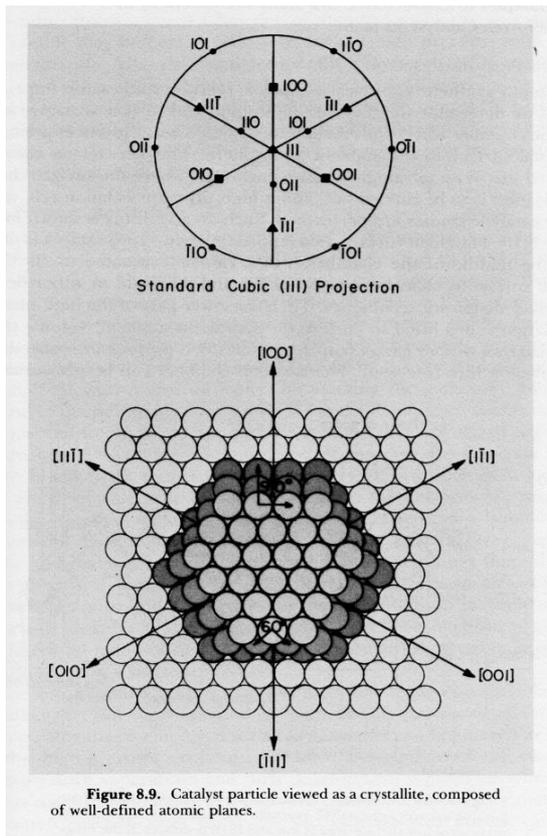
In heterogeneous catalysis the catalyst is assumed to contain stable active sites that are regenerated into their active form after each reaction cycle.

The reaction is dynamical. Reactants can diffuse after chemisorption to “high energy sites” and desorb through dynamics.

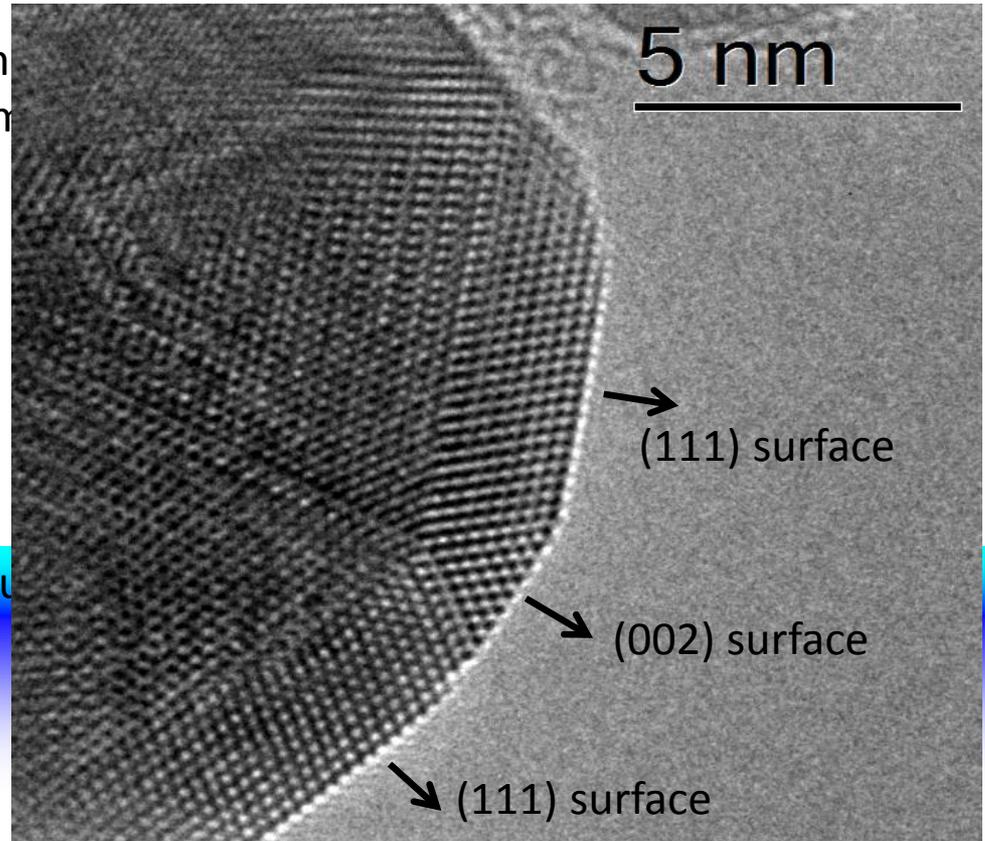
The catalyst material is static and pre-determined by synthesis: during operation no structural modification but participation of charge carrier reservoirs are assumed.

# The single crystal approach (G. Ertl)

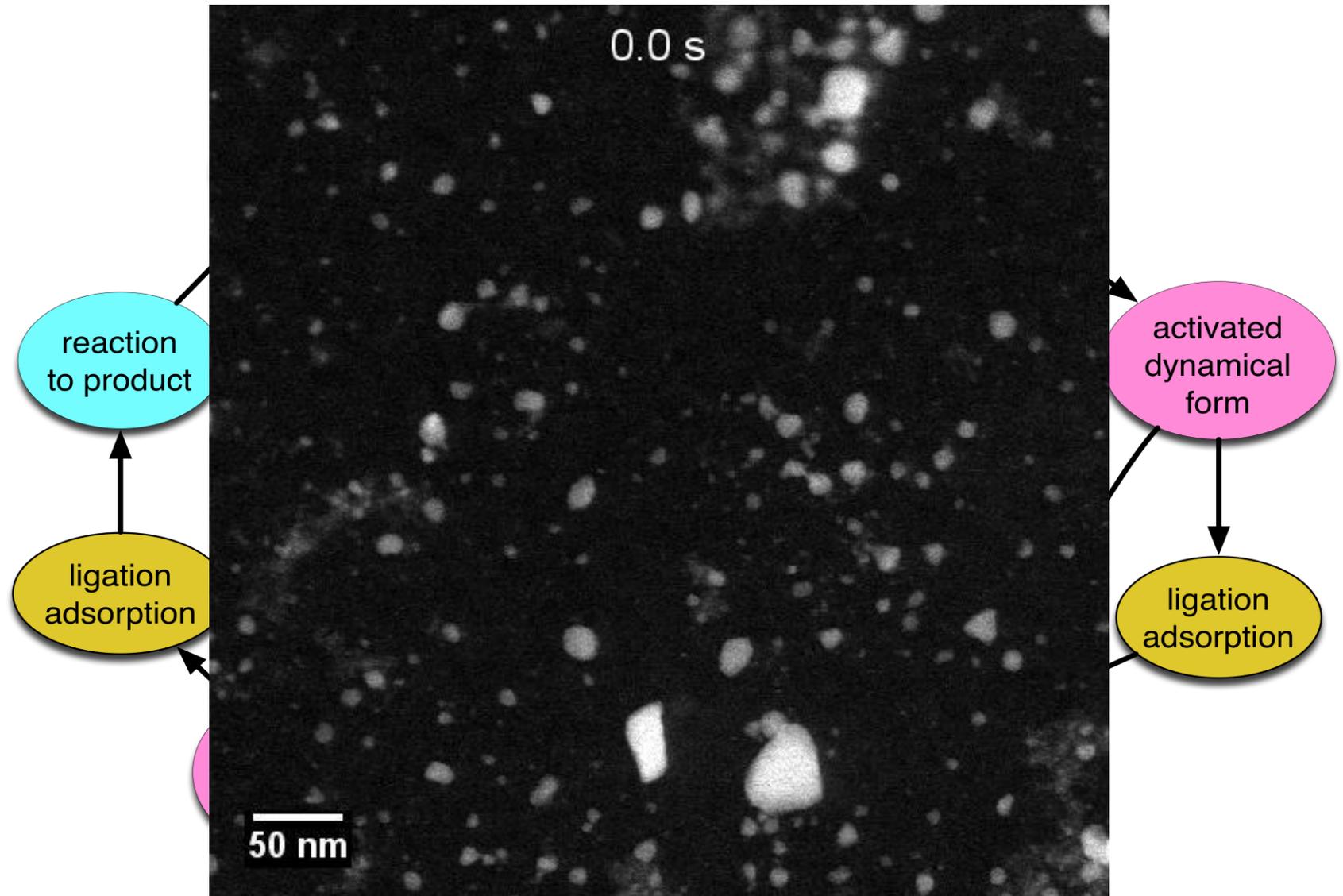
Catalysis can only be understood if we know where the atoms are



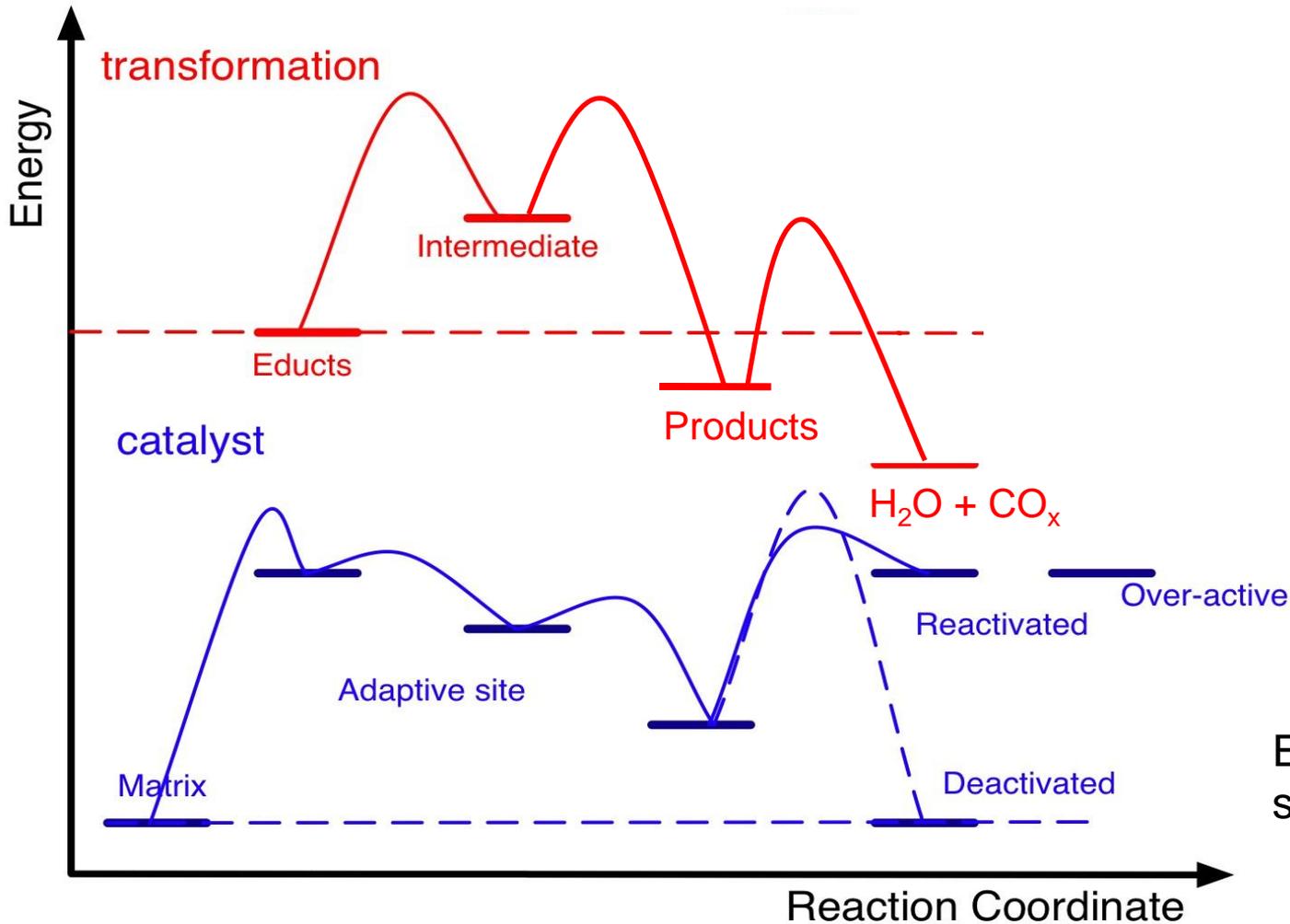
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# Catalysis as Science

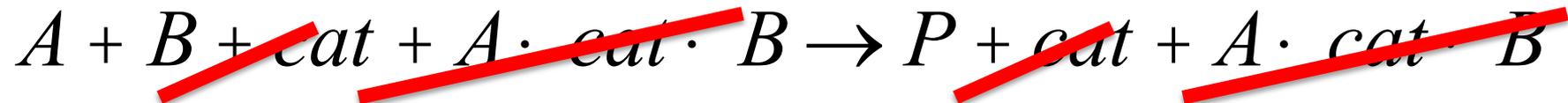


# The (standard) description of catalysis



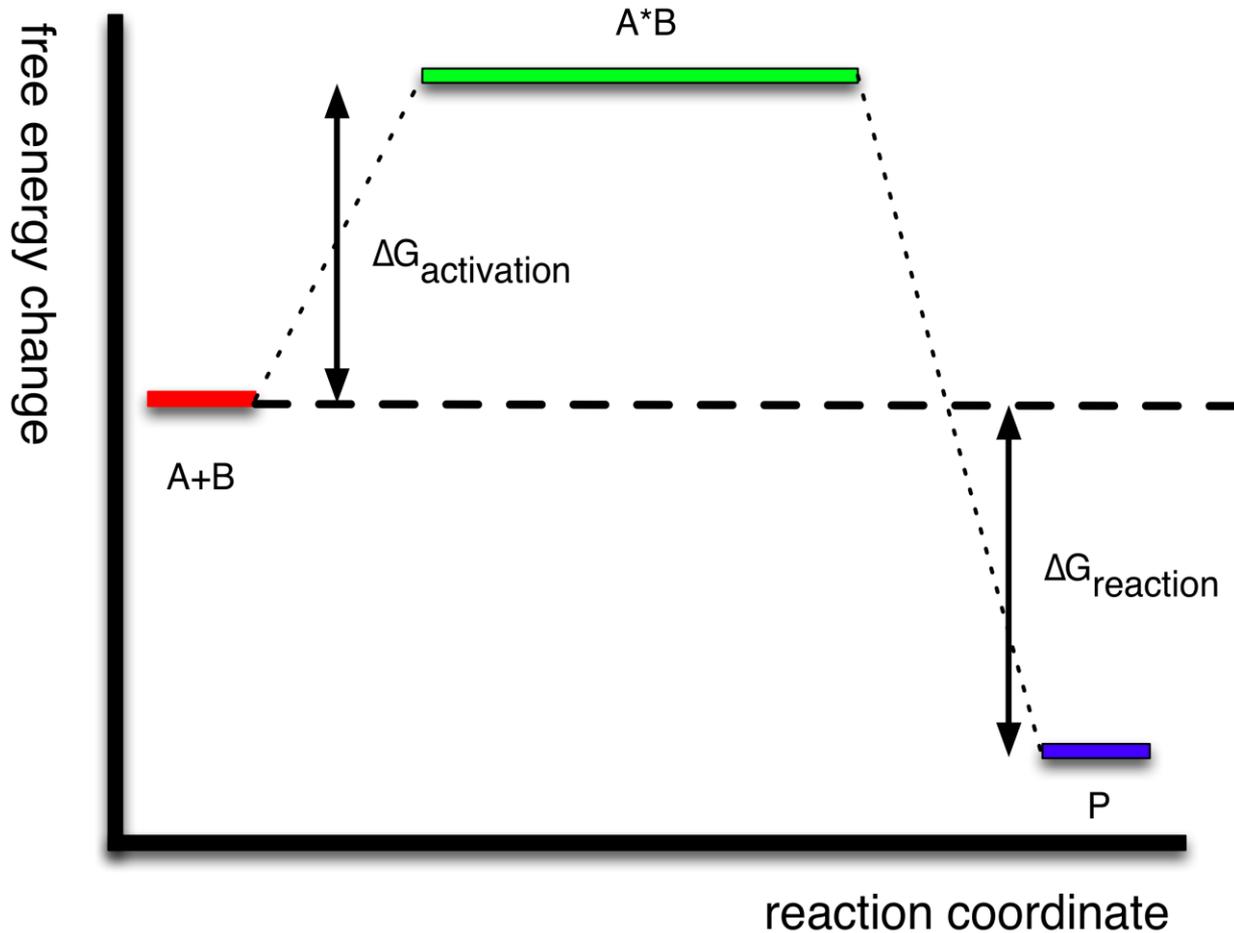
Example:  
selective oxidation

Catalysis general: not as simple as it seems

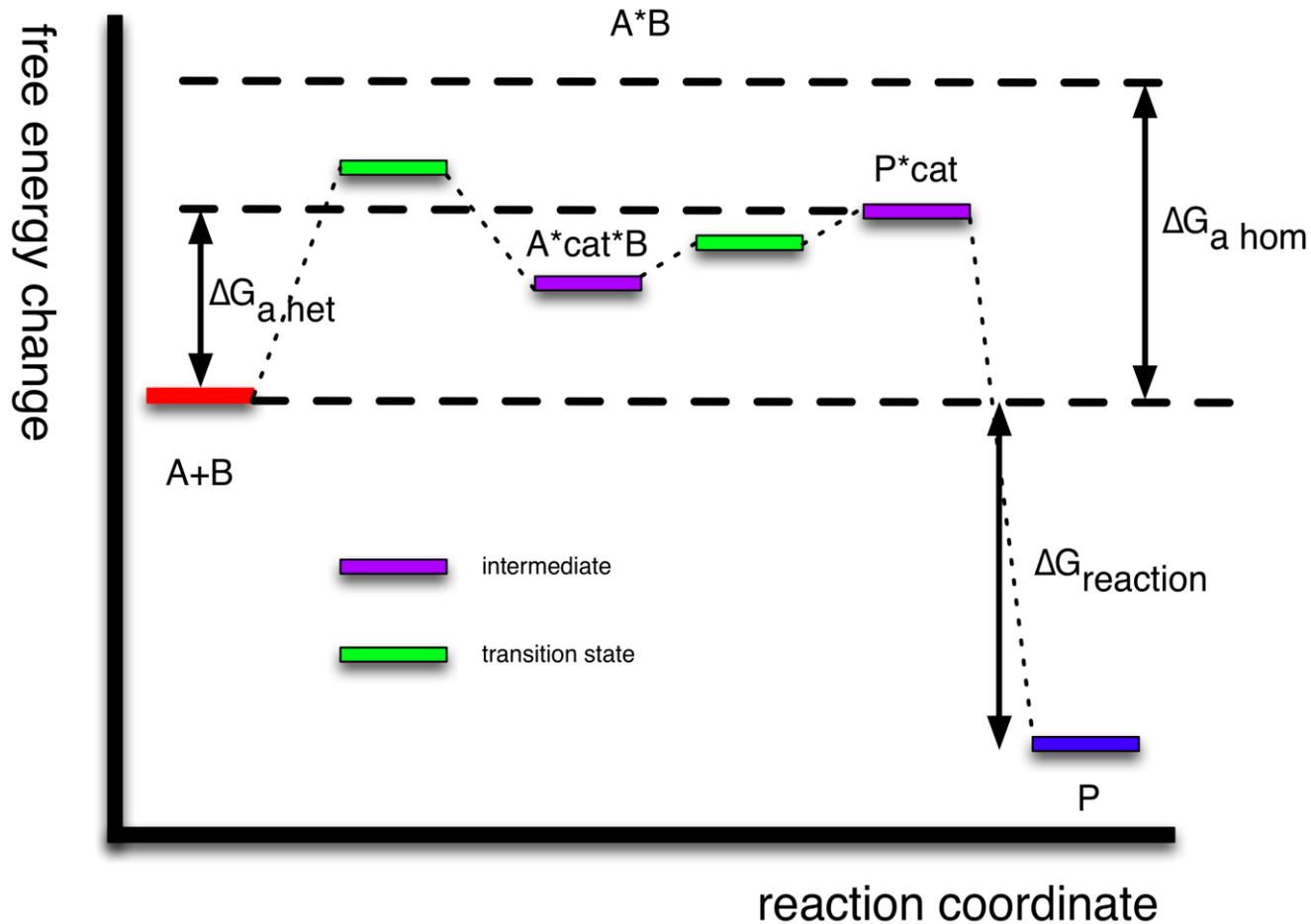


ER

# Chemistry is energy science: molecular energy quantities



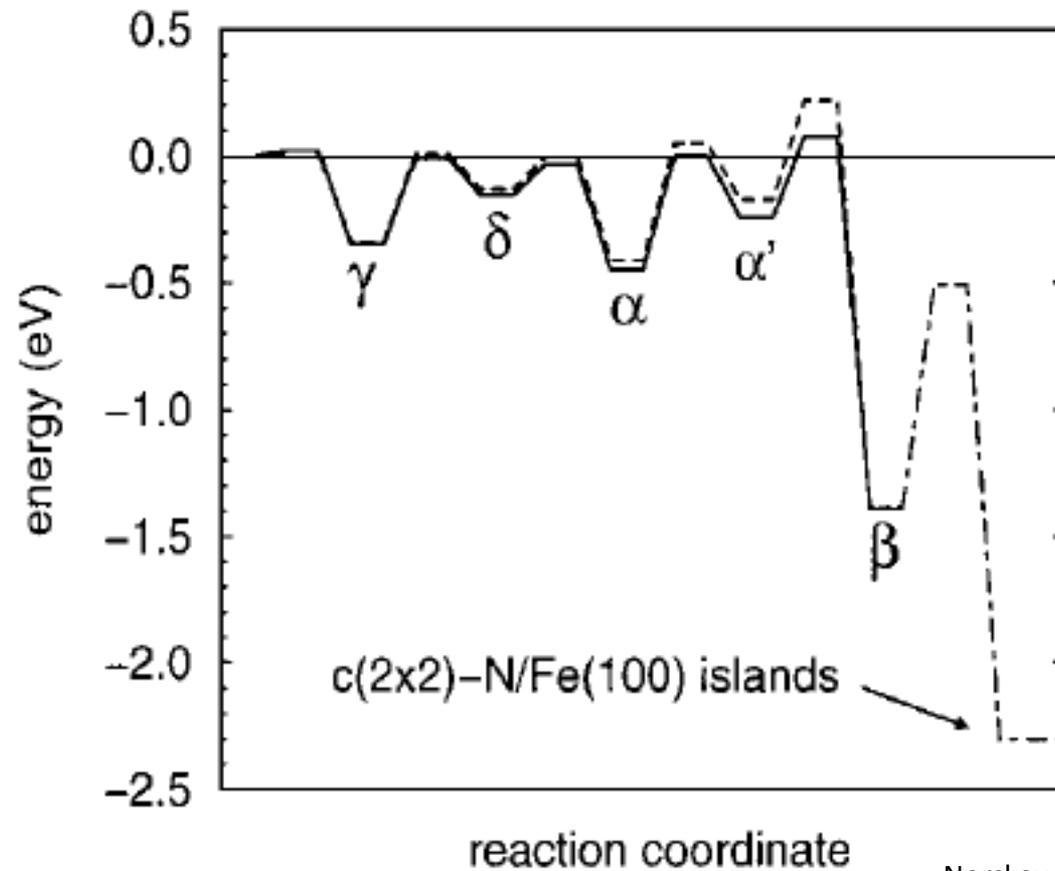
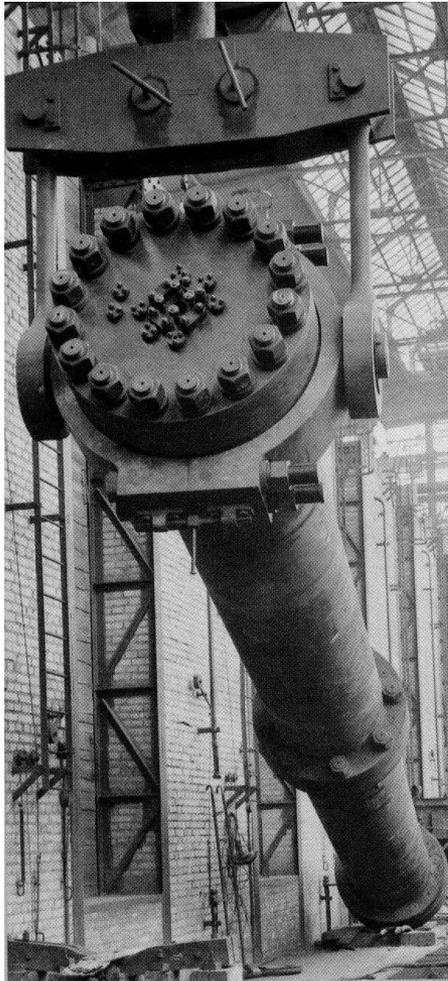
# Catalysis is energy science: management of molecular energy quantities



# Microscopic control of activation

- Two boundary cases of the activated complex between reactants and catalyst:
  - The activated complex is high in activation energy for adsorption: A
  - The activated complex is high in activation for reaction: R
- For A the overall catalysis is dominated by adsorption processes.
- The classical case of LH kinetics and the only one theoretically considered.
- For B the overall catalysis is dominated by the reaction steps involving “Taylor sites” and in most cases catalyst dynamics: the most frequent case in practical catalysis but hard to study as strongly dependent on reaction conditions.
- We will for now concentrate on the simpler case A but not forget that this is a boundary case of the general dynamic operation of a catalyst.

# Real barriers can be quite substantial

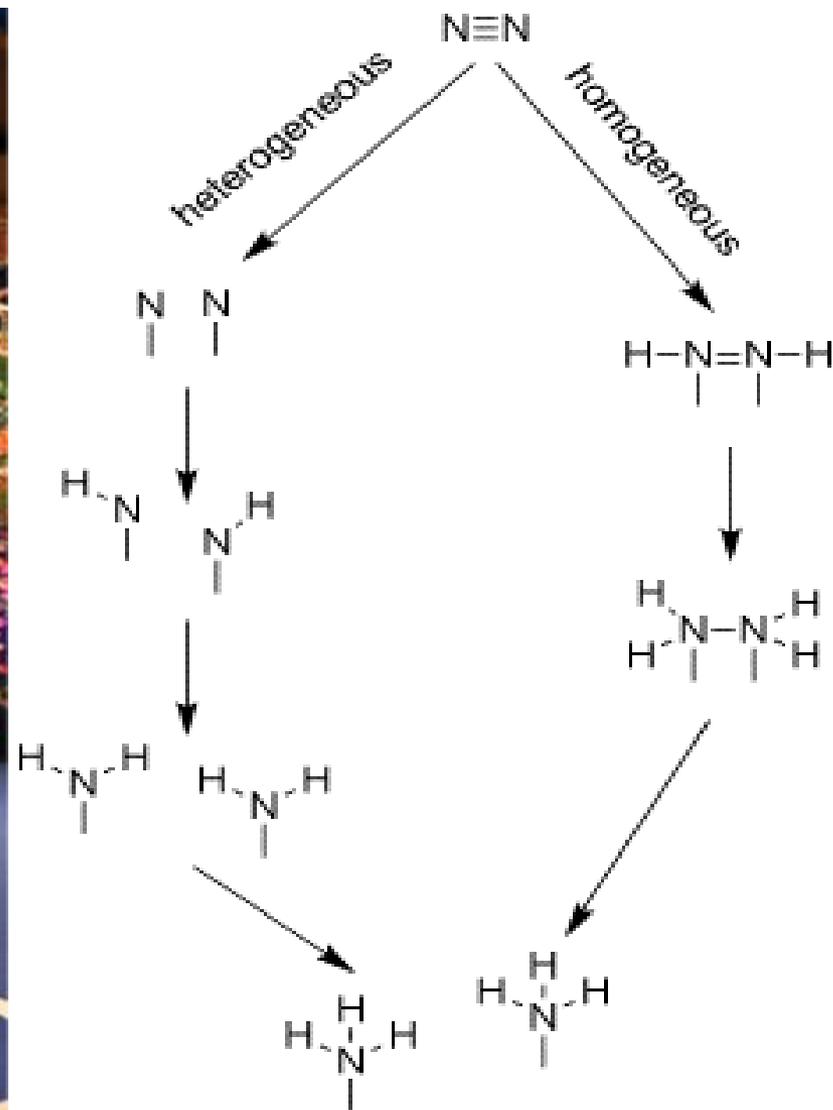


Norskov et al: 2001

# Consequence of molecular activation

- The energy difference between catalyzed and uncatalyzed processes can be very large: more than 1000kJ/mole.
- The catalyst reacts in activated processes with educts and products:
- When products are less stable than educts it will be difficult to obtain them:
- Reaction networks with multiple reactions enhance the complexity and lead to substantial amounts of the thermodynamic preferred product.
- Mostly undesired water and CO<sub>2</sub> in organic transformations.
- Catalytic activation of already activated systems (biomass) leads to enormous selectivity problems.

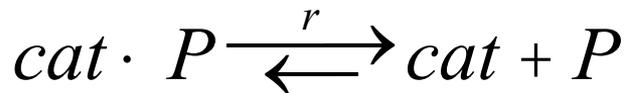
# Ammonia synthesis: our test case nature does it differently than chemical technology



# Thermodynamics and Kinetics

- It is intuitive that chemical elementary steps (what is this?) depend for their velocity on the energetic difficulty.
- Steps with large barriers (energies to be invested) are slow.
- Steps with large energy liberation are fast.
- We apply this to a catalytic process and consider the liberation of the product as relevant step.
- Then we can consider the extent of reaction by the thermodynamic mass law.
- The velocity of the reaction occurs from the partition function (statistical thermodynamics, Boltzmann law) of the educt in a translational coordinate describing the liberation of the product.
- If we then assume that the equilibrium is always at the side of the product and no back reaction should occur we can equalize the two worlds of kinetics and thermodynamics.

# Thermodynamics and kinetics: activation barrier ( $\Delta G_{\text{act het}}$ )

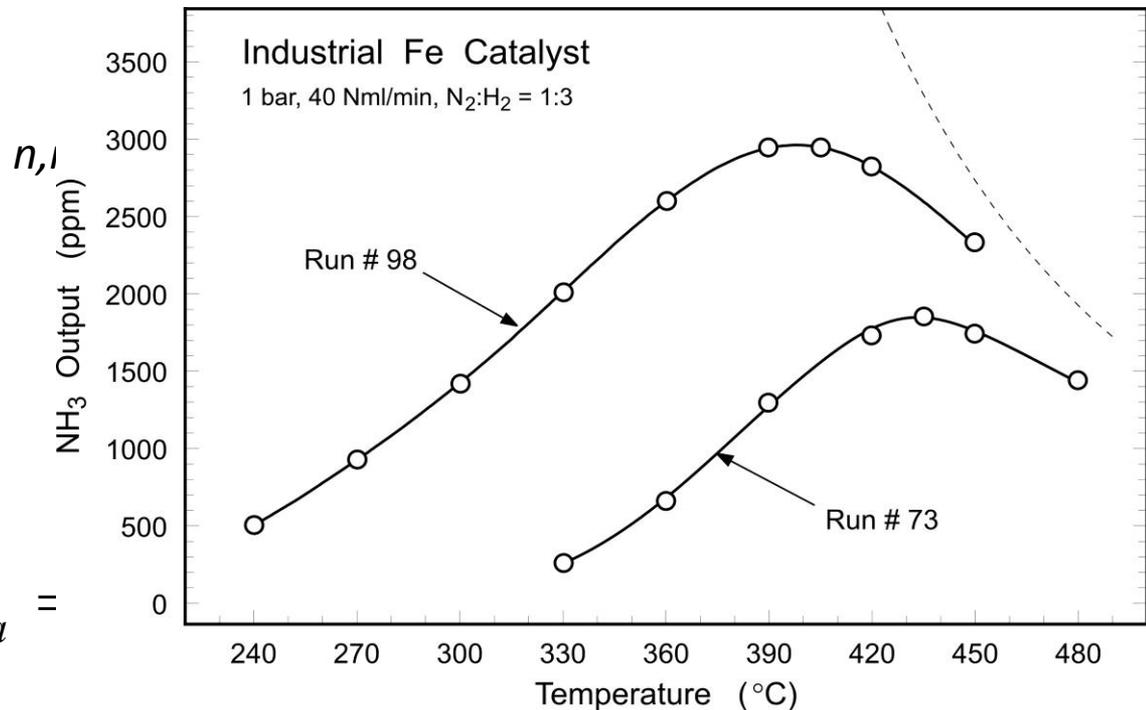


$$K = \frac{[\text{cat} \cdot \text{P}]}{[\text{cat}]^n [\text{P}]^m}$$

$$K = \frac{Z_{\text{cat} \cdot \text{P}}}{Z_{\text{cat}}^n Z_{\text{P}}^m} e^{-\frac{\Delta G_a}{RT}}$$

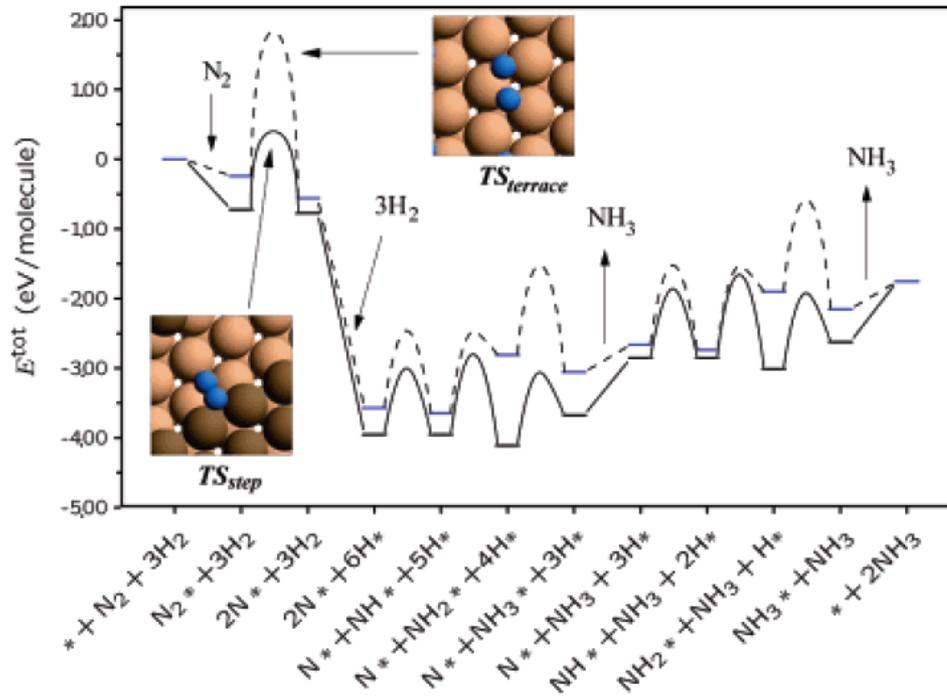
$$r = K \frac{kT}{h} \quad \text{as } \Delta G_a =$$

$$r = \frac{kT}{h} e^{-\frac{\Delta G_a}{RT}} \quad \text{equals} \quad r = A e^{-\frac{E_a}{RT}}$$



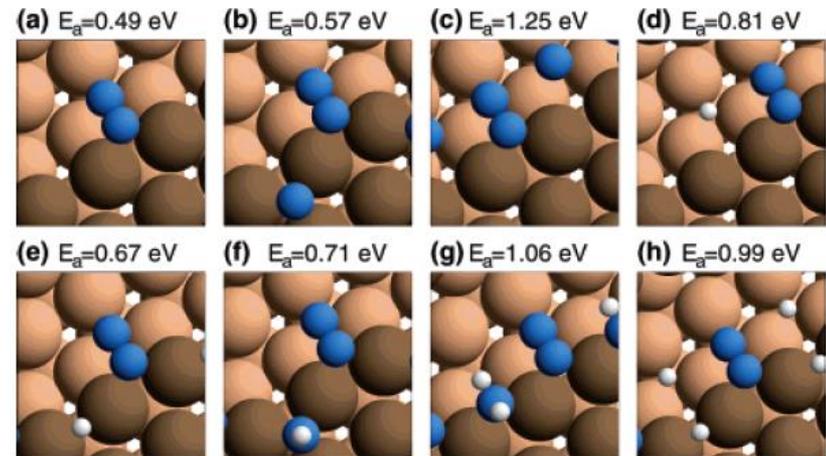
# Simplicity: ammonia synthesis

*J. Phys. Chem. B, Vol. 110, No. 36, 2006* **17721** Theoretical construction of the reaction profile of ammonia synthesis over Ru at 600 K.



Note the strong dependence of the single rds on coverage (pressure)

*J. Phys. Chem. B, Vol. 110, No. 36, 2006* **17729**



# Adsorption

- Concept of surface coverage:
- $\Theta$  is surface coverage,  $(1-\theta)$  number of free sites (reactant).
- Other reactant is number of adsorbatives (pressure or concentration).
- Then a kinetic derivation can be given.
- We consider the rate of reaction between free sites and reactants.
- The complex functional properties of the bonding and de-bonding of the adsorptive forming the adsorbate is hidden in reaction rate constants designated ads and des.

# Langmuir isotherm

$$r_{ads} = k_{ads} p (1 - Q)$$

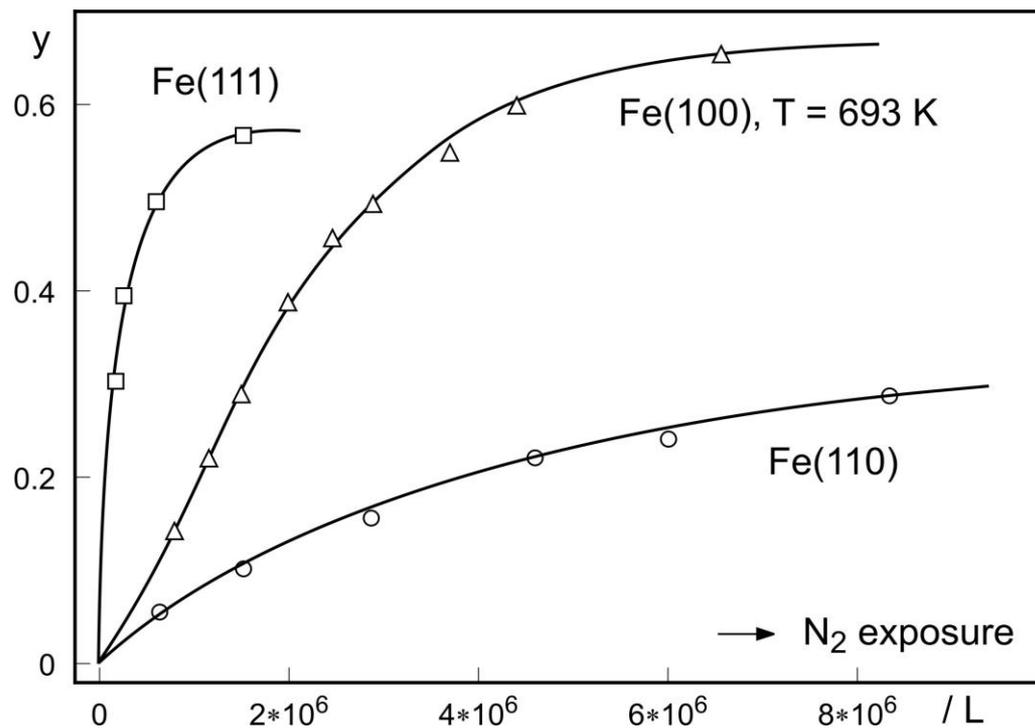
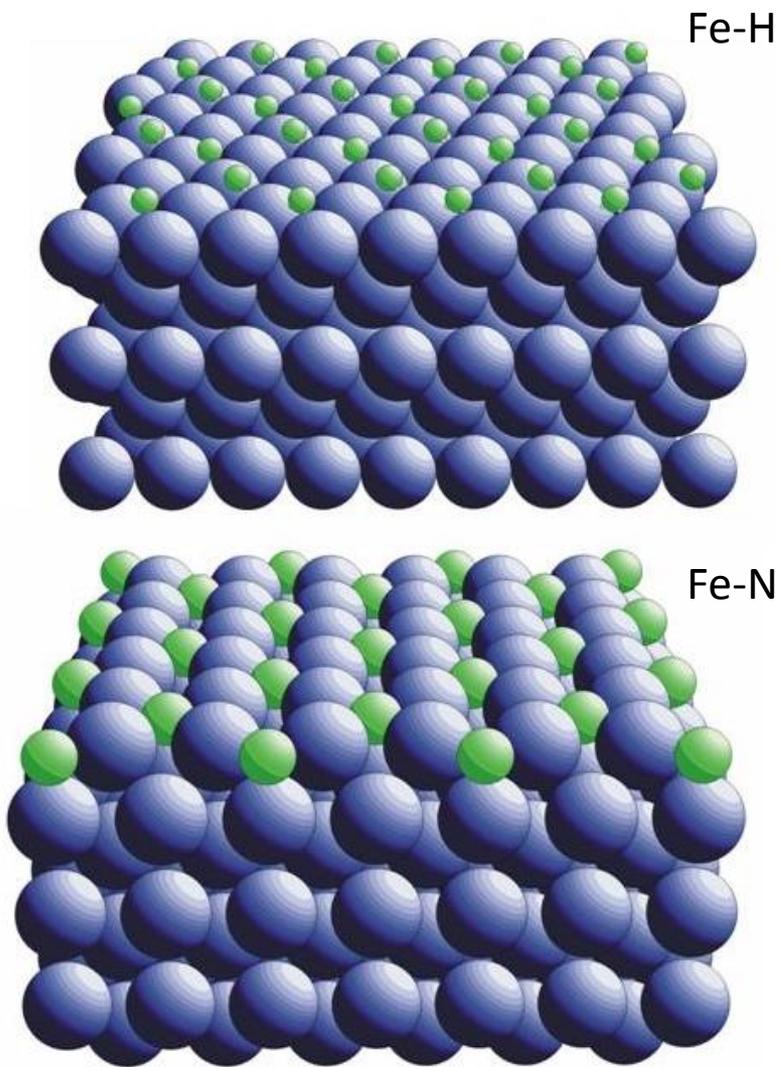
$$r_{des} = k_{des} Q$$

$$k_{ads} p (1 - Q) = k_{des} Q \quad Q = \frac{N}{N_{mono}} \quad b = \frac{k_{des}}{k_{ads}}$$

$$N = \frac{N_{mono} p}{b + p}$$

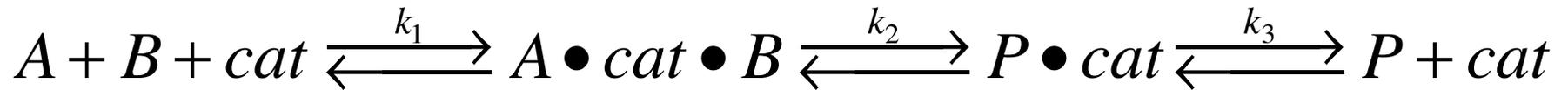
$N_{mono}$  and  $b$  are only constants for non-specific adsorption and become functions of chemical potential of adsorptive (reactants) when chemical processes occur.

# The Fe-N/H system: basis of Haber Bosch



Low pressure static data

# How catalysis works: two simple cases



# Relation of elementary steps and kinetics

$$r_1 = k_1 P_A (1 - Q_A - Q_P) \quad \textit{adsorption}$$

$$r_{-1} = k_{-1} Q_A$$

$$r_2 = k_2 Q_A \quad \textit{reaction}$$

$$r_3 = k_3 Q_P \quad \textit{desorption}$$

This rate law exhibits the same concentration behaviour as the Langmuir isotherm and the enzymatic reaction

$$r = \frac{k_2 k_3 P_A}{(k_2 + k_3) P_A + (k_1 + k_2) \frac{k_3}{k_1}}$$

# Case analysis of rate law:

Note: the simplest possible catalytic reaction

$$P_A \ll \frac{k_{-1} + k_2}{k_2 + k_3} \frac{k_3}{k_1} \quad \text{low pressure}$$

$$r \gg \frac{k_1 k_2}{k_{-1} + k_2} P_A \quad \text{first order}$$

k1 = adsorption

k2 = reaction

k3 = desorption

$$P_A \gg \frac{k_{-1} + k_2}{k_2 + k_3} \frac{k_3}{k_1} \quad \text{high pressure}$$

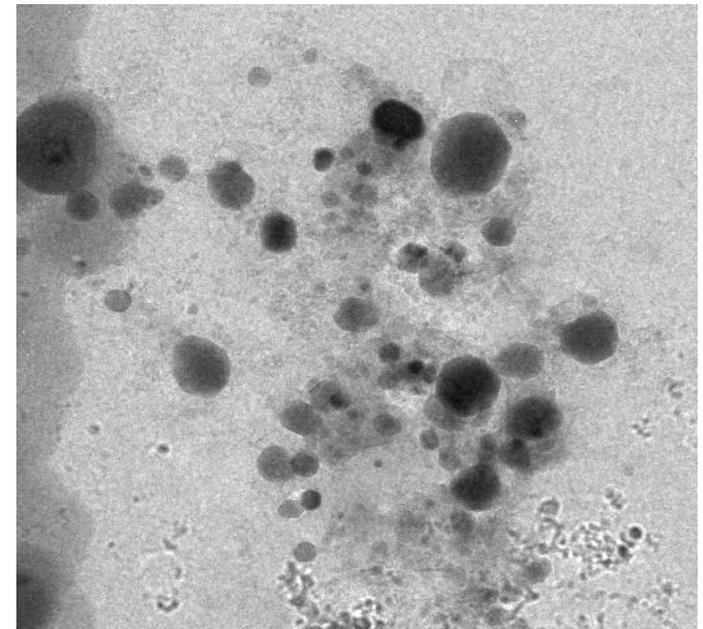
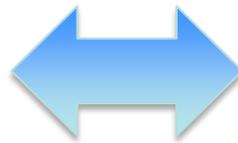
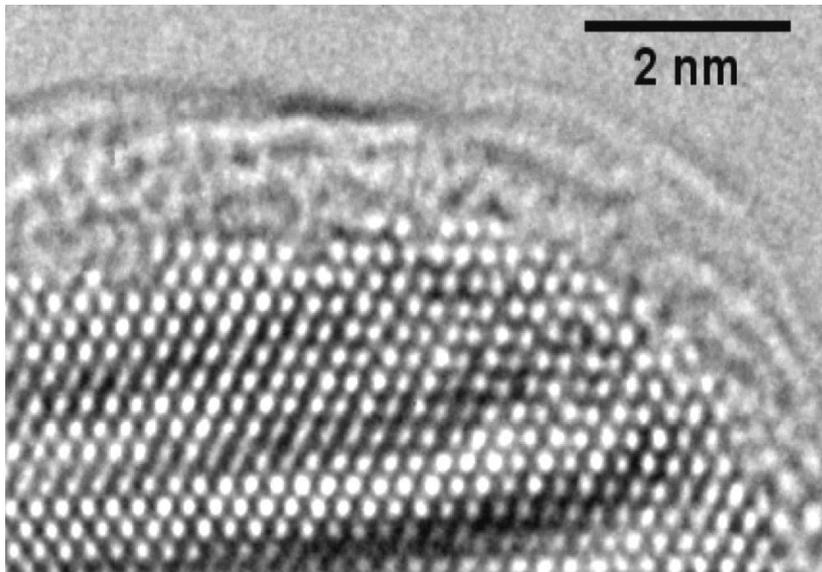
$$r \gg \frac{k_2 k_3}{k_2 + k_3} \quad \text{zero order}$$

It is apparent that from quantitative analysis of such rate laws it is impossible to learn something about the molecular properties of the reaction:

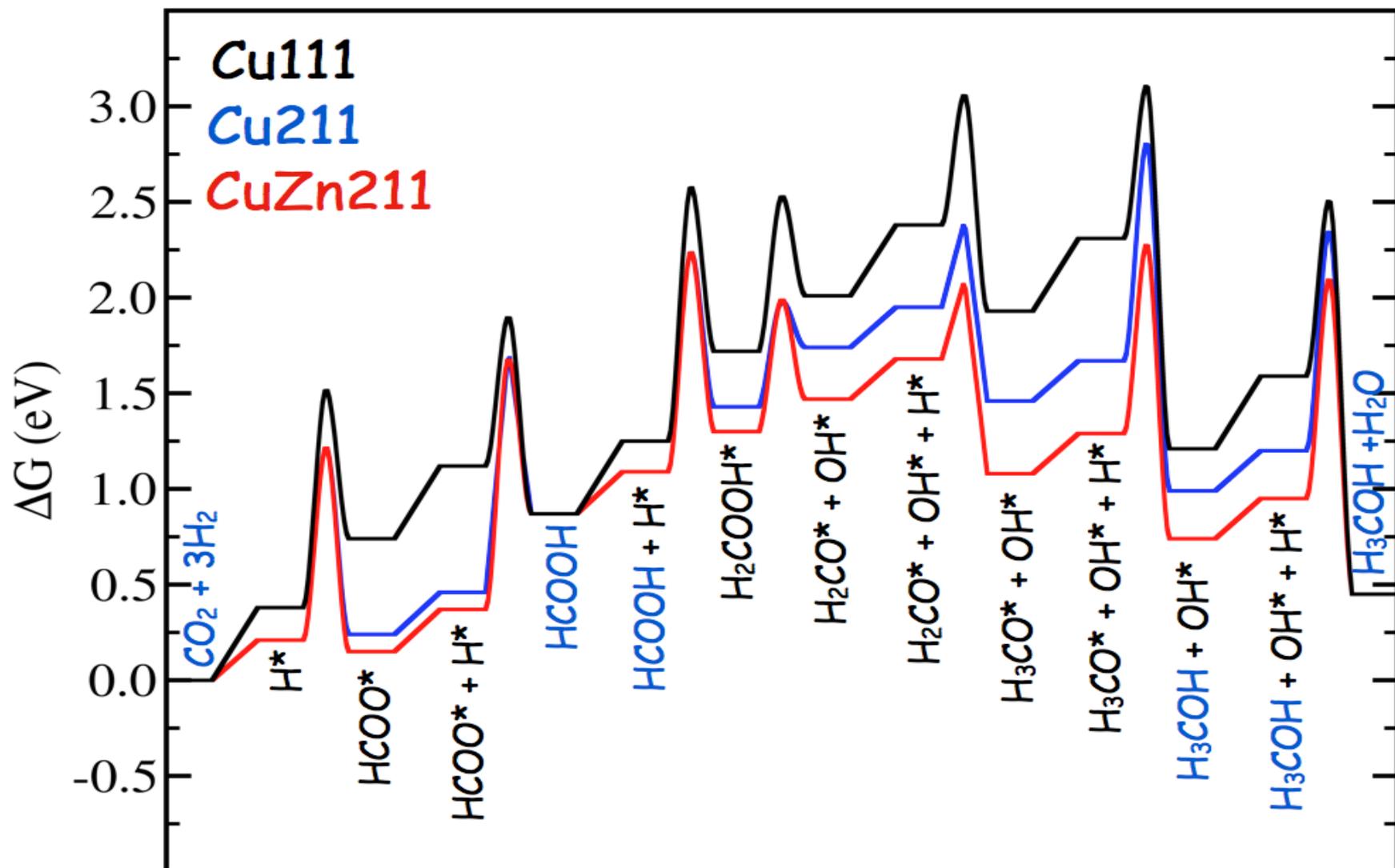
What is a „reaction mechanism“?  
Why do we do kinetic modelling?

# Time gap of structure

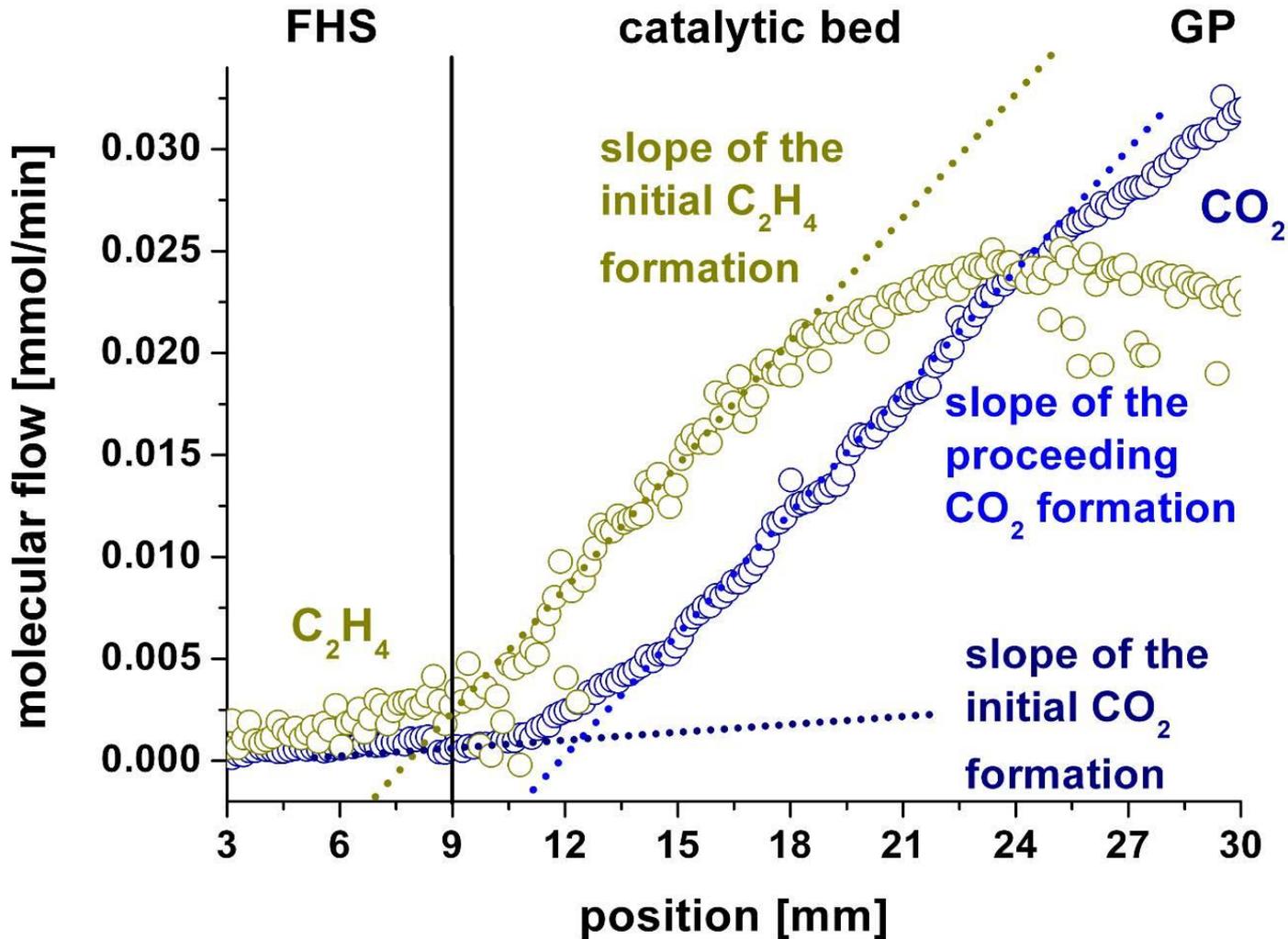
- We tend to infer that rigorous catalysis science can only be done if we know the exact location of atoms.
- We accept real structure as high energy sites.
- But we ignore the „time gap“ of dynamics occurring under elevated chemical potentials of reactants.



# Catalysis - a multi-scale process



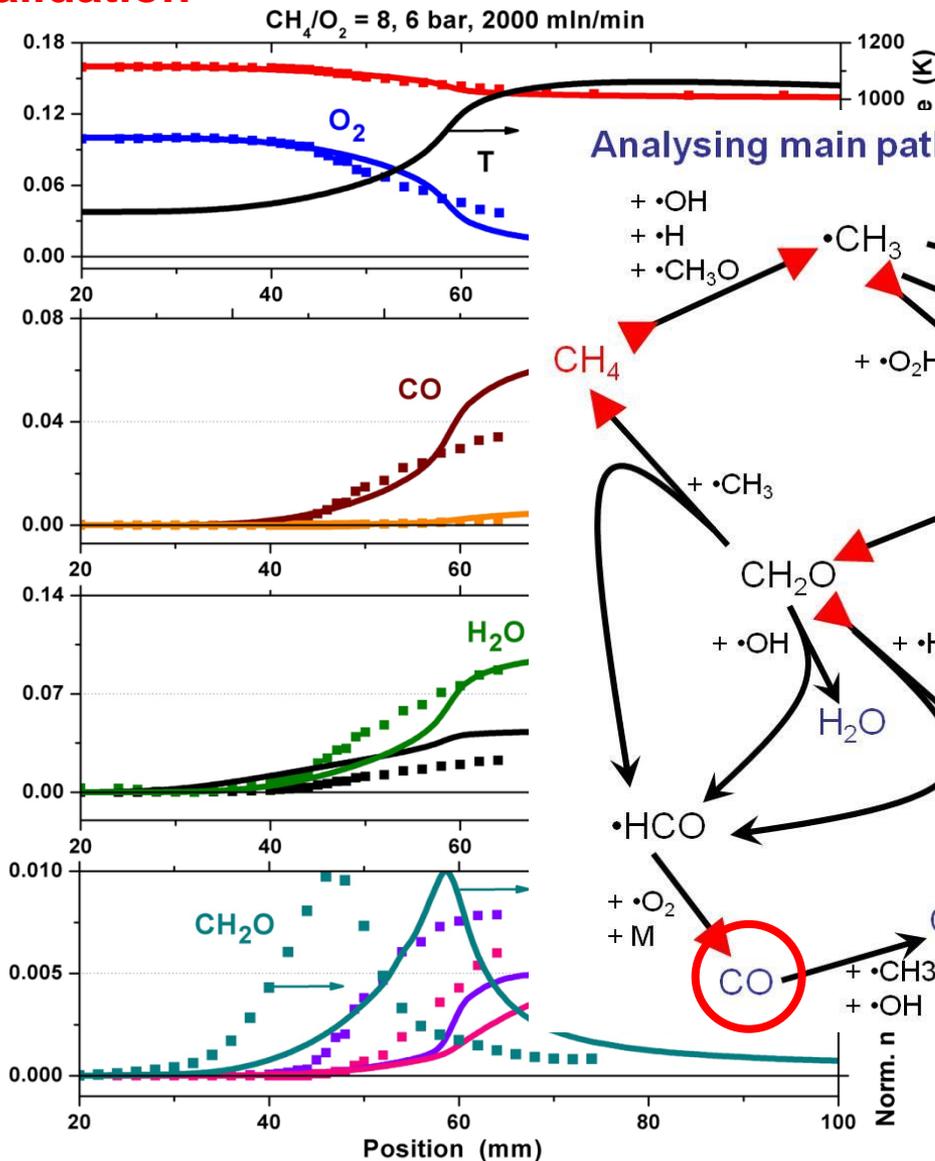
# Mean field? The profile reactor



Ethane ODH  
MoO<sub>3</sub> supported  
773 K 1:1 feed mix

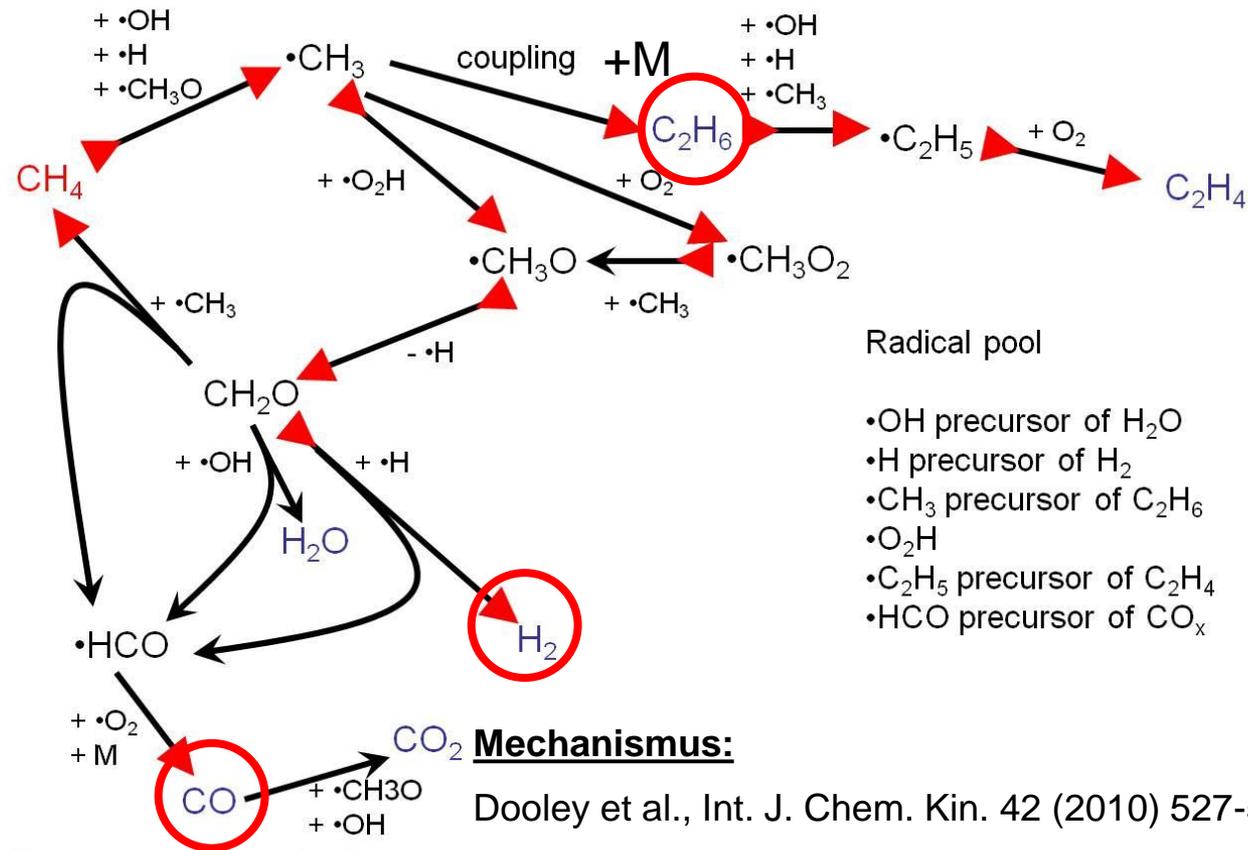
# Oxidative Coupling of Methane (OCM) $\Rightarrow$ A Peculiar Catalytic Reaction

## validation



## reaction path analysis

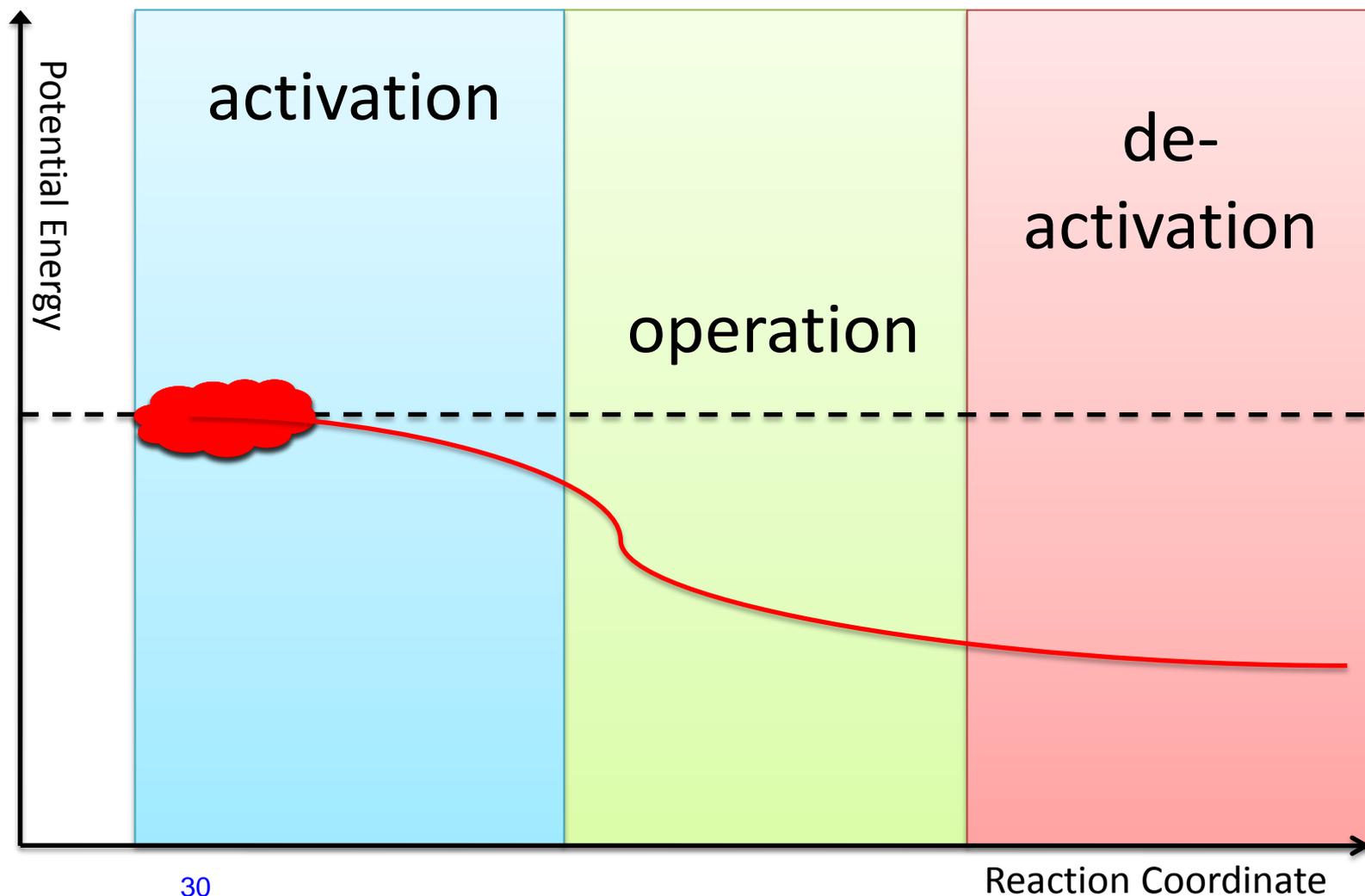
Analysing main pathways from rates of production (CH<sub>4</sub> 74 %, O<sub>2</sub> 5 %)



# Active sites

- The central concept in all types of catalysis.
- Act as coordination centres allowing to exchange adsorbates (fragments) and electrons (oxidation state).
- Are modified during chemical bond rearrangement.
- In a catalytic cycle they are regenerated in to their most active initial state.
- Adaptivity required as mostly the reaction product is more reactive than the starting species: selectivity through autogenous partial deactivation.

# Mode of operation of an active phase: A frustrated structural transition



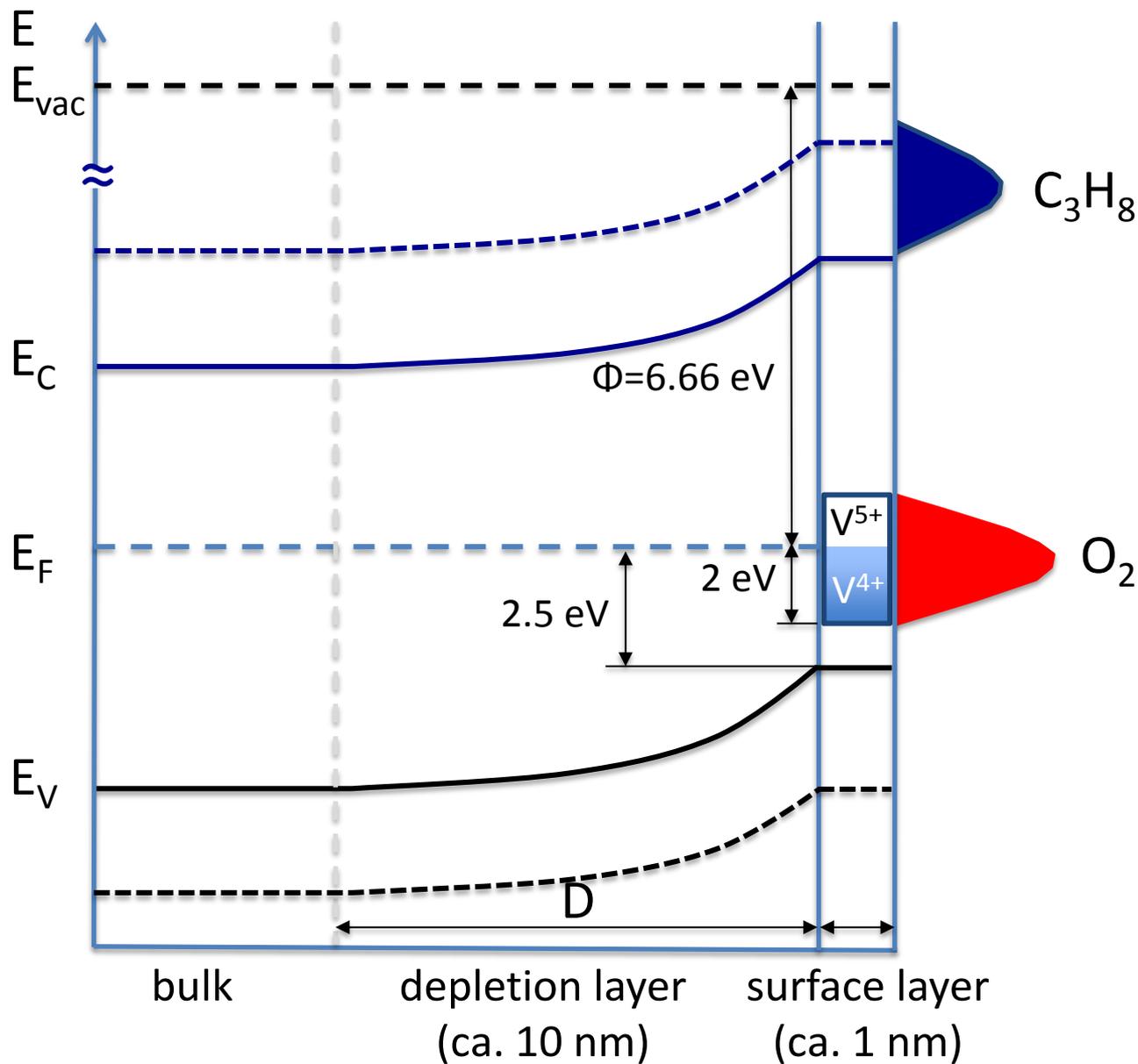
# Catalytic materials

- Catalysts are materials that can re-form active sites several times : the „catalytic cycle“ as kinetic model: how does this work?
- The details of this re-generation are unclear but decisive for understanding the role of a material as catalyst.
- The “standard model” of catalysis assumes a stable active site that does not need any regeneration other than separation of the bond between reactant and catalyst.
- Reactions requiring only dissociation as difficult steps follow this process: ammonia synthesis, CO oxidation SO<sub>2</sub> oxidation.
- Most other reactions where associations are complex and can lead to different products (hydrocarbon transformations) do not follow the standard model.

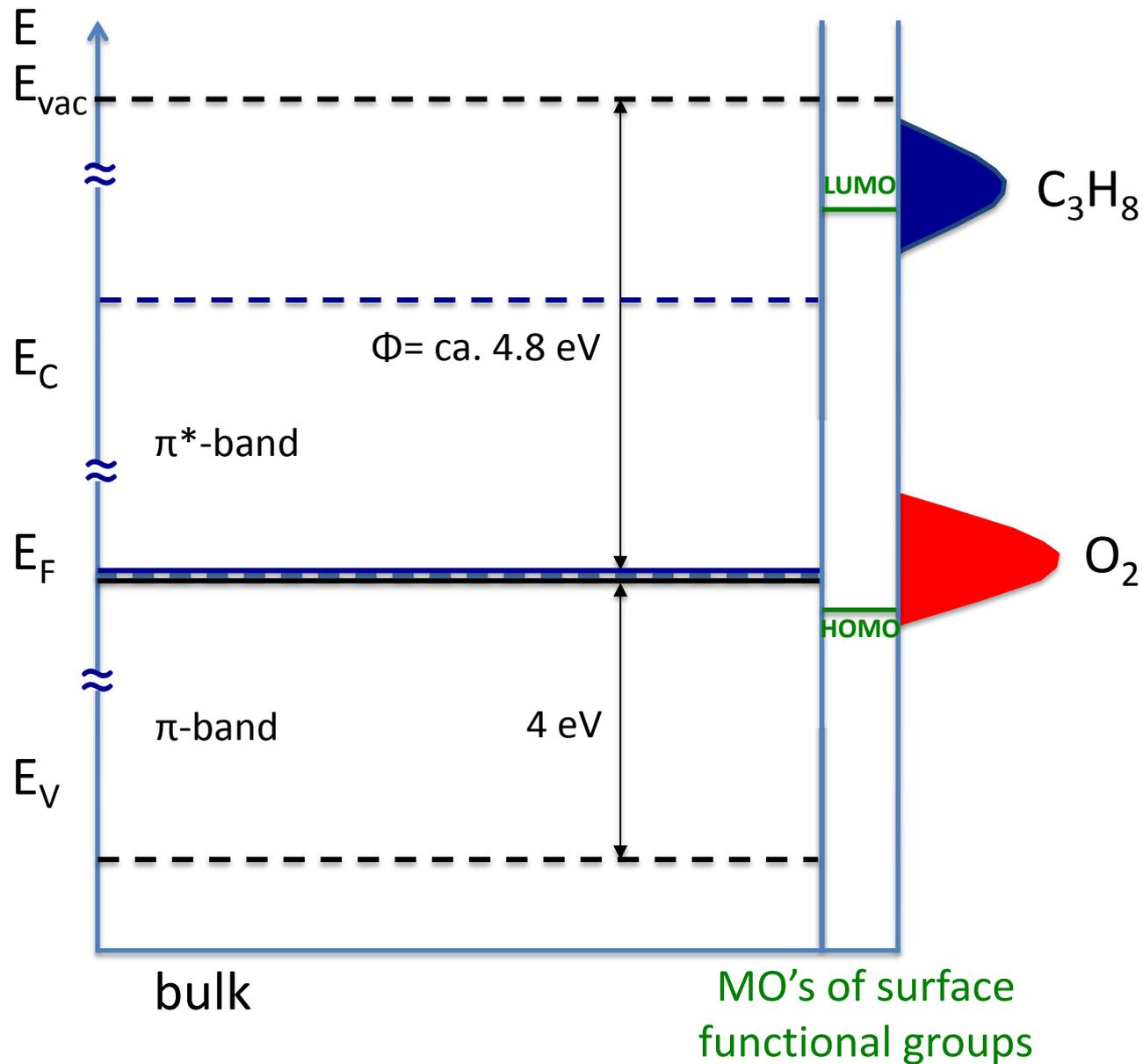
# Realistic Materials

- Most catalysts are nanostructures of active phases supported on a phase with many functions.
- Usually „single site“ concept as molecular search for a minimum of atoms active in a catalytic cycle.
- Historically active atoms were „antennas“ for the underlying band structure of the whole solid.
- The reality lies in-between: both aspects cooperate.

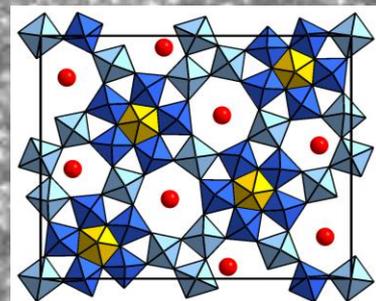
# Prototypical situations



# Prototypical situations



5 nm



# Dem Anwenden muss das Erkennen vorausgehen

Max Planck



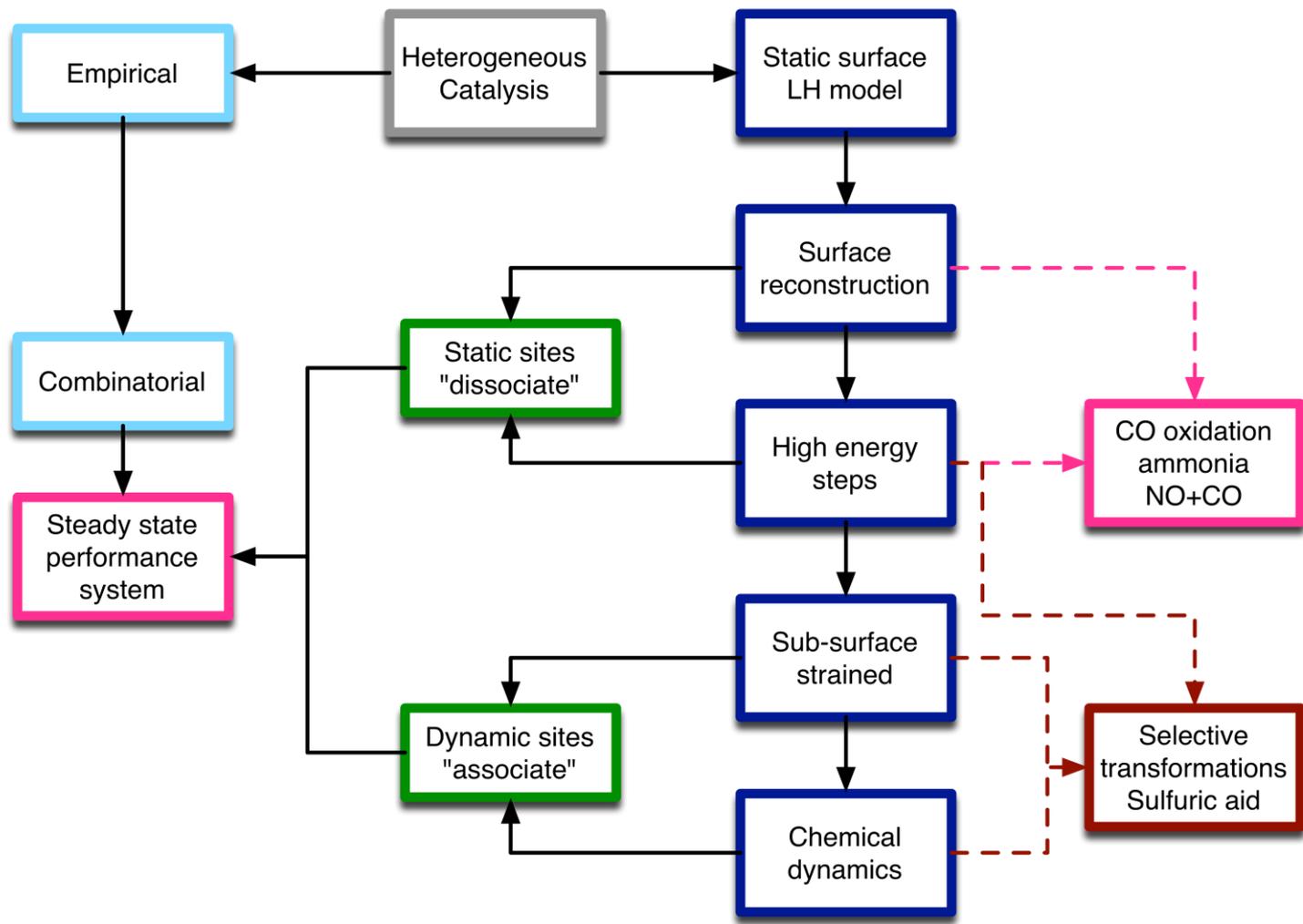
Mache die Dinge so einfach wie möglich aber nicht einfacher

Albert Einstein

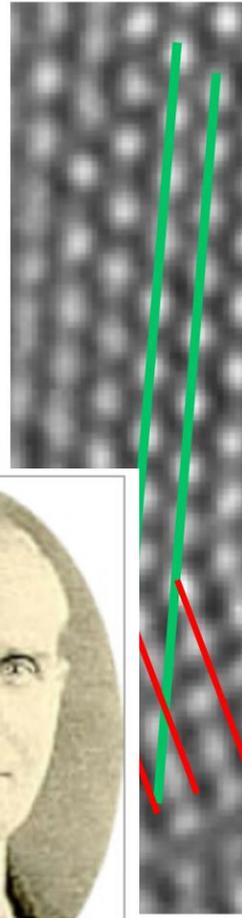
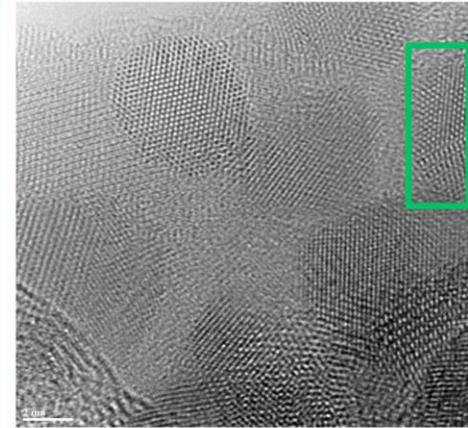
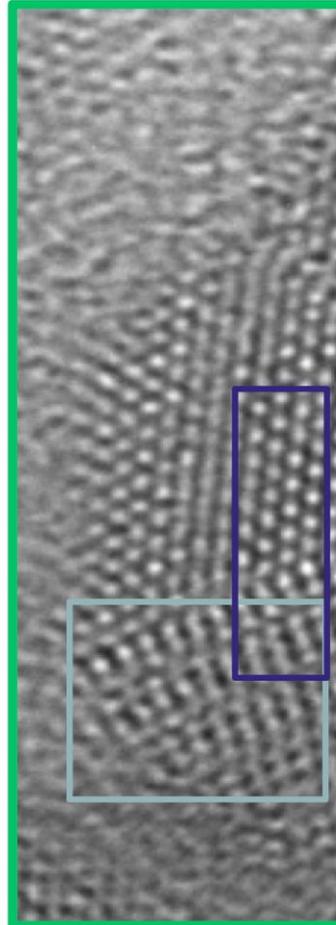
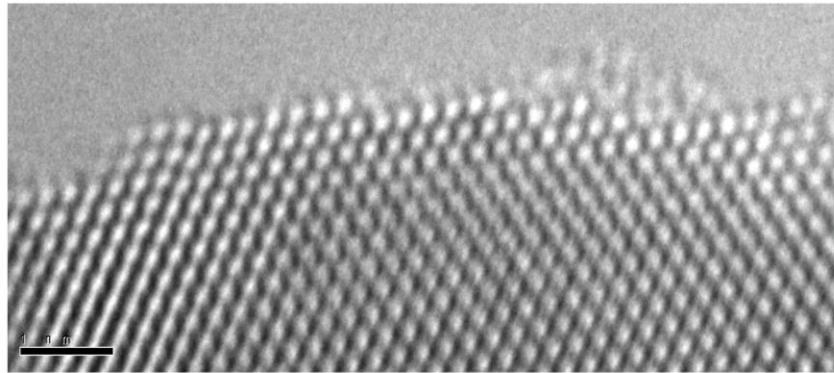
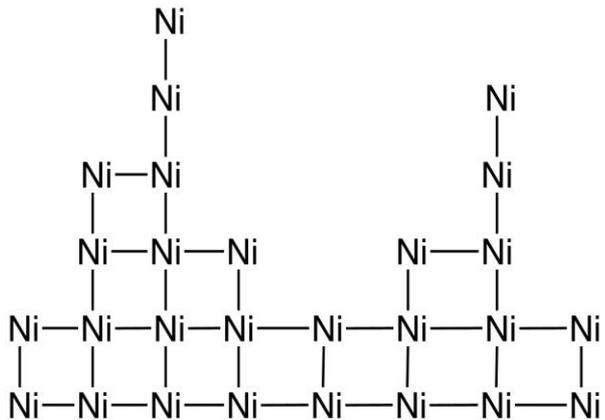
Thank You

# From concepts to observation

Structural complexity needs to be rigorously accounted for



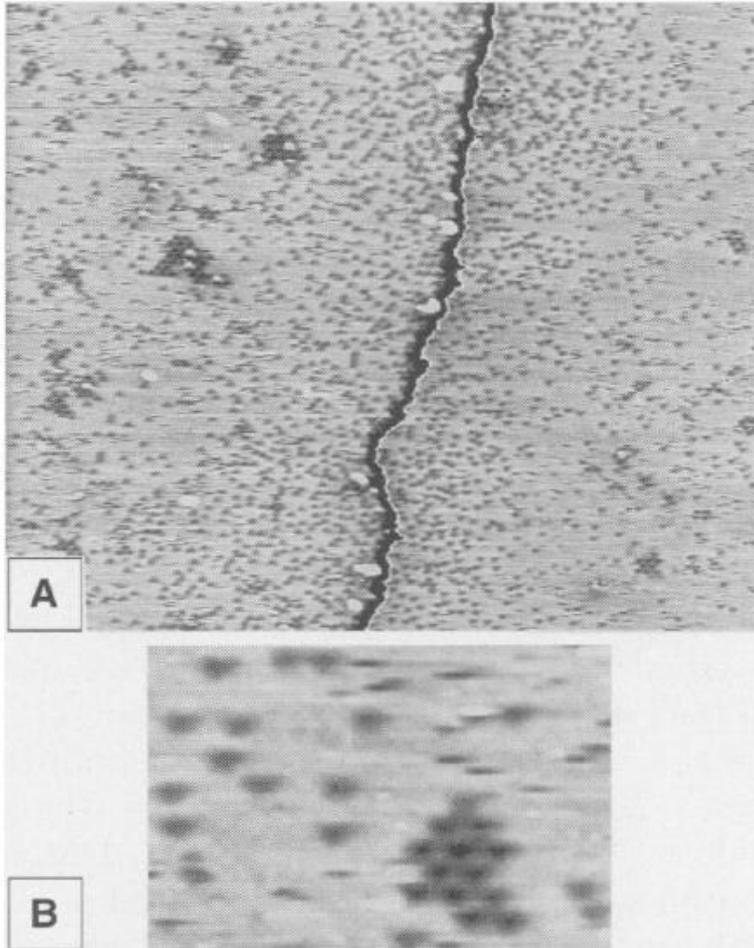
# Active sites: aristocratic



Hughes Stott Taylor

- In metals potential sites detectable (AC-HRTEM).
- In compounds much more involved (termination layer).

# Steps



Discover by STM that steps are the dissociating functions even on single crystal surfaces.

Evidence that “defects” are important for reactivity.

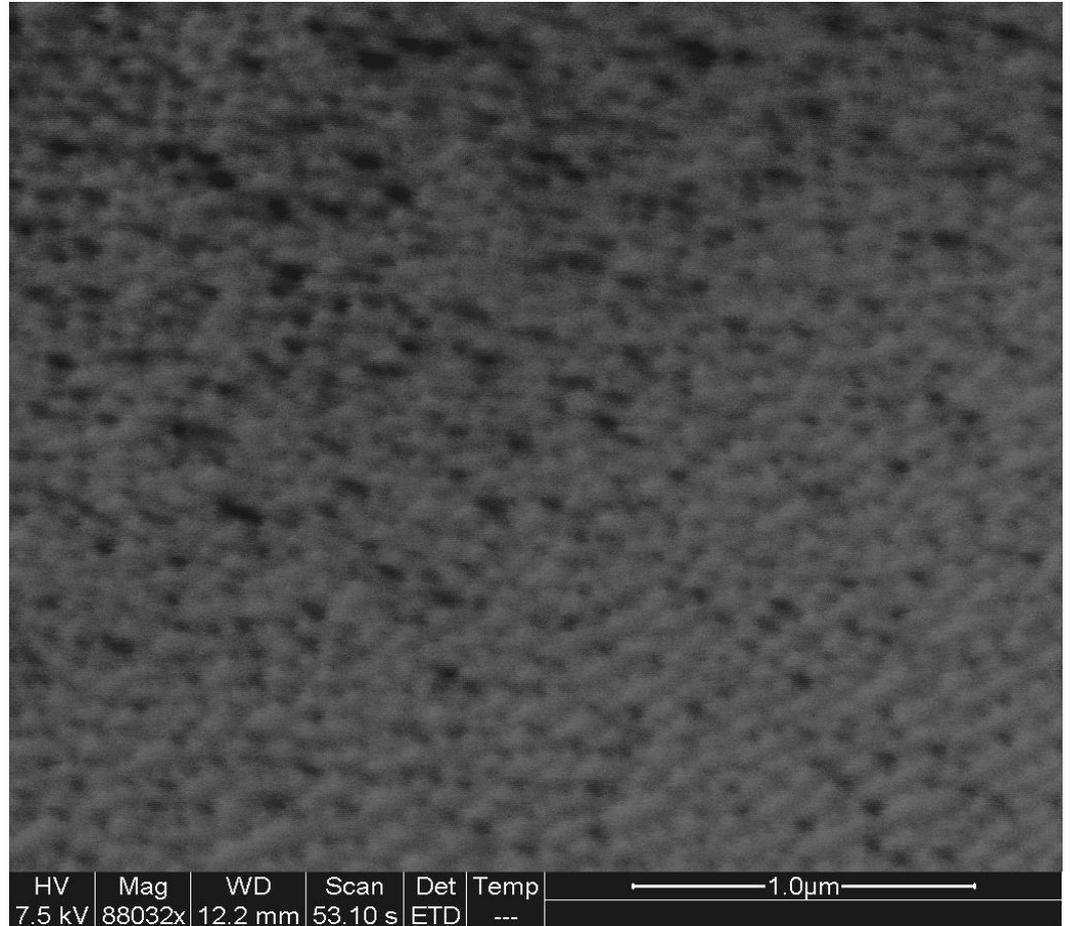
Was also found by Somorjai earlier indirectly during hydrocarbon conversions on Pt and Pd single crystals (selectivity control).

Ertl, Wintterlin, science 1989

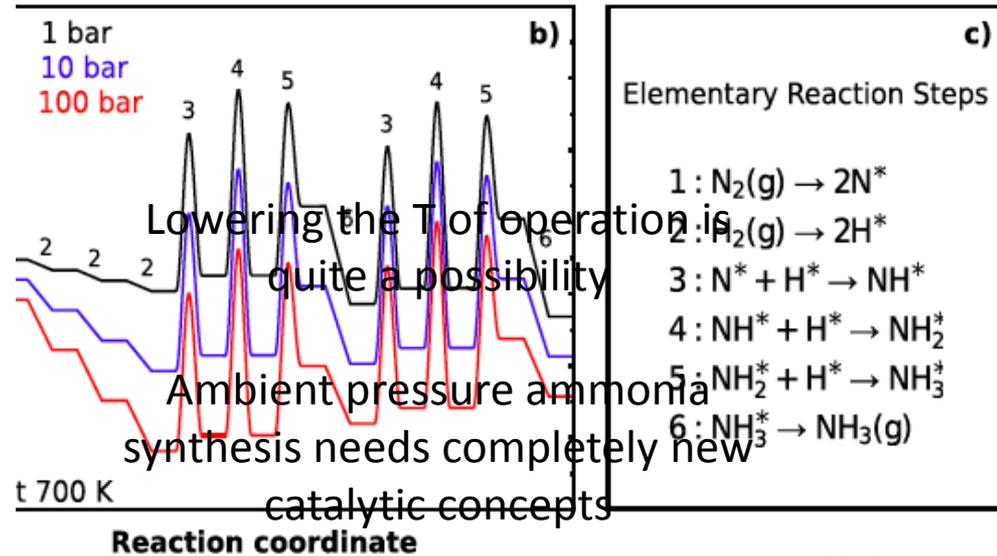
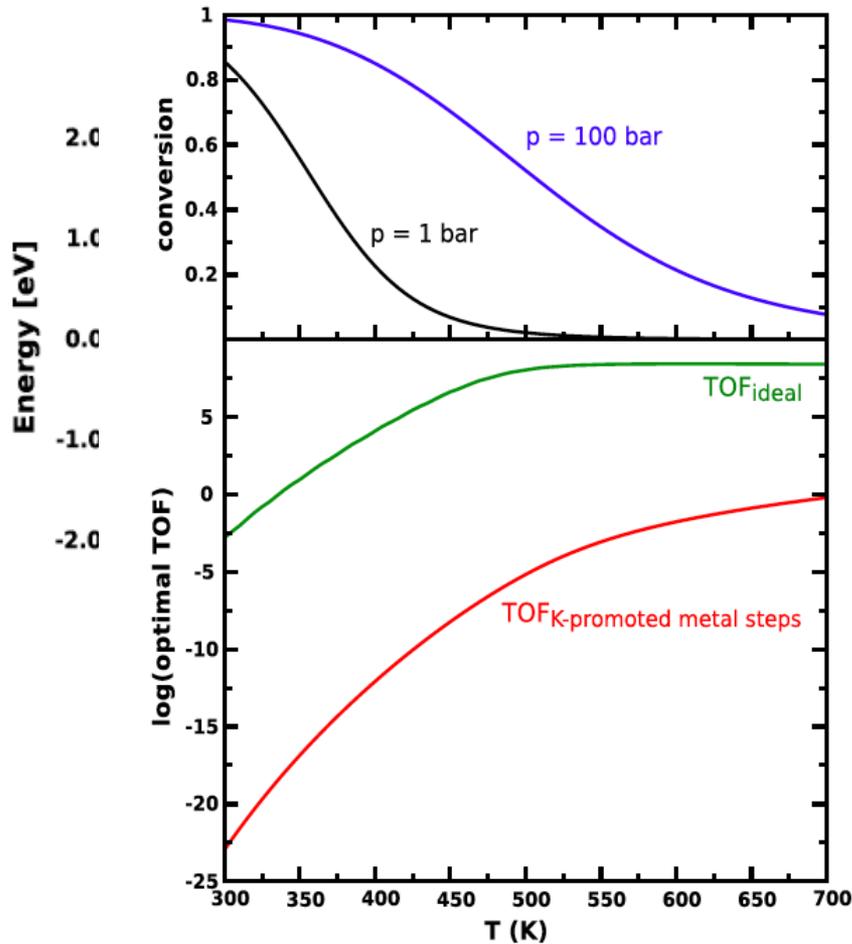
Ru (0001) and NO

# Reactive states of metals: stability

- Heating in vacuum removes the defective real structure of a metal surface and transforms it into its pure non-reactive form:
- Under chemical potential this process is dynamical leading to a fluctuating state of the system between the initial and final state seen in this video



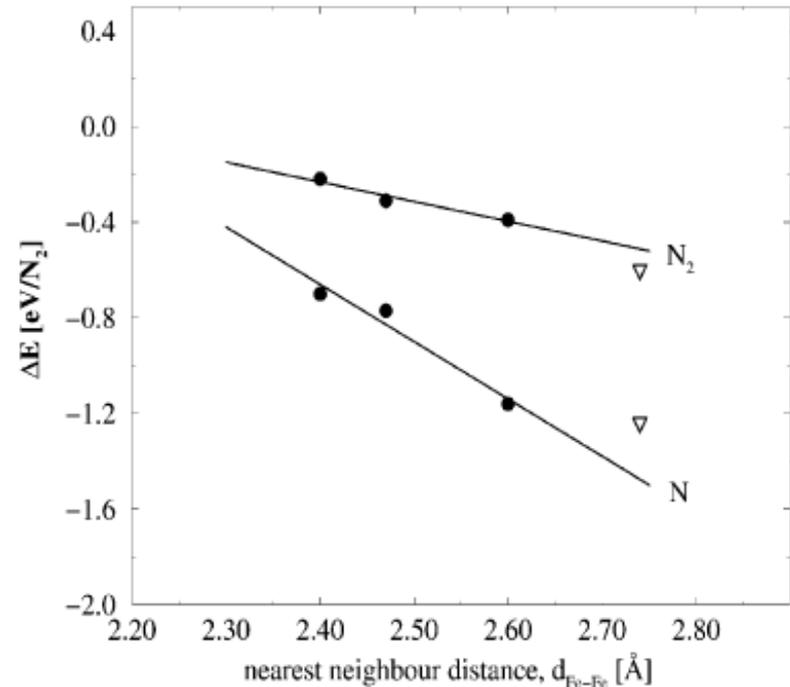
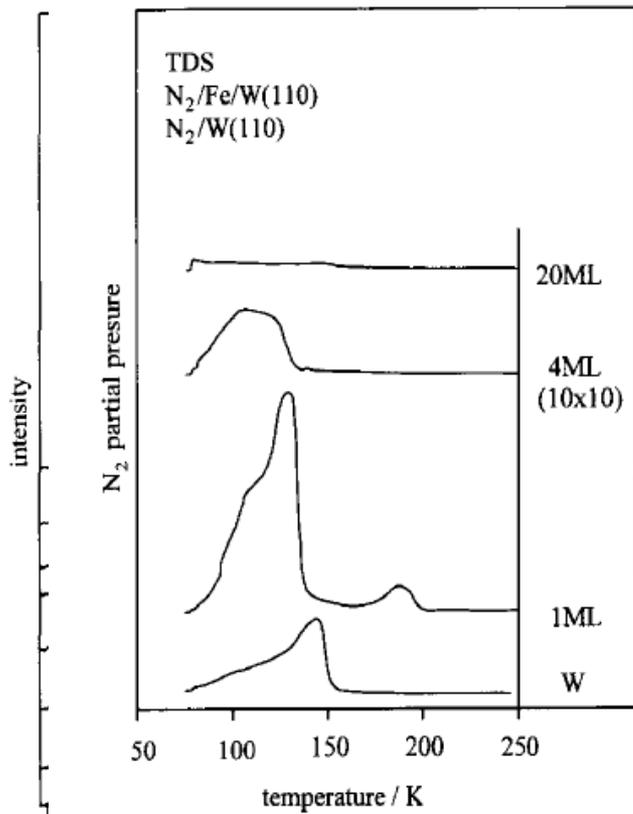
# Theory: What could be possible in Haber-Bosch



Norskov et al. 2013

activation is the sole challenge  
 enters into play: mind ammonia decomposition

# Precision in materials: strained iron



Norskov et al. 1999

Strained iron is a much better catalyst.

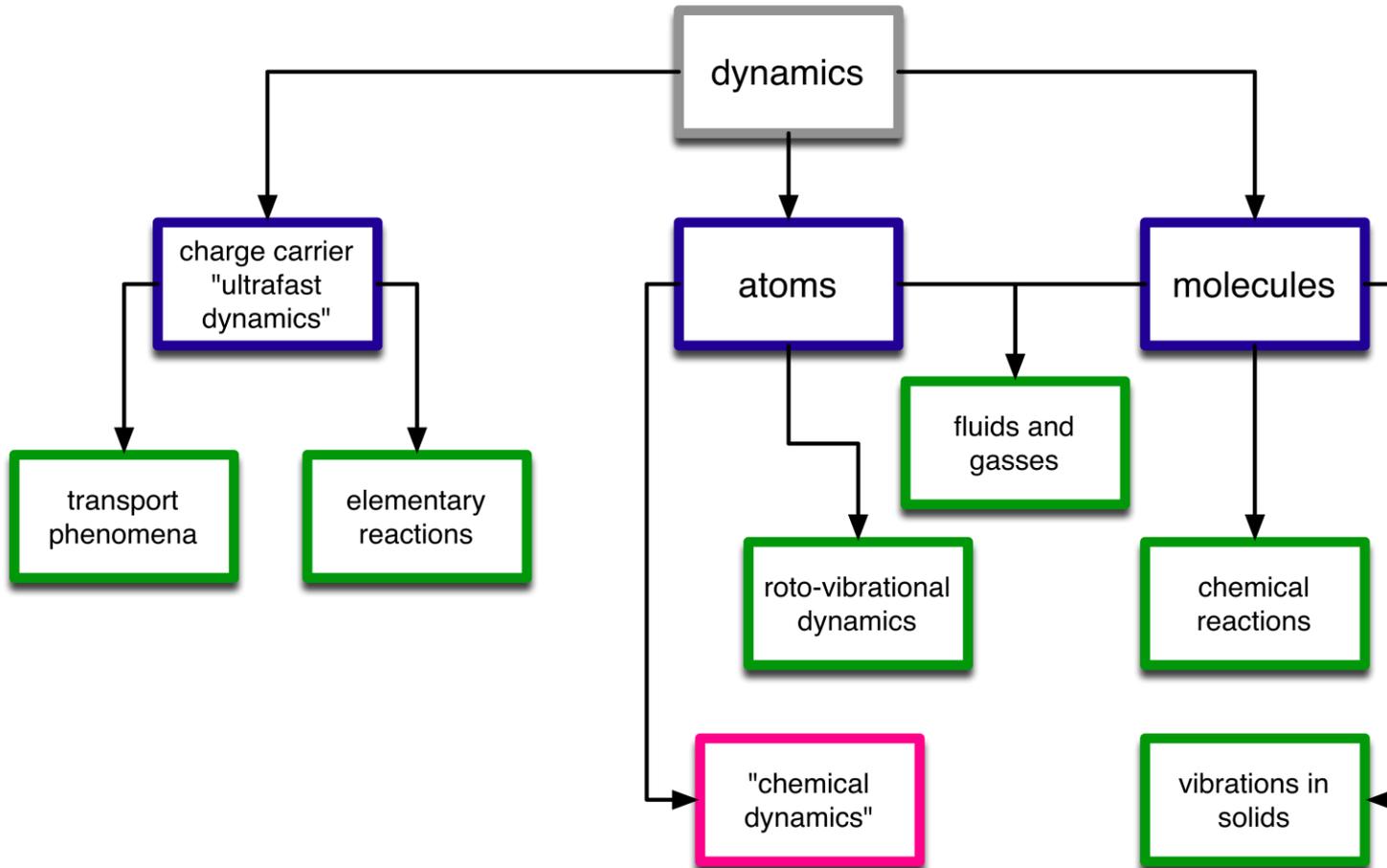
Experimental and theoretical evidence support this.

Challenge: find a suitable compound, as iron metal will be deactivated by nitridation.

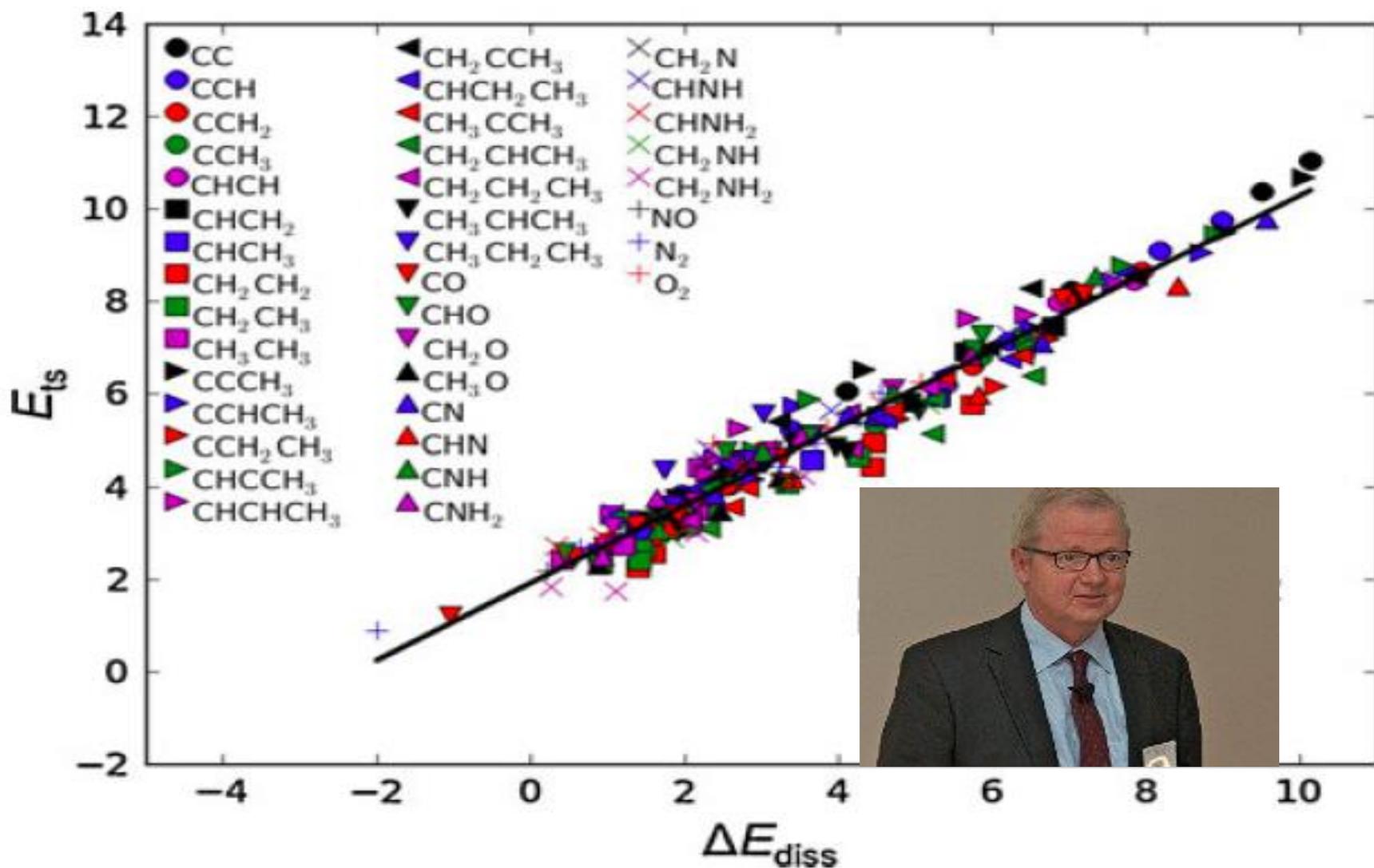
# Dynamics and „excited states“

- Dynamics is not kinetics:
- Process following a potential gradient is kinetics.
- Process fluctuating around an equilibrium structure is dynamics.
- Chemical dynamics is a combination:
- Structural fluctuation as consequence of response of chemical potential:
- Transient states between chemically stable states are relevant: “excited states”.
- Ordered translational structure is a boundary case in catalysis (good for adsorption, poorer for reaction).

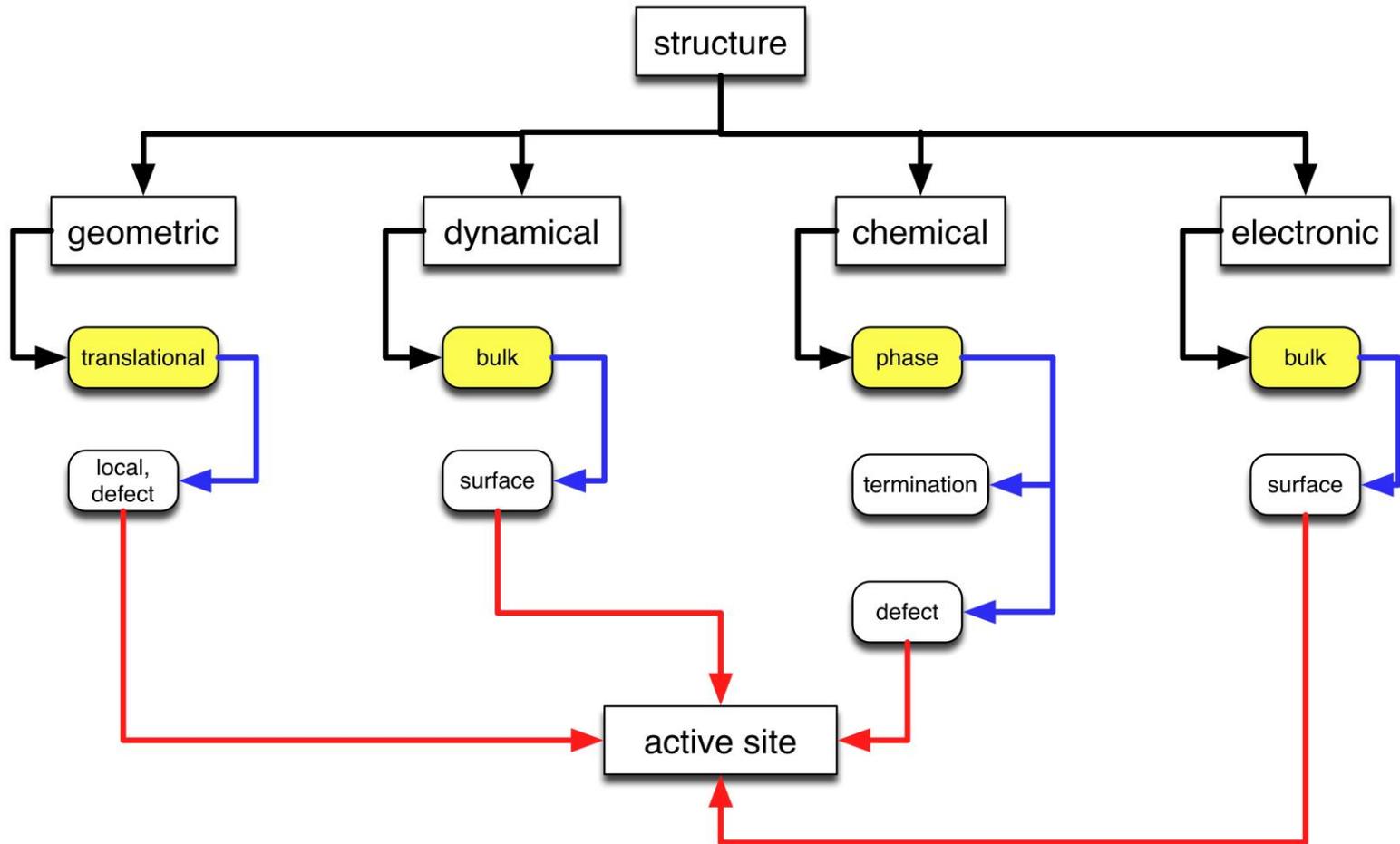
# Dynamics: a hype term?



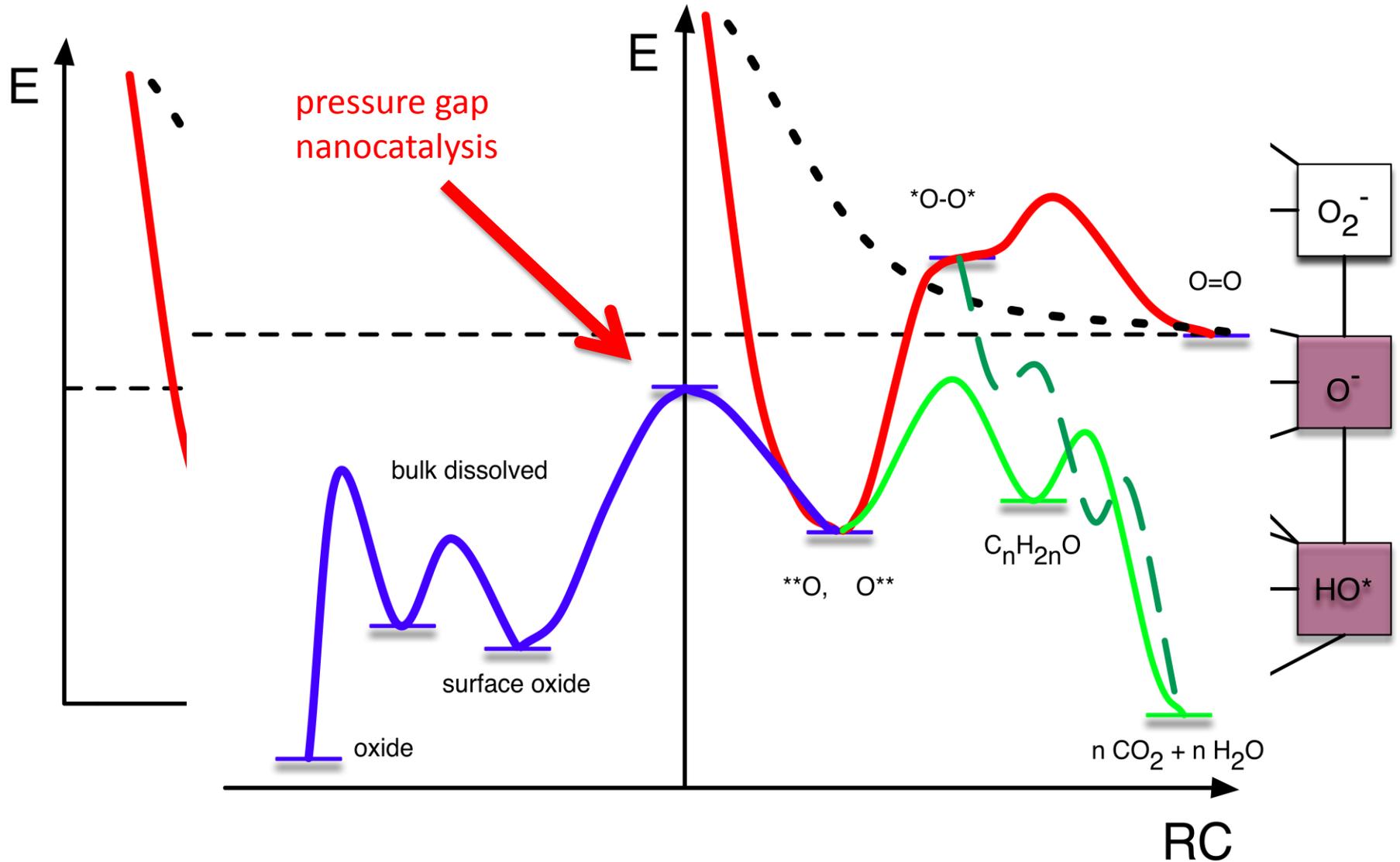
# Is dynamics relevant ?



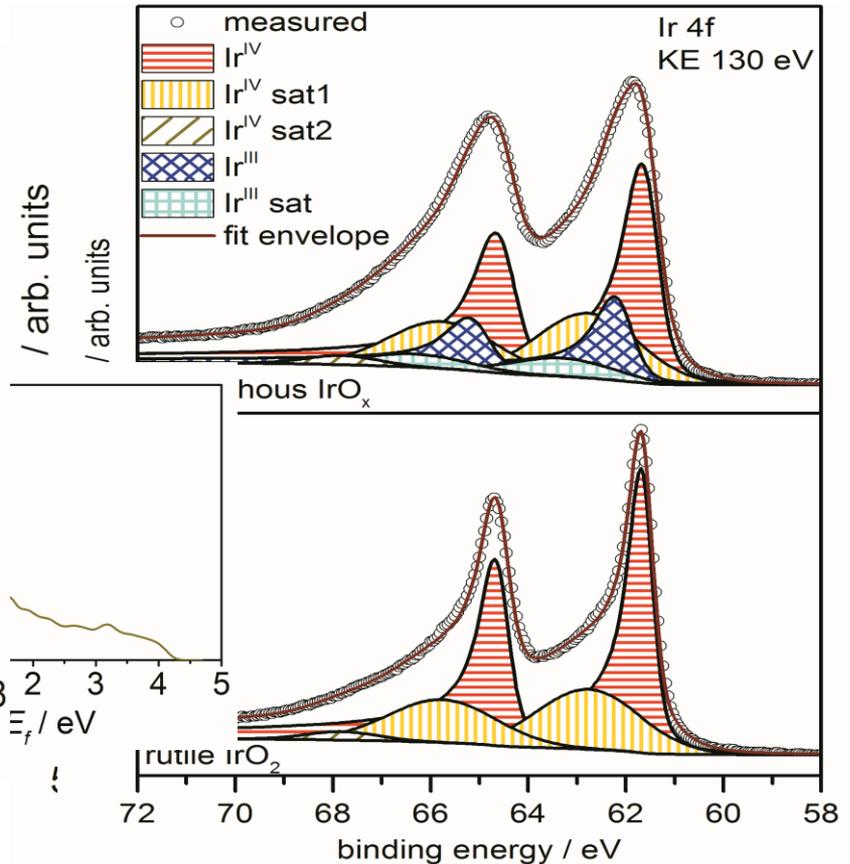
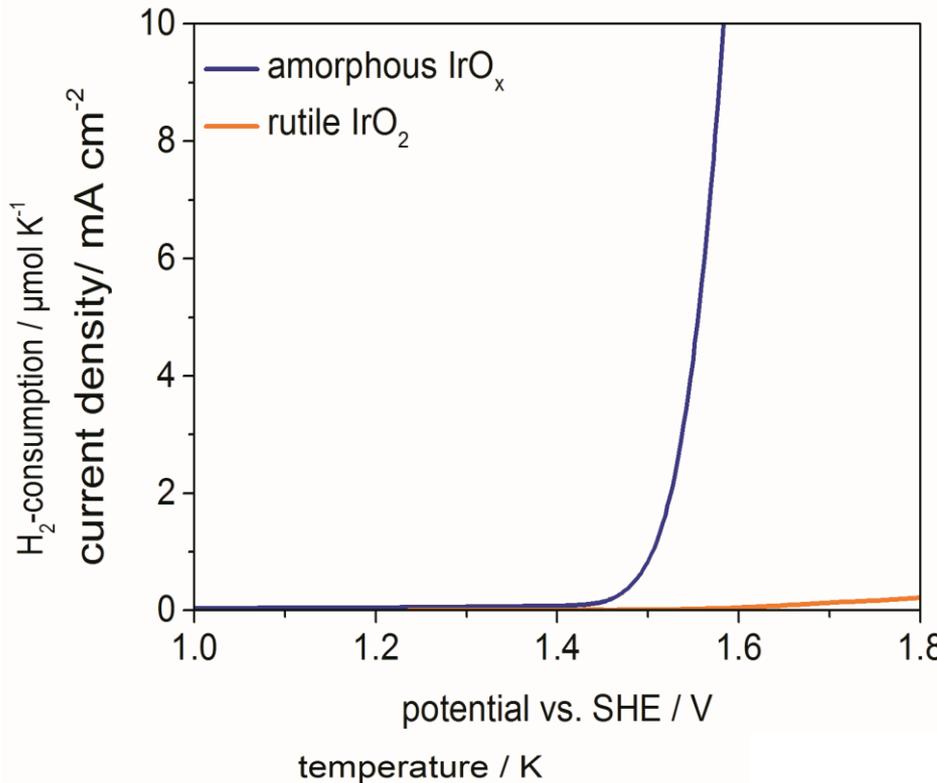
# Structure



# The simple reaction $O_2 \rightleftharpoons 2O$ : What about the catalyst ?

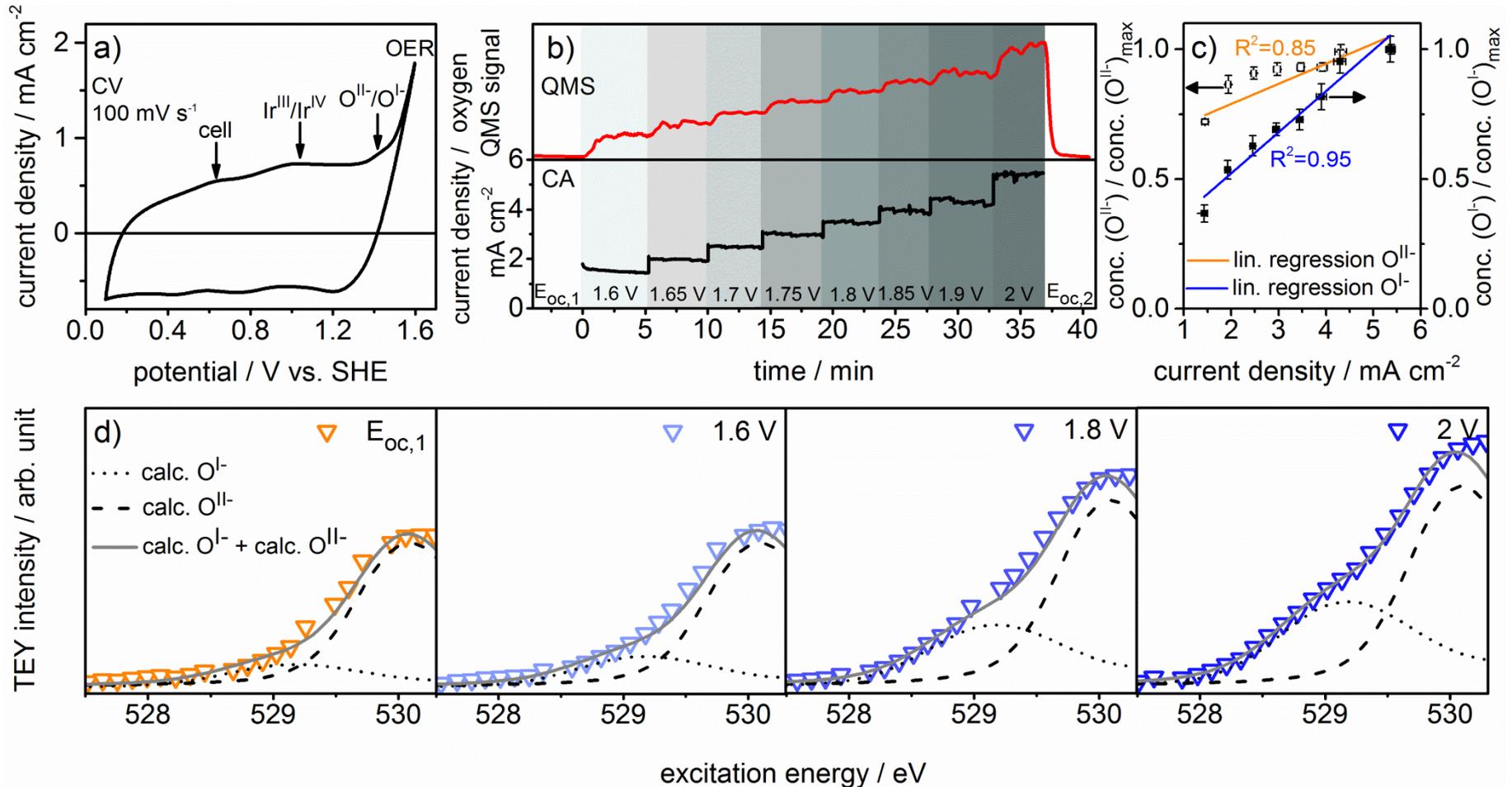


# A worked example: IrO<sub>2</sub> as OER catalyst



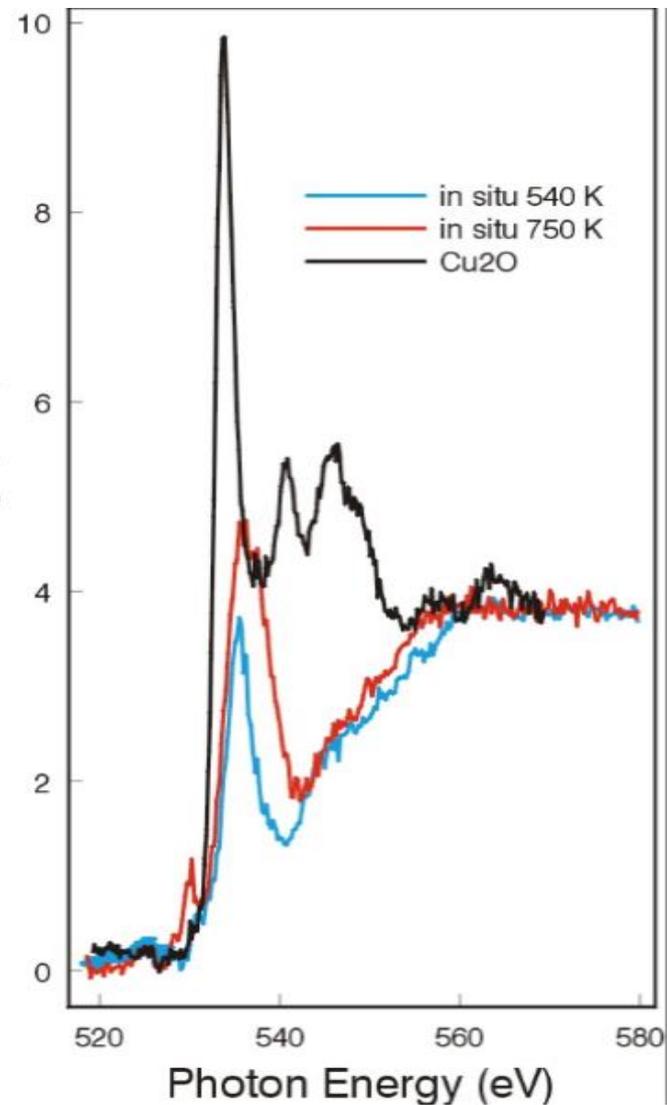
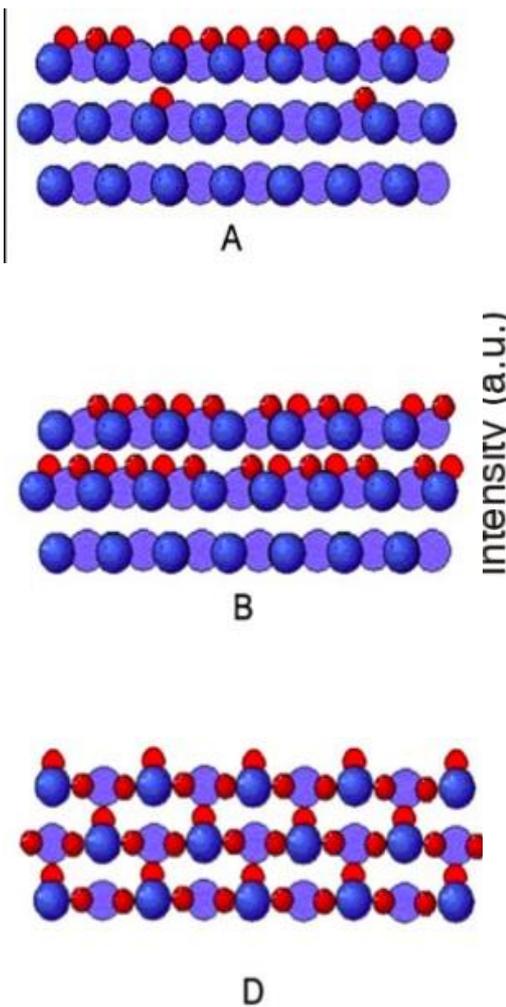
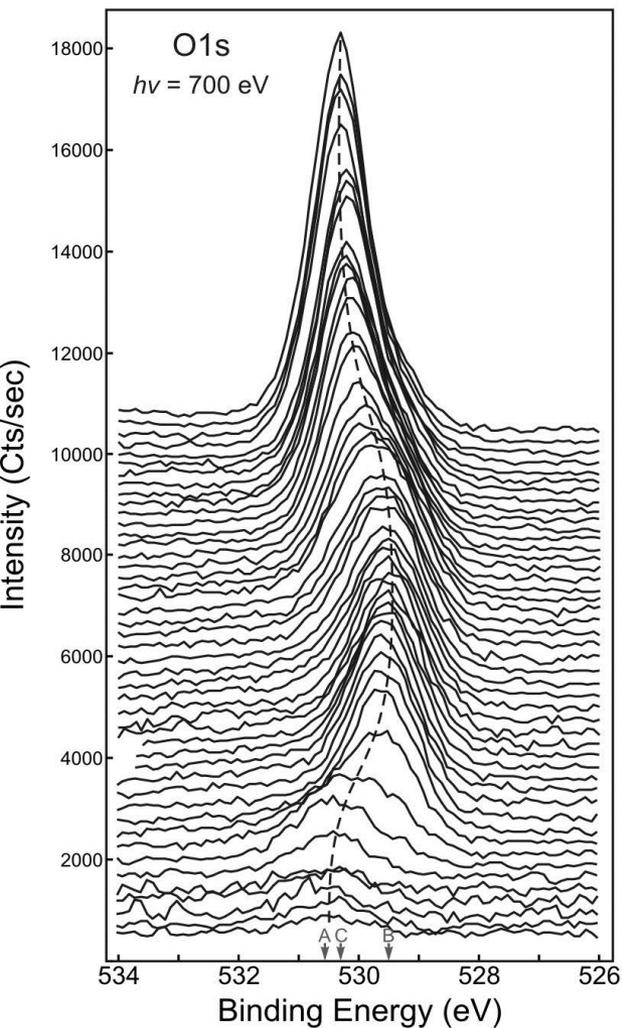
- Ir oxide exists as stoichiometric rutile phase considered as active phase.
- It reveals a low activity in OER in comparison to an „amorphous phase“
- Metastable, loaded with defects in the cation- and anion sublattices.
- Reaction is defect-driven: how well described in conventional model studies?

# O<sup>-I</sup> as active species for OER

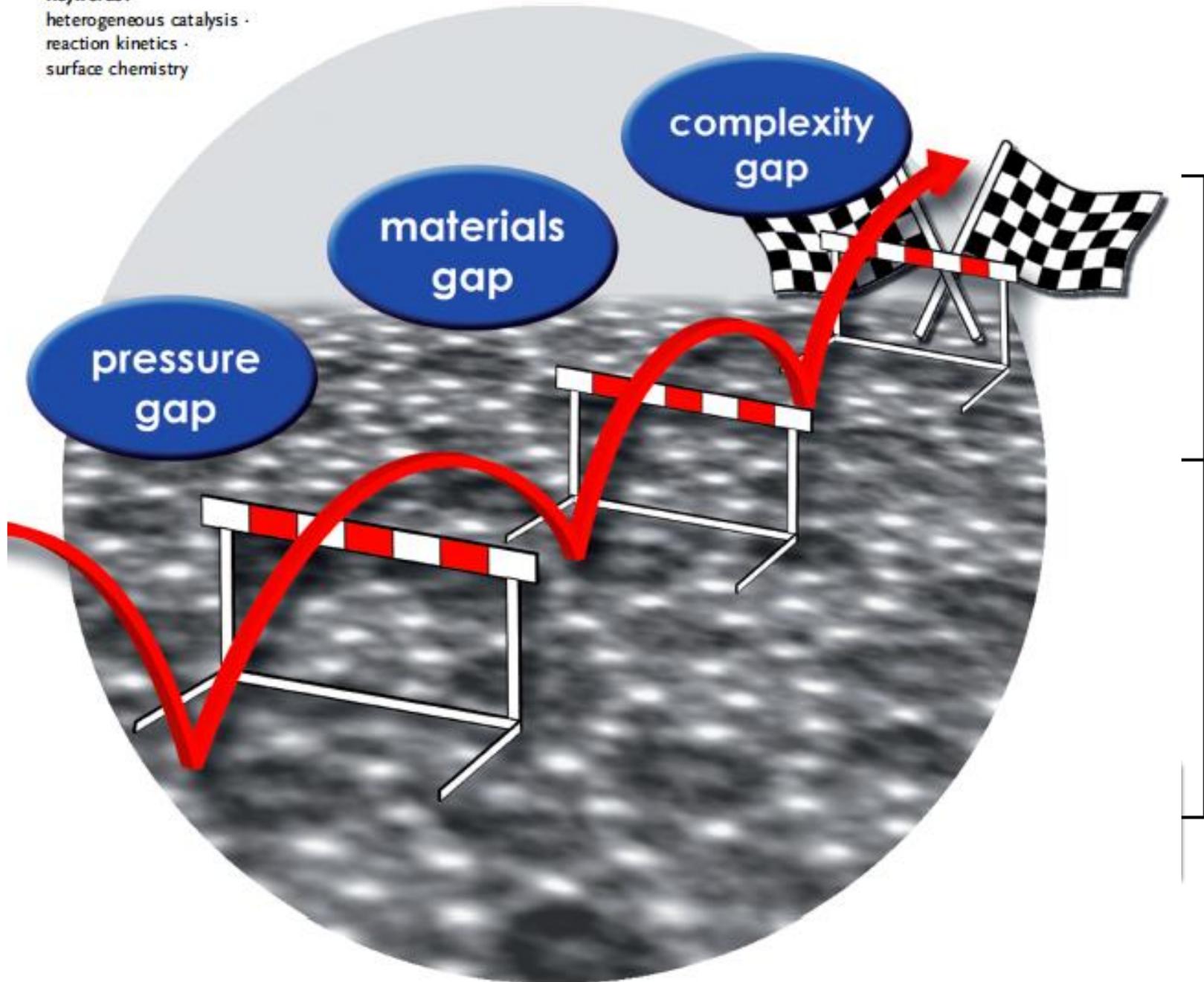


- Observing a 3-electrode cell and Pt//nafion//Ir device during operation by NEXAFS at O-K edge: in 0.1 n sulphuric acid, very low synchrotron light dose.
- All other spectroscopic signatures are poorly sensitive due to lack of chemical information of due to overload with other oxygen species (water, nafion, oxygen).

# Stages of metal oxidation: Cu

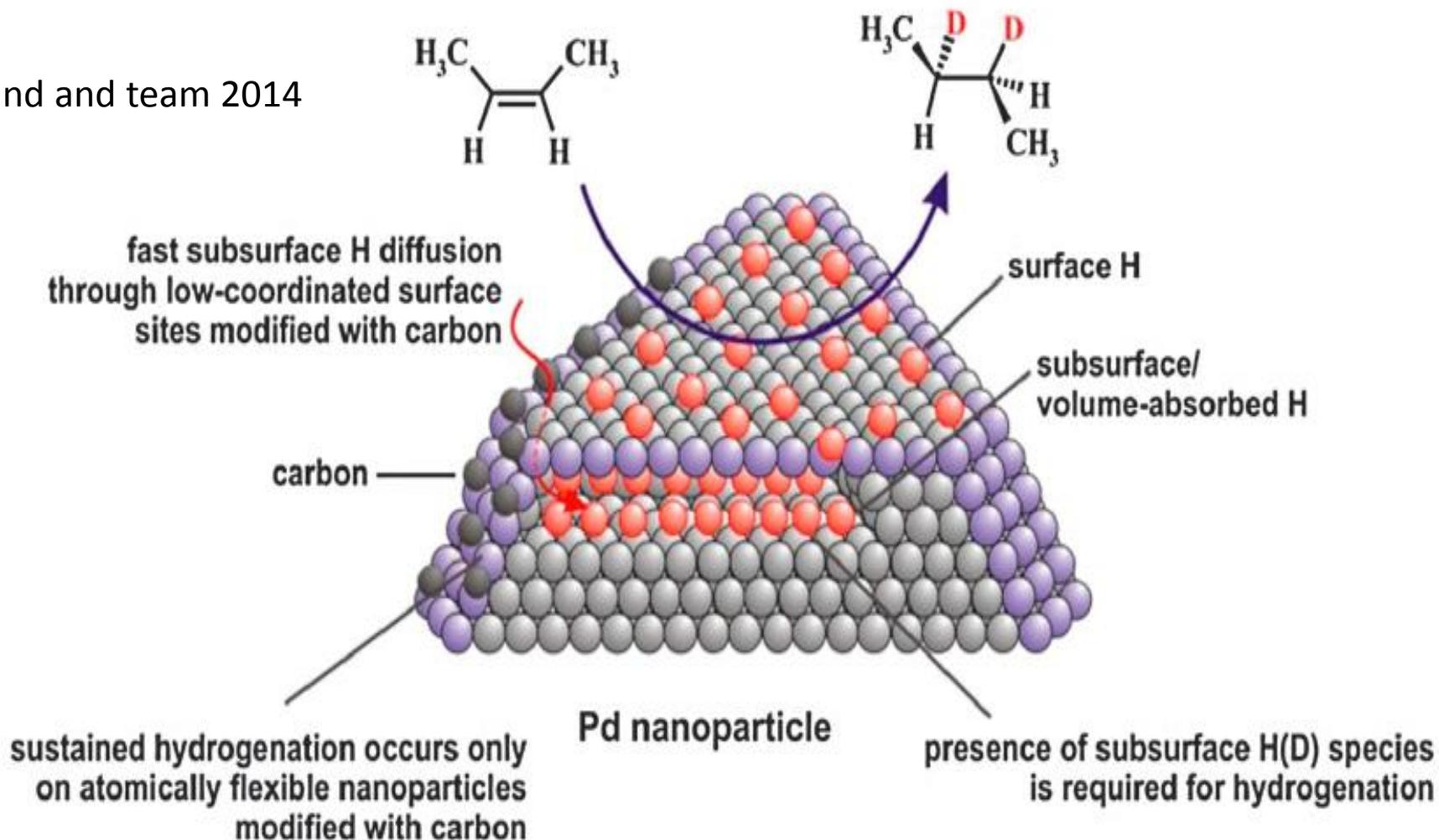


Keywords:  
heterogeneous catalysis ·  
reaction kinetics ·  
surface chemistry



# Is the static model of a catalyst only valid under model conditions?

H.J. Freund and team 2014





# Langmuir Isotherm trends

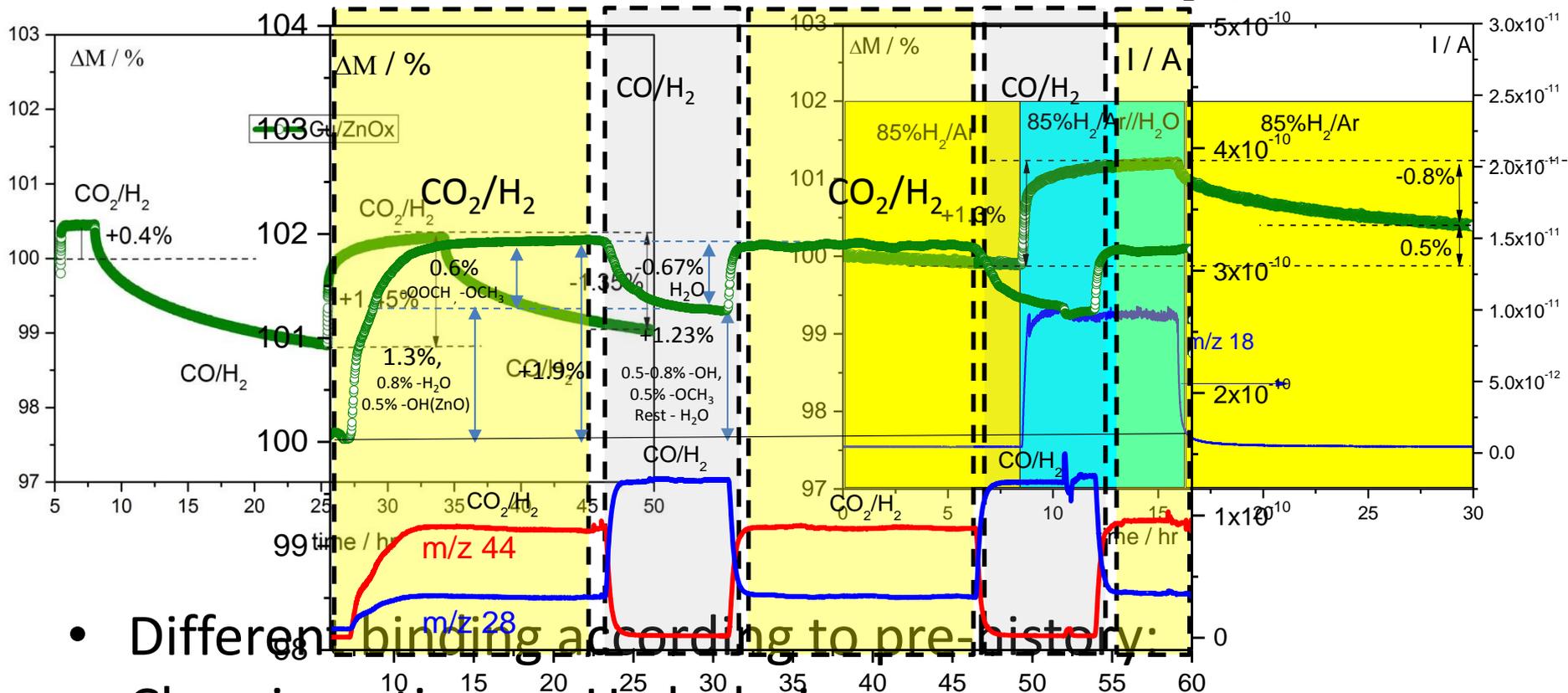
Sample	CO <sub>2</sub>	CO	Property
Cu/MgO	$7.3 \times 10^{-9}$	$1.3 \times 10^{-9}$	K <sub>ads 303</sub>
Cu/MgO/Zn	$1.2 \times 10^{-8}$	$3 \times 10^{-15}$	
Cu/MgO	57 a	59 b	Q (kJ/mol) <sub>303</sub>
Cu/MgO/Zn	71 a	98 b	
Cu/ZnO/Al	---	157 b	a at $1 \times 10^{-6}$ mol/g
Cu nano	---	48 a	b at $2 \times 10^{-5}$ mol/g

# Water on Cu/ZnO/Al

In-situ TG Experiment: 30bar, 230°C, 200Nml/min, 400mg

RWGS reaction (250°C, 1bar)

Addition of 1.5% H<sub>2</sub>O (250°C, 1bar)



- Different binding according to pre-history:
- Chemisorption vs. Hydrolysis
- Limiting for MeOH synthesis temperature