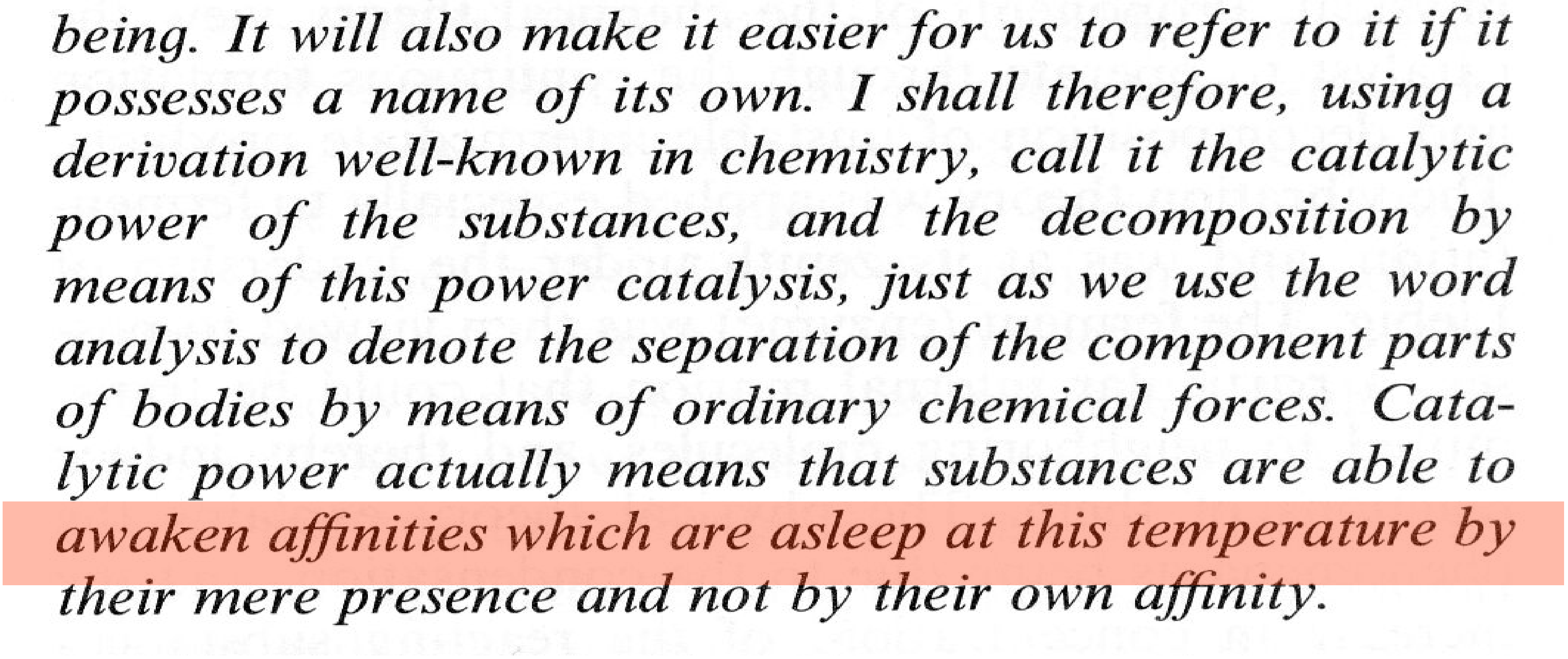
Concepts

- Catalysis is a science based on concepts that are partly founded in theory.
- This well-founded part is the result of surface science and of quantum theory and is valid for processes with adsorption / activation as rate-controlling step without selectivity.
- Catalysis is a multi-scale phenomenon and requires thus simultaneous research in several chemical disciplines.

Concepts

- The concepts developed differently in different disciplines of catalysis:
  - Homogeneous
  - Heterogeneous
  - Biological.
- Common to all: catalysis is a kinetic effect and cannot modify thermodynamic limits.

Definitions



being. It will also make it easier for us to refer to it if it possesses a name of its own. I shall therefore, using a derivation well-known in chemistry, call it the catalytic power of the substances, and the decomposition by means of this power catalysis, just as we use the word analysis to denote the separation of the component parts of bodies by means of ordinary chemical forces. Catalytic power actually means that substances are able to awaken affinities which are asleep at this temperature by their mere presence and not by their own affinity.

Berzelius, 1820

How does this work?

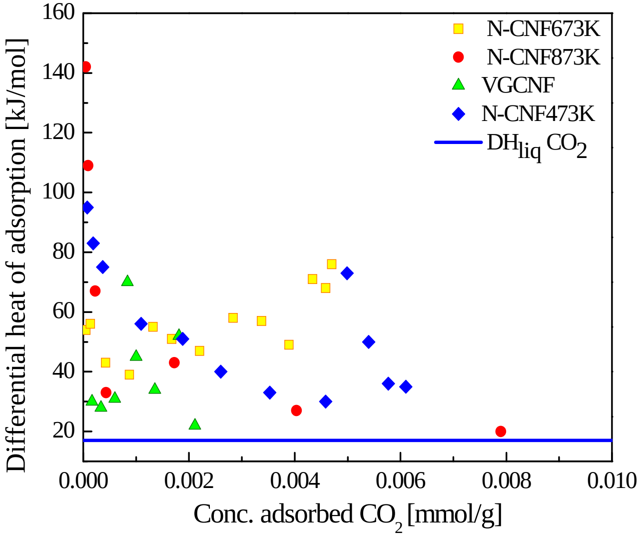
Functional answer by physical chemistry (potential energy)

Chemical answer?

Activity and selectivity

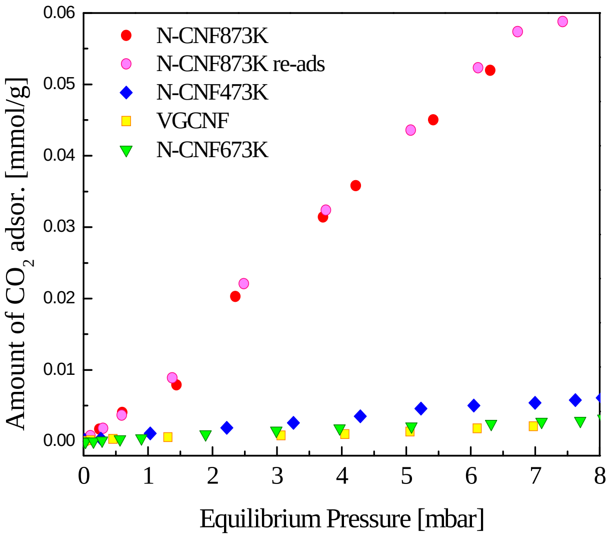
- Catalyst quality according to yield per unit
  - Mass: well measurable
  - Total surface area: more realistic
  - Active surface area: sometimes possible
  - Active site most desired: not countable (tof concept)
- No absolute measure possible for any catalyst today!!
- Selectivity is fraction of atoms (!!) from feed that are found in the desired product:
  - Analytical accuracy and definition ambiguities.

Counting active sites
Acid-base chemistry of N CNT:



Microcalorimetry with CO$_2$

RSA 2 m^2/g
TSA: 55 m^2/g



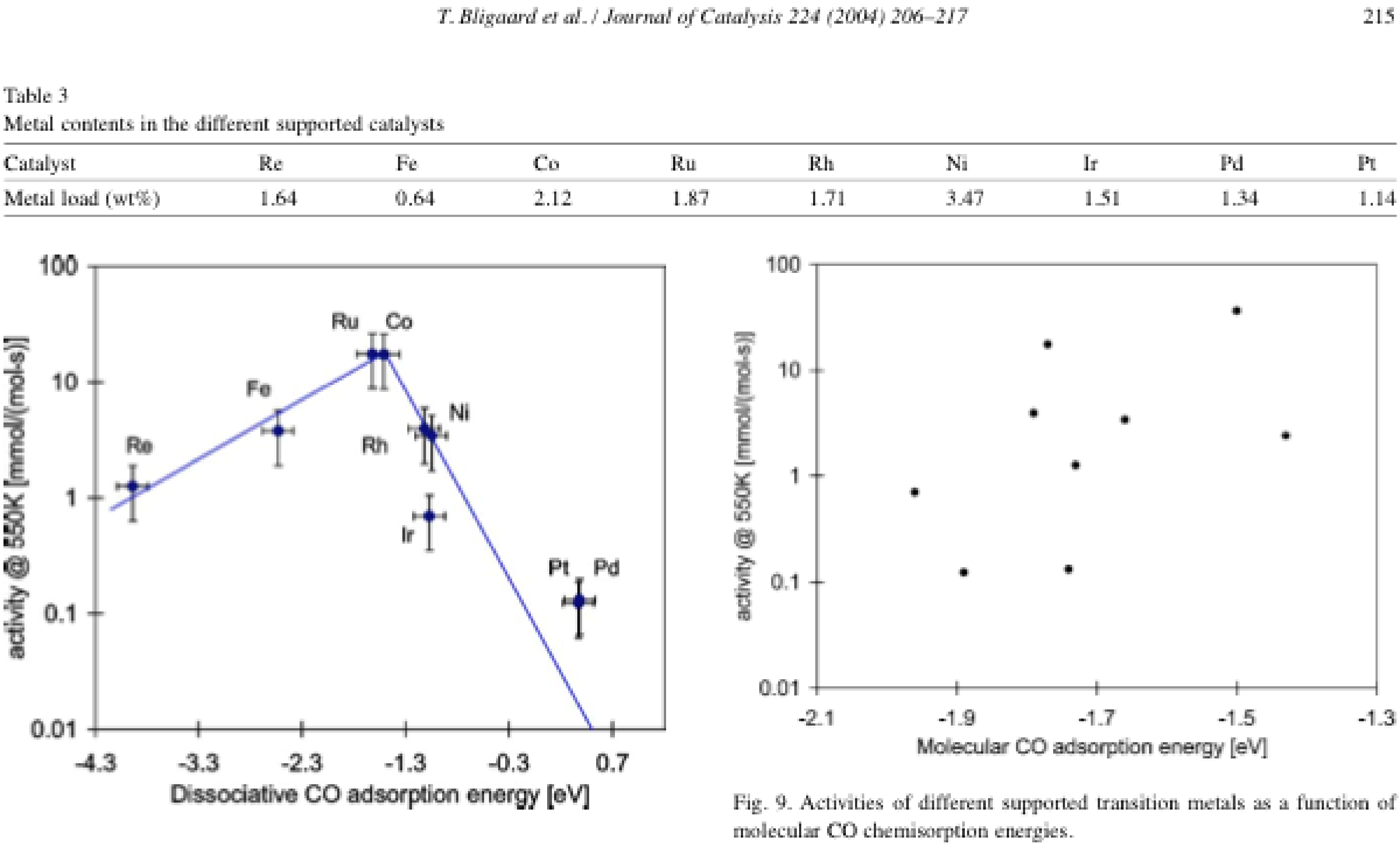
Sample	Liquid phase titration		Gas phase Microcalorimetry	
	mol basic site/g	pKa	Amount of CO$_2$ mol/g	Initial differential heat of adsorption KJ/mol
N-CNF473K	$4.5*10^{-4}$	7,9; 7.8	$5*10^{-6}$	90
N-CNF673K	6*10-4	8.2; 8	$1.5*10^{-6}$	50
N-CNF873K	$1*10^{-3}$	8.35; 8.34	$8*10^{-6}$	150

Chemical dynamics: difference in gas or protolytic liquid water

Basic concepts

- Catalysts bring together reactants by adsorption.
- At special high energy sites (“active sites”) adsorbates can react (exchange atoms in molecular entities).
- Catalysts operate cyclically recuperating the active site.
- Excessive strength of adsorption kills catalyst by poisoning the active site.

Example: CO methanation



T. Bligaard et al. / Journal of Catalysis 224 (2004) 206–217 215

Table 3
Metal contents in the different supported catalysts

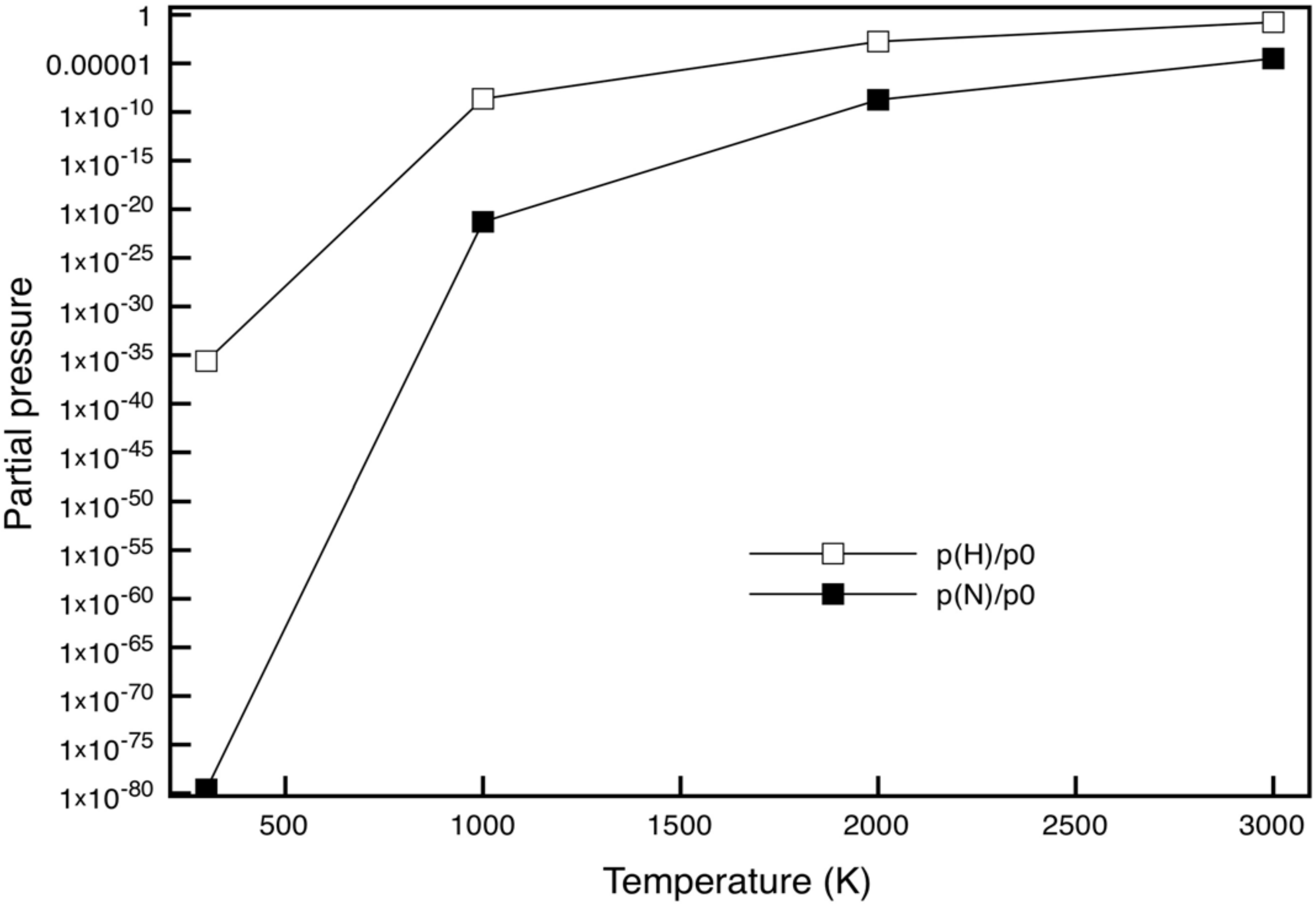
Catalyst	Re	Fe	Co	Ru	Rh	Ni	Ir	Pd	Pt
Metal load (wt%)	1.64	0.64	2.12	1.87	1.71	3.47	1.51	1.34	1.14

Fig. 9. Activities of different supported transition metals as a function of molecular CO chemisorption energies.

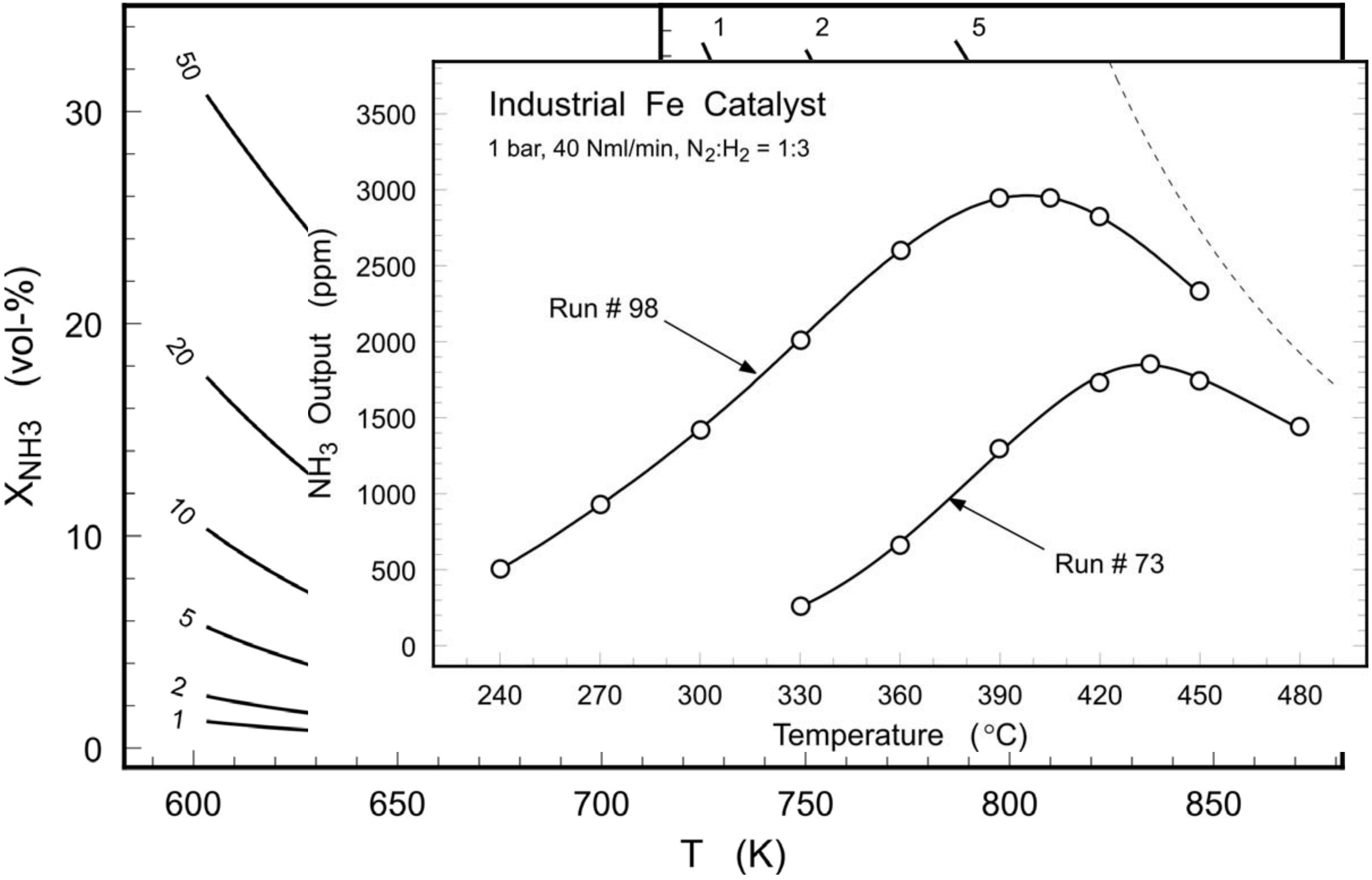
Heterogeneous catalysis

- Two concepts for active sites:
  - Mean field approximation: all sites are equal and all geometric sites are active (Langmuir model).
  - Active sites are embedded in non-active surface sites allowing adsorption (checkerboard model, Taylor model).
- All theory and most model systems operate with the Langmuir model, Taylor model mostly qualitative: CO oxidation, gold catalysis: “perimeter models”.

Why we need catalysis:N/H uncatalyzed is unreactive



Why we need a catalyst: Haber-Bosch



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State of science

- All practical catalysts (high-performance) are found by empirical methods.
- Despite enormous factual knowledge no rigorous understanding of structure function relations; design?
- Models are still the only way to relate the knowledge of surface science to the application of catalysis leading to “generic” knowledge.
- The reasons for the “gaps” between model studies and high performance catalysis should become apparent.

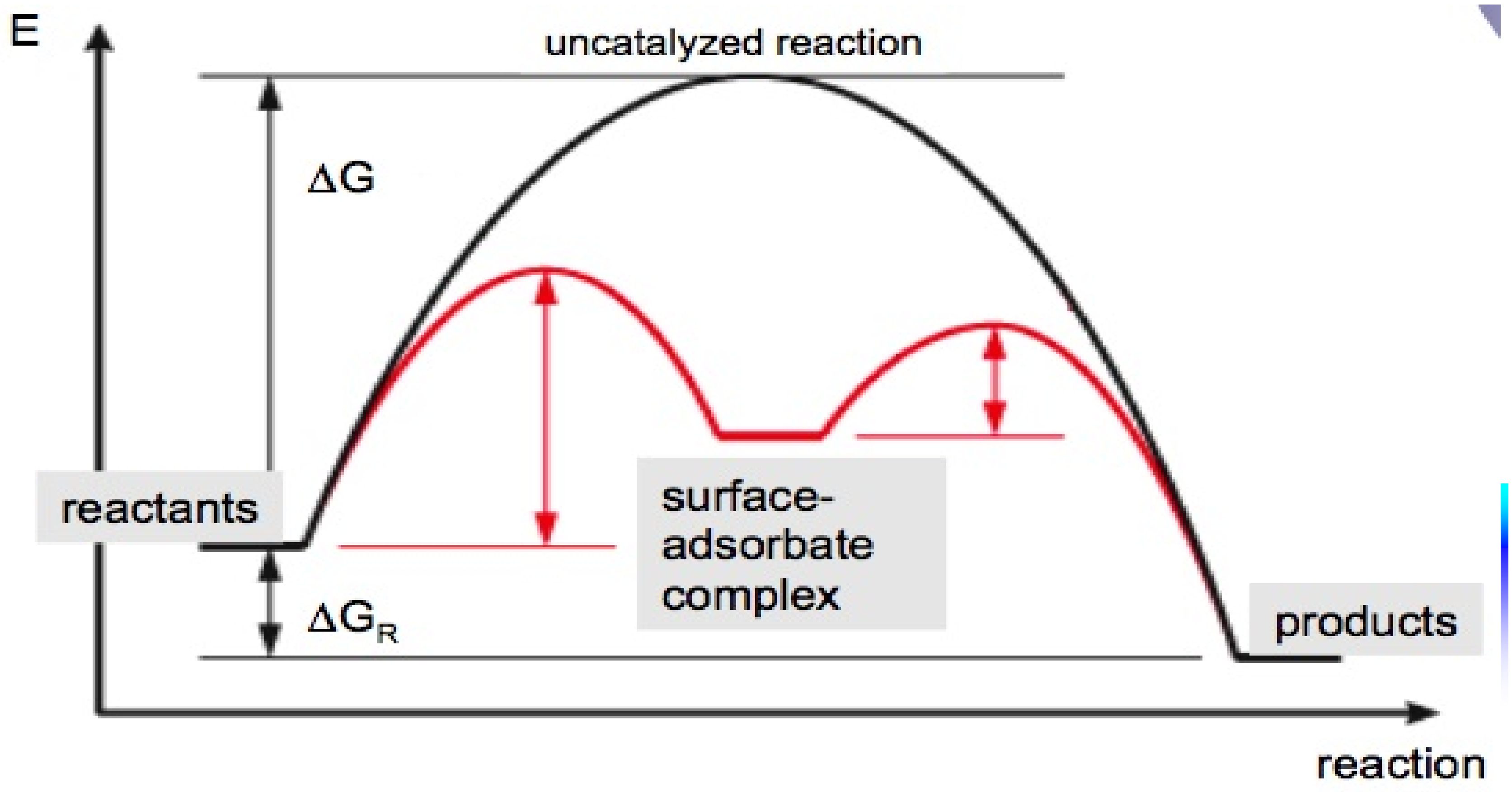
Model systems

- are “real” (contrast to real systems) but are usually not functional
- serve as static counterpart for reacting systems
- are evaluated with simplified reactions
- are used under conditions (low T, low p) that minimize substrate adsorbate and adsorbate-adsorbate interactons
- are made to a maximum structural definition (equals minimal reactivity)
- Can be materials or theory or “concepts”

The standard model (Langmuir, Taylor, Ertl)

- A heterogeneous catalysts can be approximated by a single crystal surface.
- The terminating atoms are all equal and active.
- Adsorption strength may change this: perimeter of islands in CO oxidation; (dynamics).
- Surface atoms can be defined precisely with atom co-ordinates.
- They can be studied by surface science structural tools.
- Single crystal approach.

Function of a catalyst: Static SM



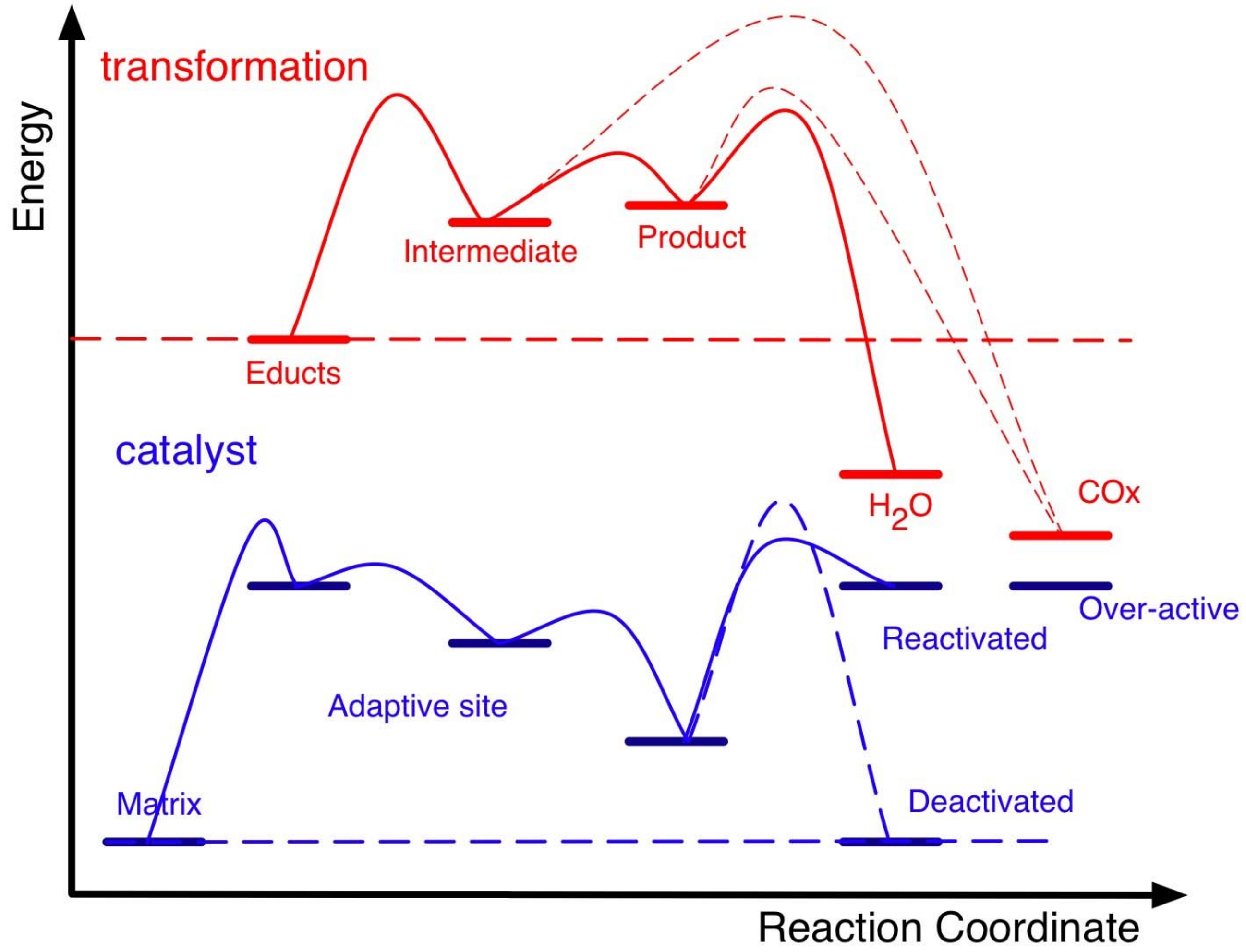
Adsorbate structures dynamical (chemical waves)

Bulk is “irrelevant”, no chemical transformations sub-surface

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.

Selective oxidation: Coupling of transformation and material



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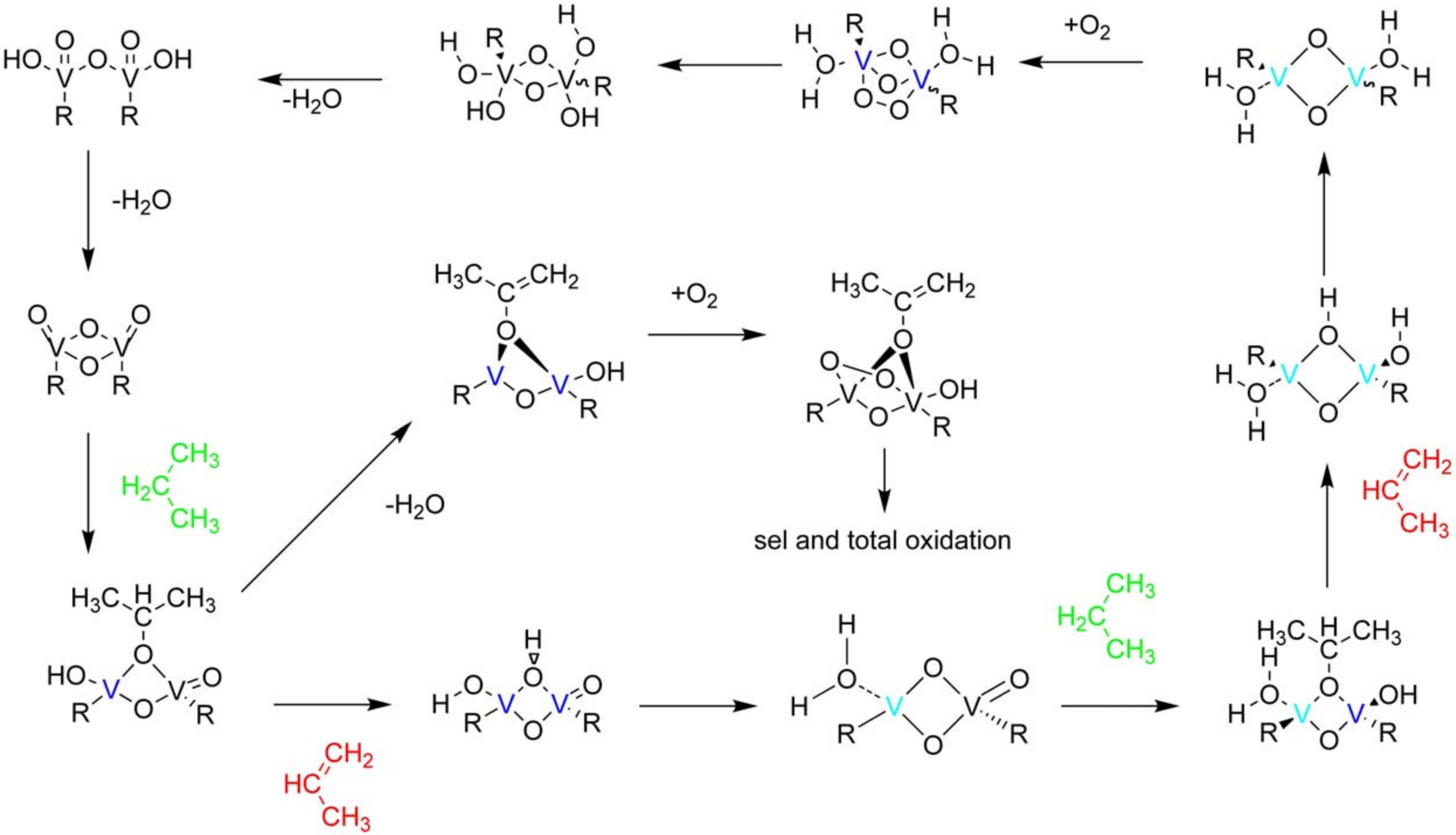
Reaction pathway



Dynamics and adaptation

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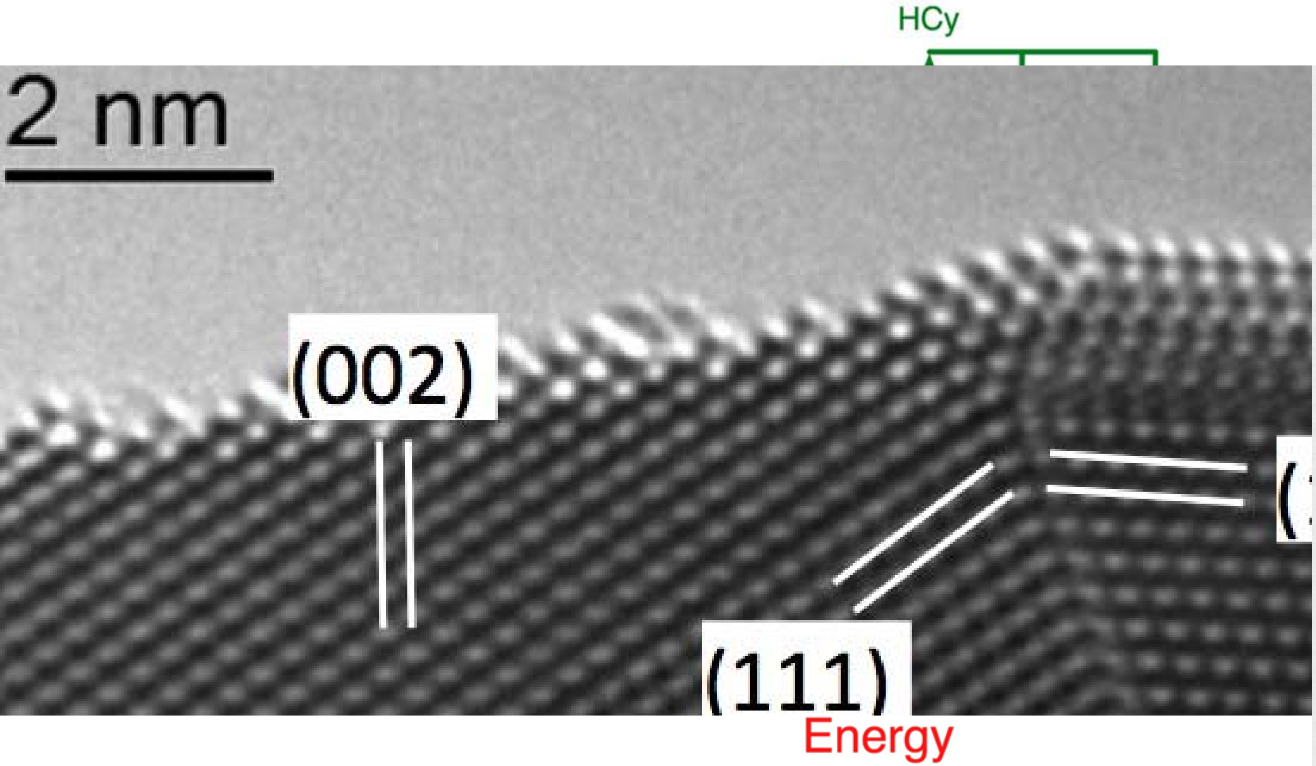
A generalized model of an active catalyst



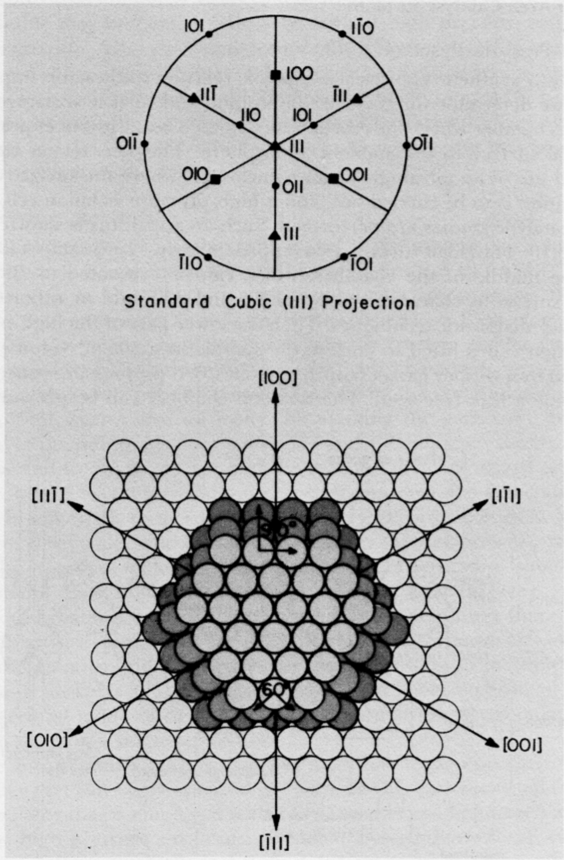


Figure 8.9. Catalyst particle viewed as a crystallite, composed of well-defined atomic planes.

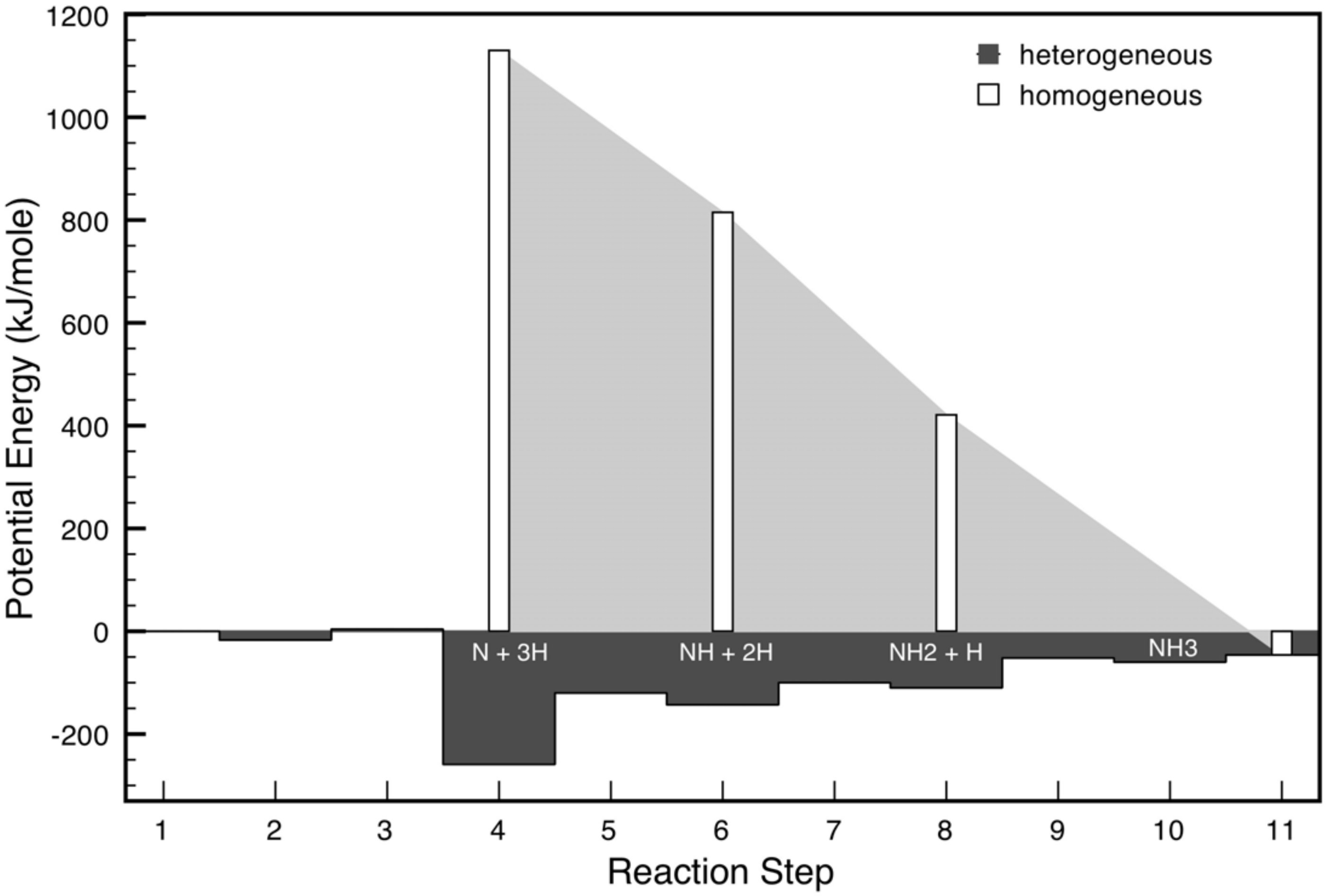
catalysts are multiply dynamical in bulk
structures (activation, deactiva
knowledge gaps from static m

Somorjai 1981

Numerical models

- Microkinetics with a set of elementary steps derived from surface science experiments
- Identification of the rds from energetics
- Ab-inito calculation of critical steps and their transition states
- Incorporation of experimental values from key steps (adsorption, activation)
- Prediction of rates from statistical methods
- Comparison with experiments (see textbook Chorkendorff and Niemantsverdriet)
- In fortunate cases hierarchical theoretical models without any experimental values

Why we need a cataylst: Haber Bosch



Elementary steps of ammonia synthesis

N_2 + cat → N_2 (ads) (1)

N_2 (ads) + cat → 2N(ads) (3)

H_2 + 2cat → 2H(ads)

N(ads) + H(ads) → NH(ads) + cat (4)

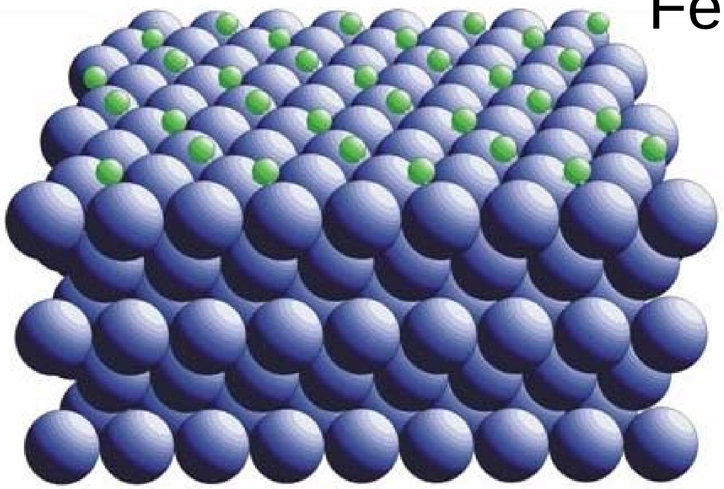
NH(ads) + H(ads) → NH_2(ads) + cat (6)

NH_2(ads) + H(ads) → NH_3(ads) + cat (8)

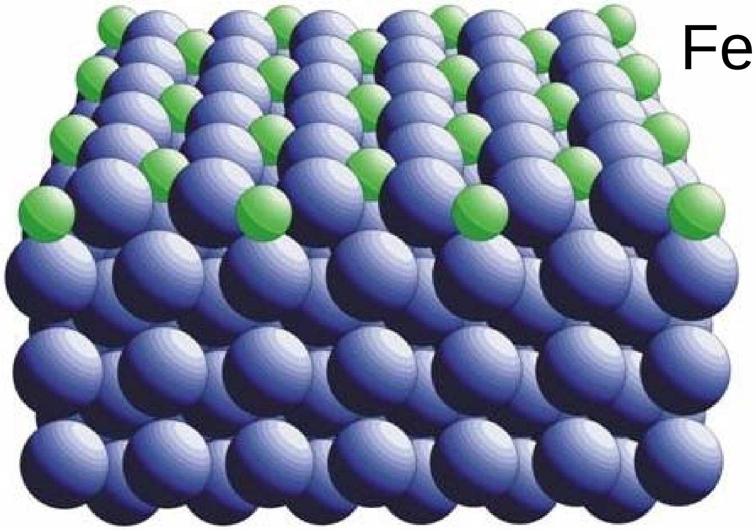
NH_3(ads) → NH_3 + cat (11)

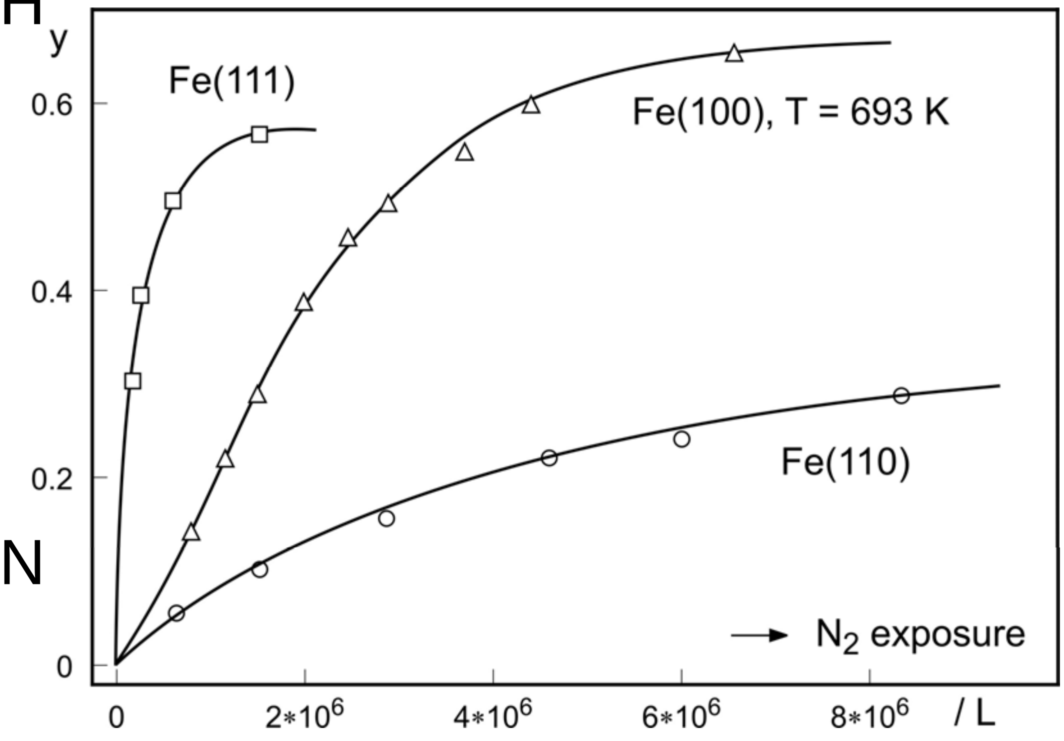
Surface science and ammonia synthesis

Fe-H



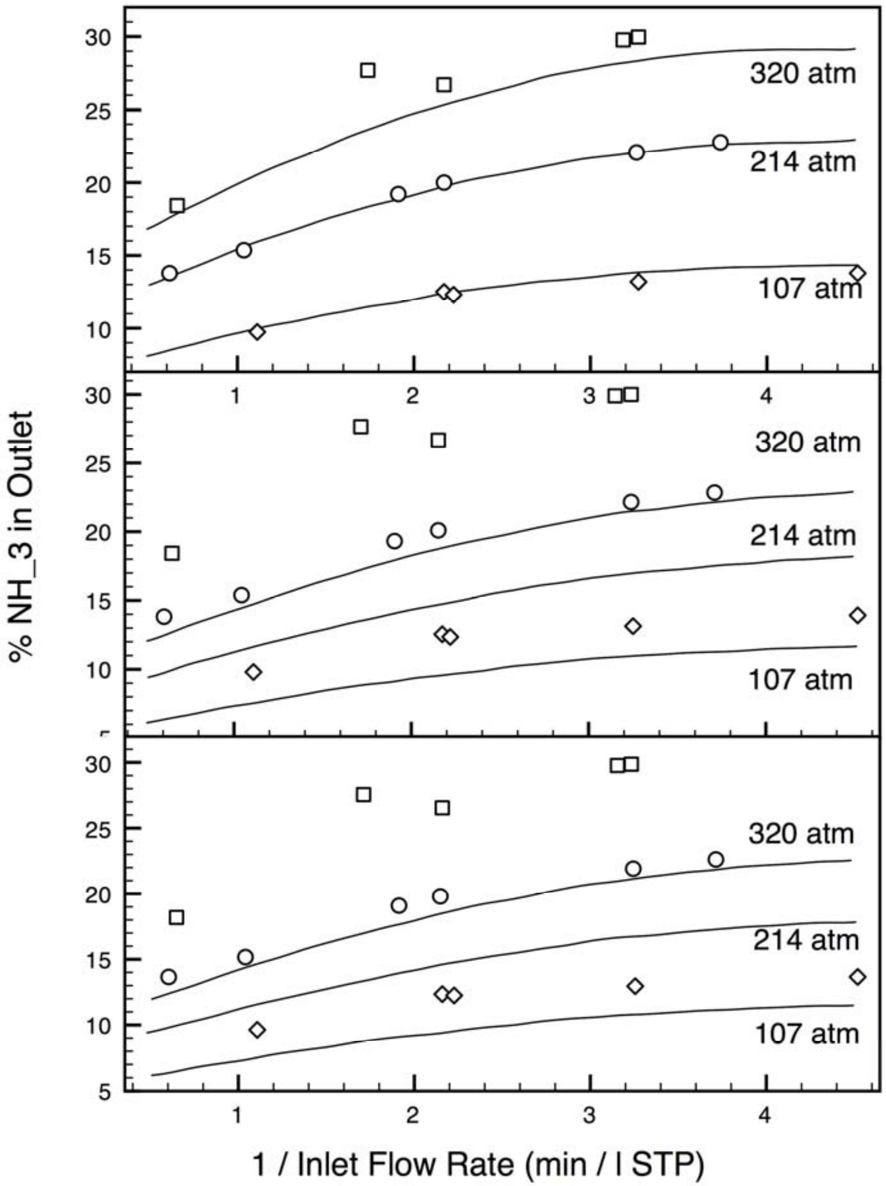
Fe-N





Low pressure static data

The result of a model



Norskov et al (1994):

Based on the surface science data of Ertl et a.l and a microkinetic model (Dumesic et al) it was possible to describe the experimental observations (points) by ab-initio models without any fitting (!) of parameters

Models differ slightly in assumptions about hydrogen activation and activation barriers of nitrogen activation: data of Ertl et al:

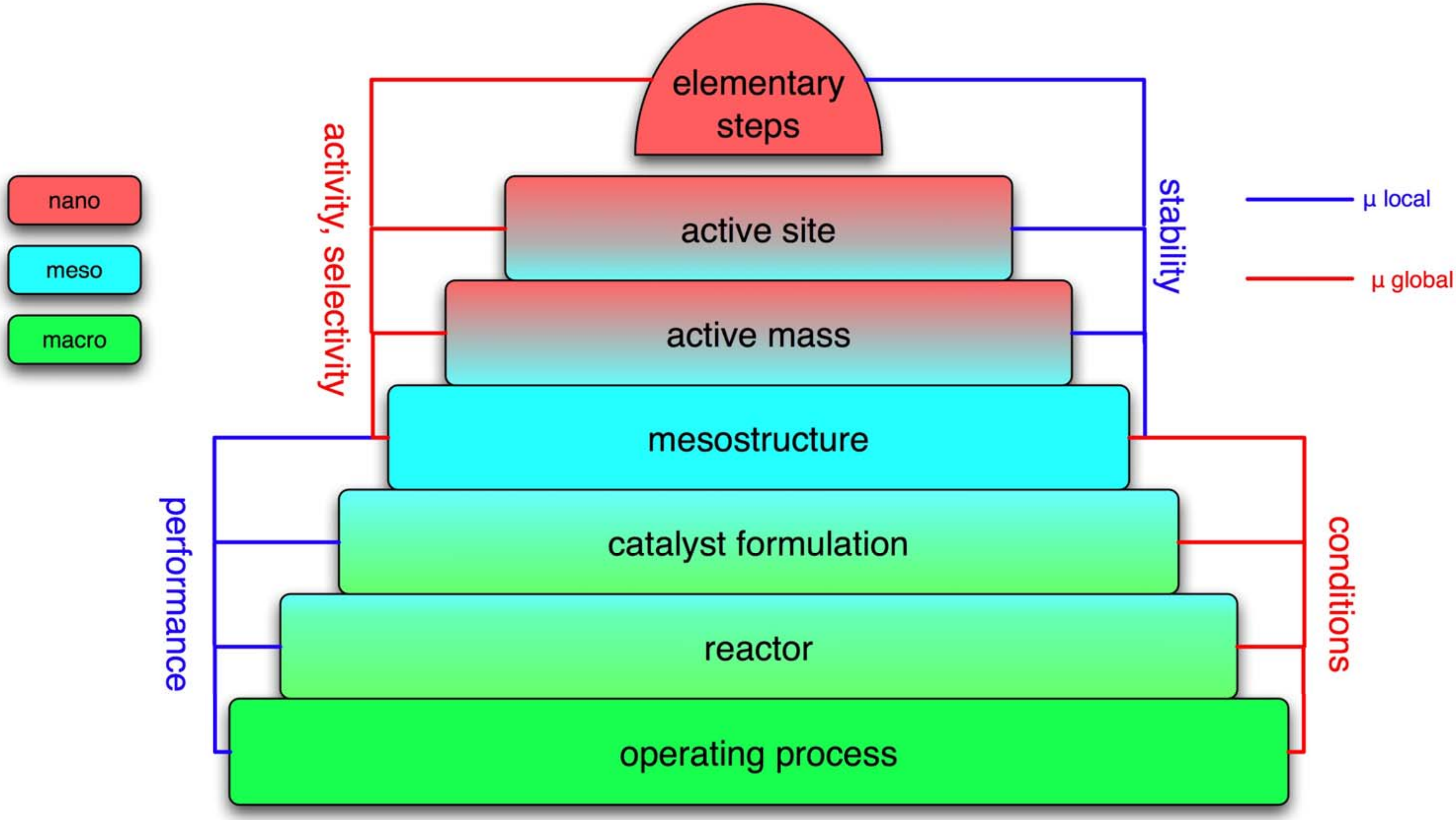
The classical description of a reaction

Ammonia synthesis from Nielsen et al (1972)

$$r = \frac{k_a^* \, a_{N_2} - k_b^* \left(a_{NH_3}\right)^2 / \left(a_{H_2}\right)^3}{\left[1 + k_c^* \left(a_{NH_3}\right) / \left(a_{H_2}\right)^{\gamma}\right]^{2\alpha}}$$

Fitting to experimental data
3 rate constants
Stoichiometry parameter γ
Inhomogeniety parameter (Temkin) α

Catalysis is a multi-scale phenomenon



🟥 nano
🟦 meso
🟩 macro

elementary steps
active site
active mass
mesostructure
catalyst formulation
reactor
operating process

activity, selectivity
stability
performance
conditions

μ local
μ global

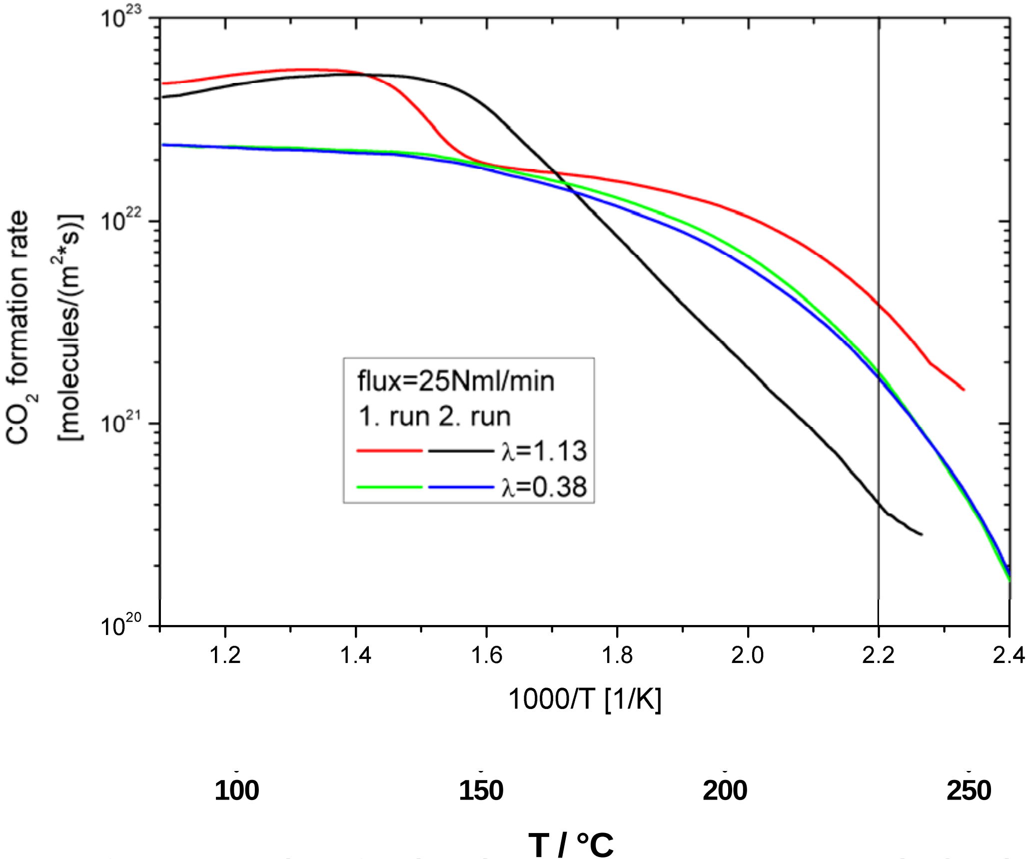
Conclusions I

- Catalysis still lacks a rigorous general concept of its operation that links the principal function (ES decoupling) to the material properties enabling that function (active sites).
- Core issue is the dynamic nature of catalysts: active sites form from precursors and reactants.
- Active sites are dynamical and adaptive within a catalytic cycle.
- Energy match between orbitals of catalyst and reactant must be accurate and requires fine-tuning: property distribution through “defects” (engineering?).

Conclusions II

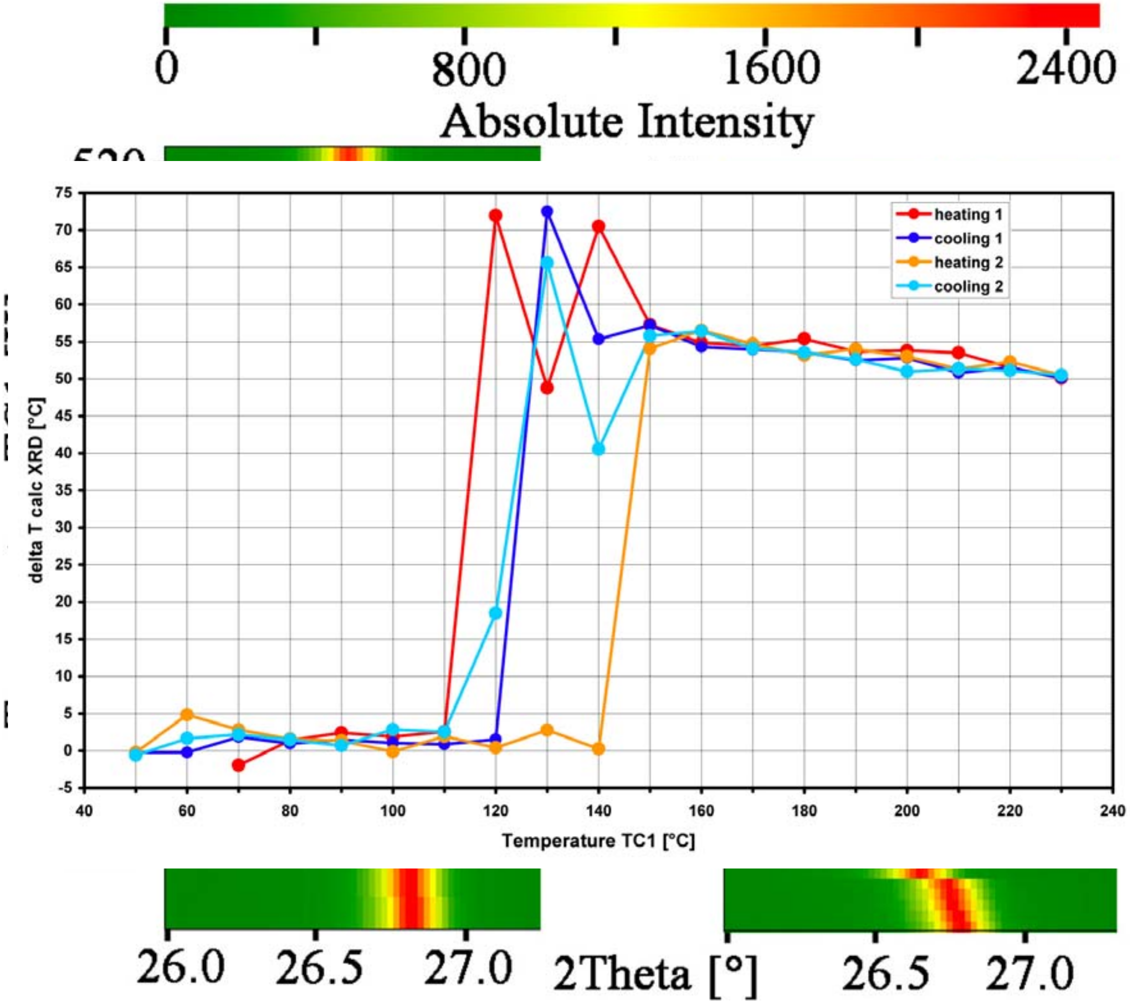
- We understand concepts of catalysis such as active sites, adsorption, checkerboard structures.
- We have quantitative models for simple cases where no selectivity occurs and where dynamics does not change structure in the window of relevant parameters.
- The chemical complexity of active sites in demanding reactions and the absence of a general model that couples properties of catalyst and reactants are missing for a design stage of catalysis.
- More empirical work is less useful than conceptual work mapping out the essence of complexity.
- A theory is emerging allowing to solve these issues.

CO oxidation: a test reaction



Careful execution for isothermal non-transport limited performance

Energy transport in CO oxidation



Lattice constant of diluent BN as internal thermometer:

Massive macroscopic deviations in temperature

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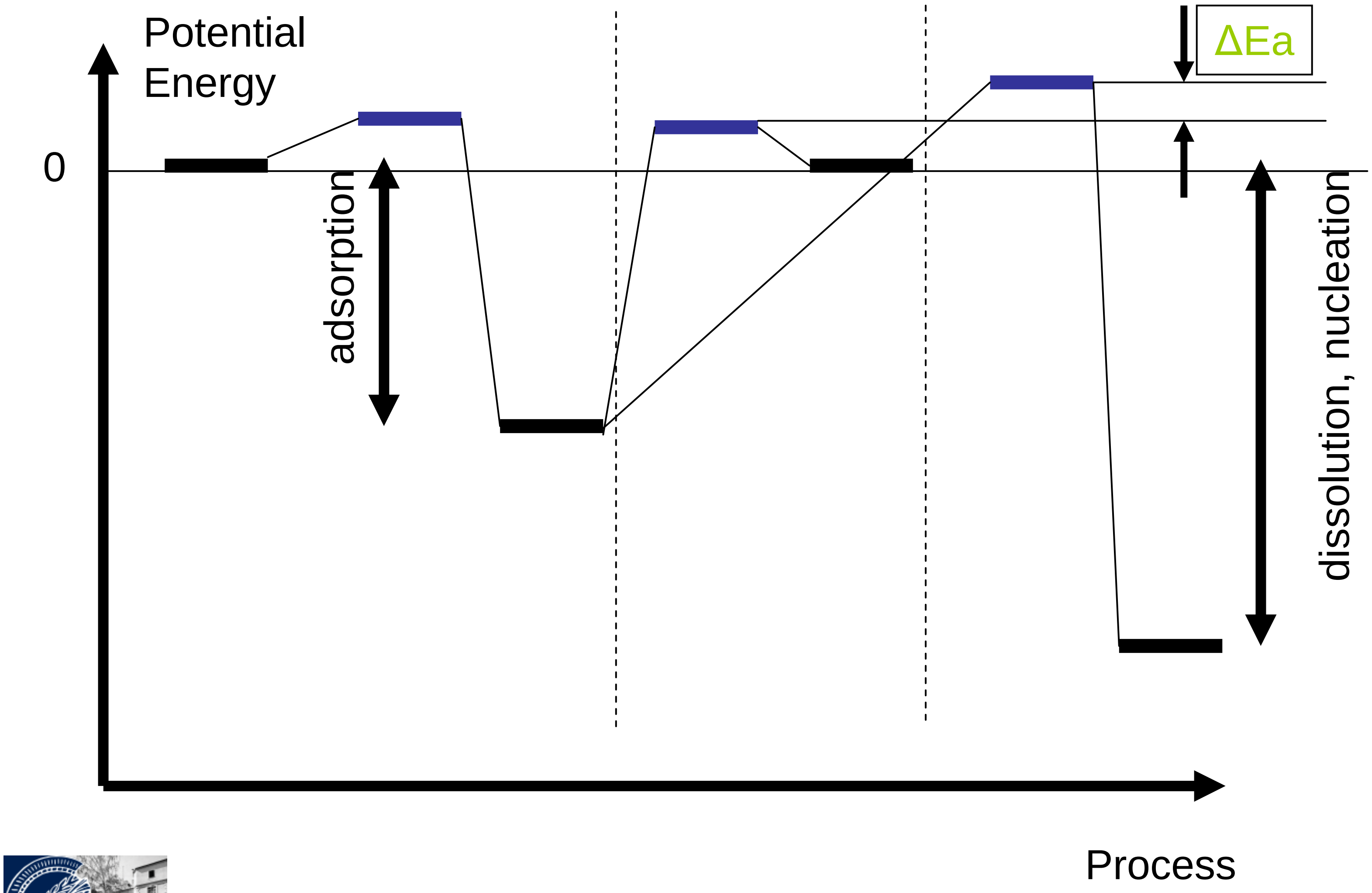
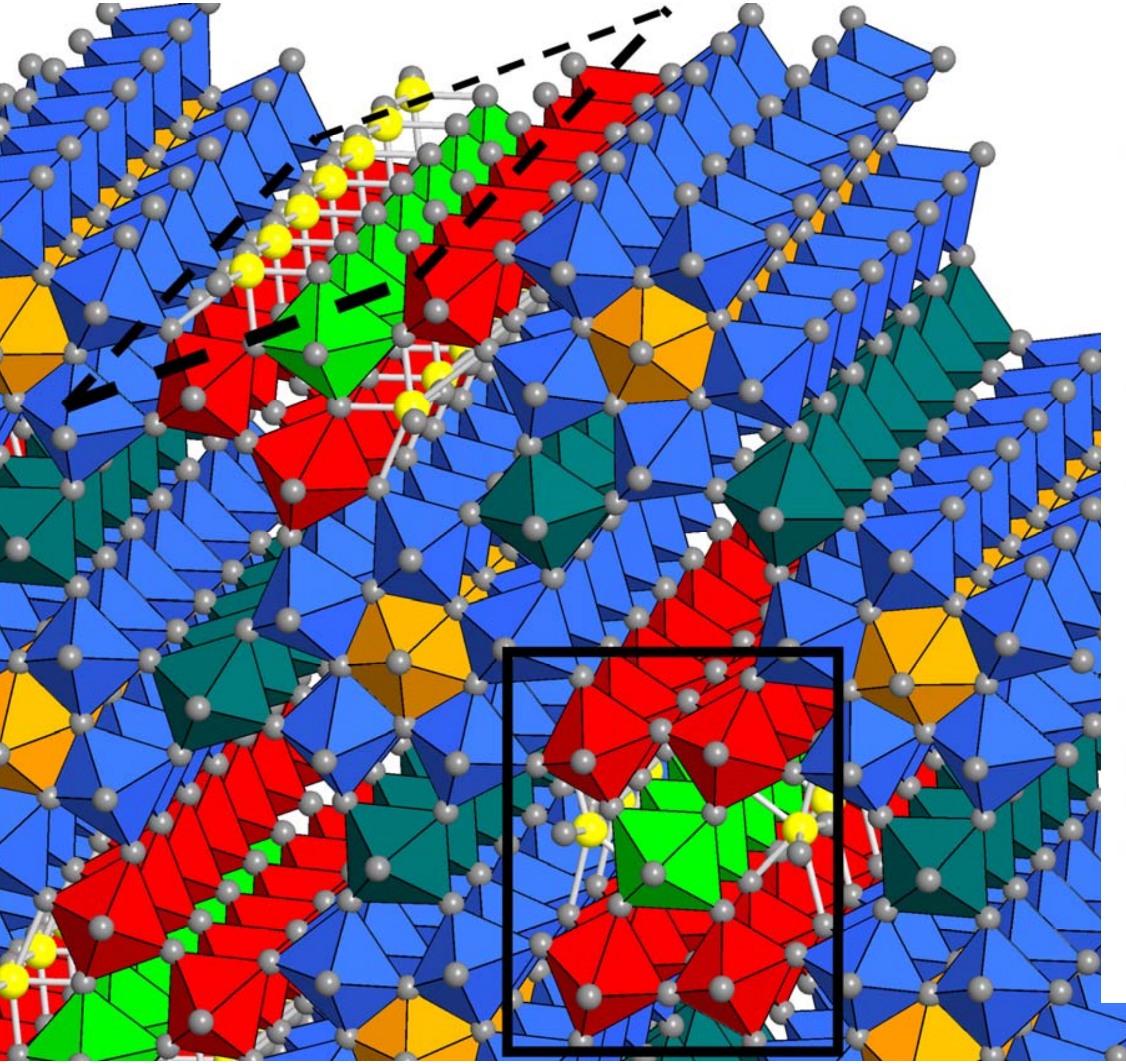
Dynamics of catalysts

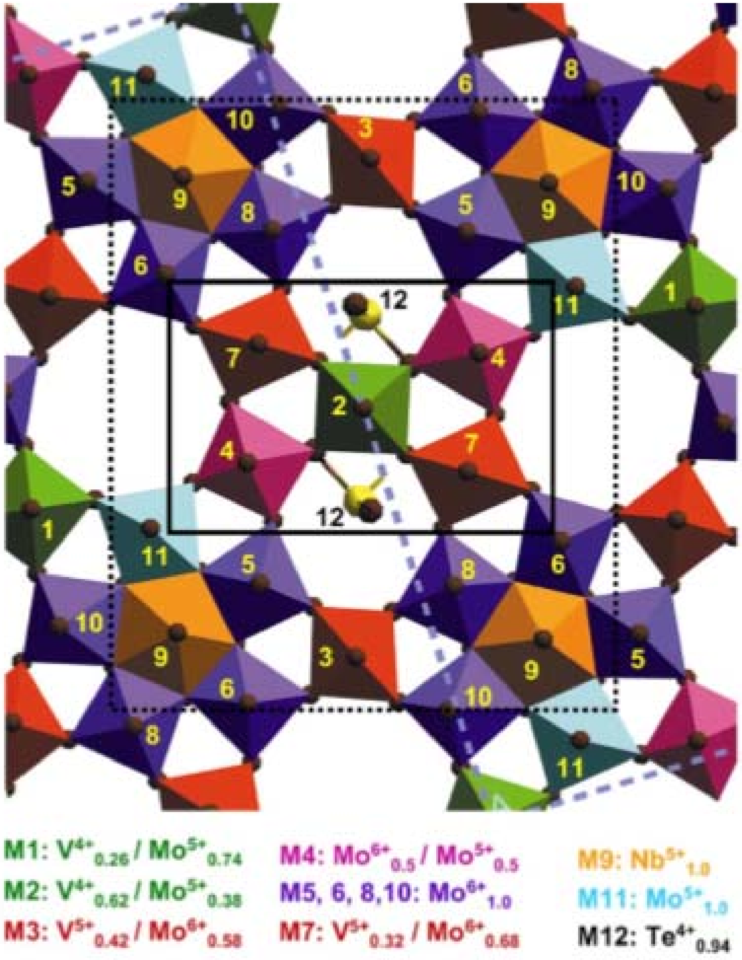


Catalyst Materials

- Catalysts must be metastable for activity (non-equilibrium): (translational structure?)
- Complex structures allow for for a matrix and dynamical active surfaces.
- Phase purity is critical for the lifetime of a catalyst achieving the desired reaction (oxide systems, phase cooperation?).
- Nanostructuring of active component optimizes catalytic cycles (kinetics of reactant –catalyst interaction).

The active site feature

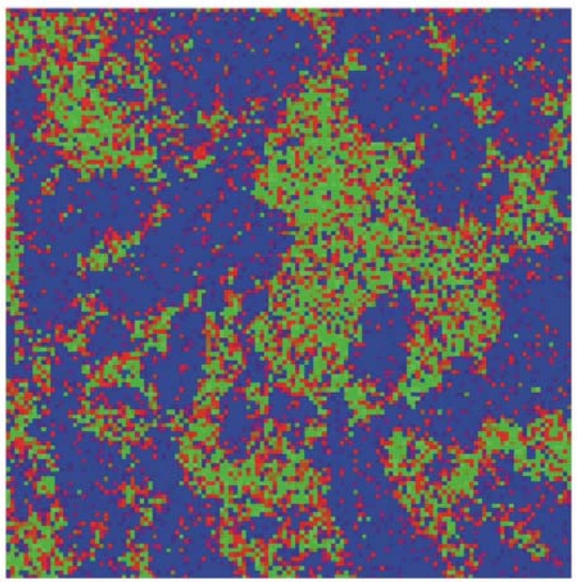




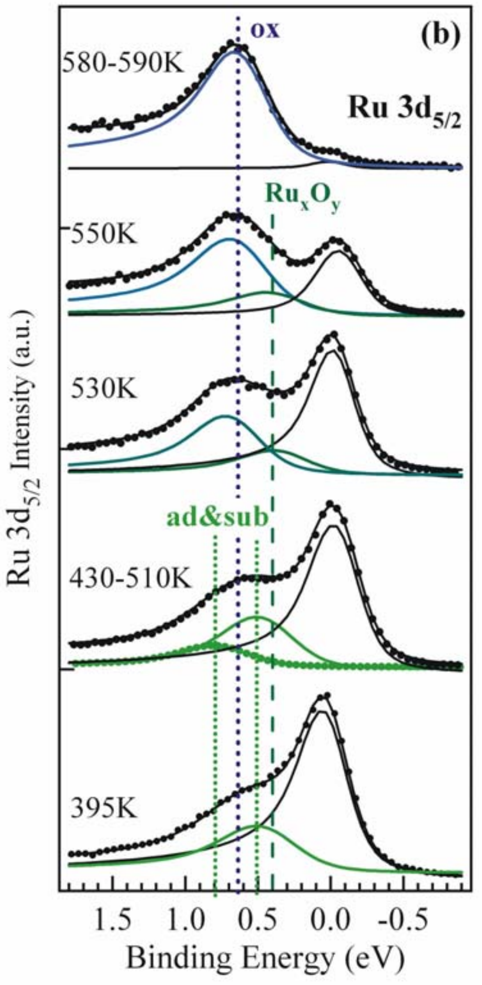
The gaps

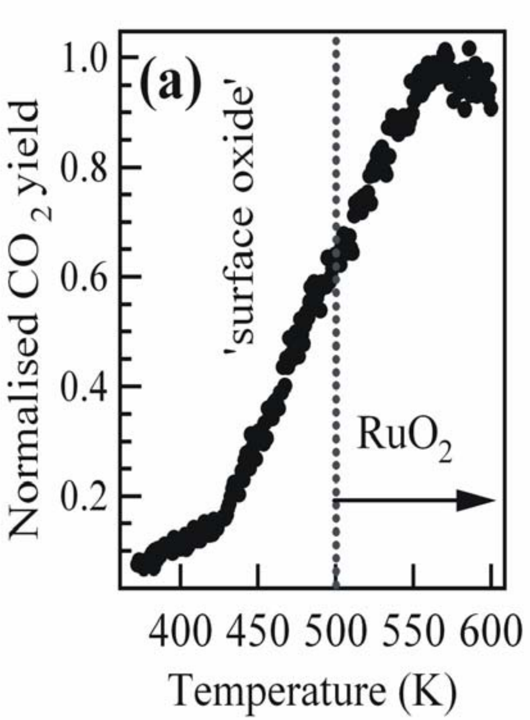
- Catalysts tend to react at elevated chemical potentials of reactants with some constituents:
  - Metal to oxide (surface oxide)
  - Metal to carbide (sol. sln.)
  - Metal to hydride (sol. sln)
  - Oxide to sub-oxide.
- At higher T, p catalysts change their material properties; highly active states at intermediate structures; at extreme conditions deactivation.

Ru in CO oxidation: metal?



In-situ surface analysis reveals that at steady state conditions a mixture (dynamical) of surface states exists: Taylor´s checkerboard





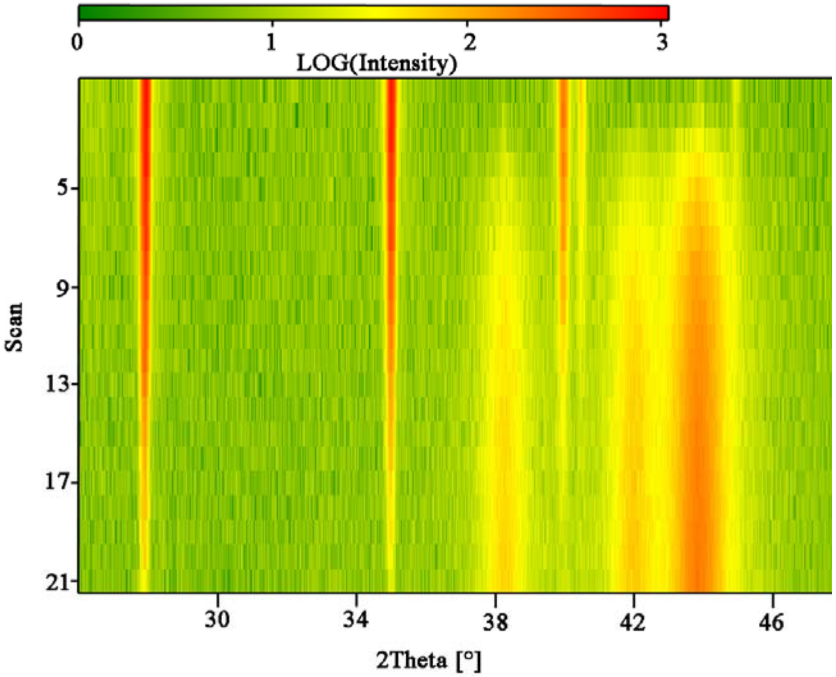
There is no structure sensitivity nor phase correlation with activity

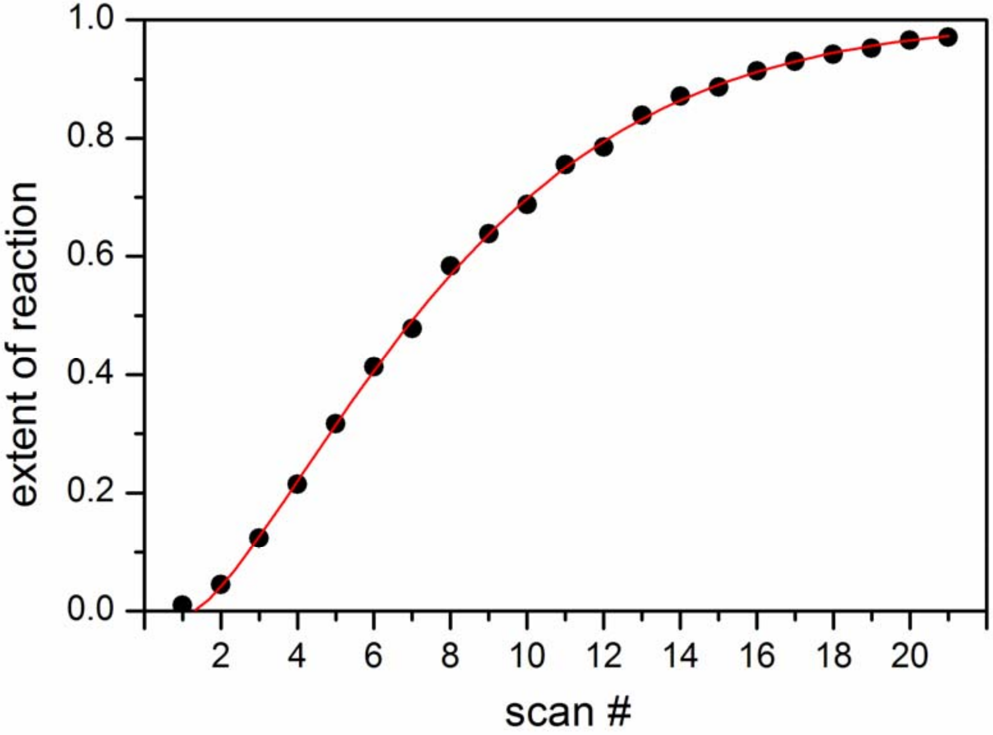
Isothermal reduction during TOS

Model: Avrami-Erofeev

$$\xi = 1 - e^{-k*(t-t_0)^n}$$

ξ Extent of reaction





RuO2 5363

Barely detectable amount of metal in oxide drives ignition

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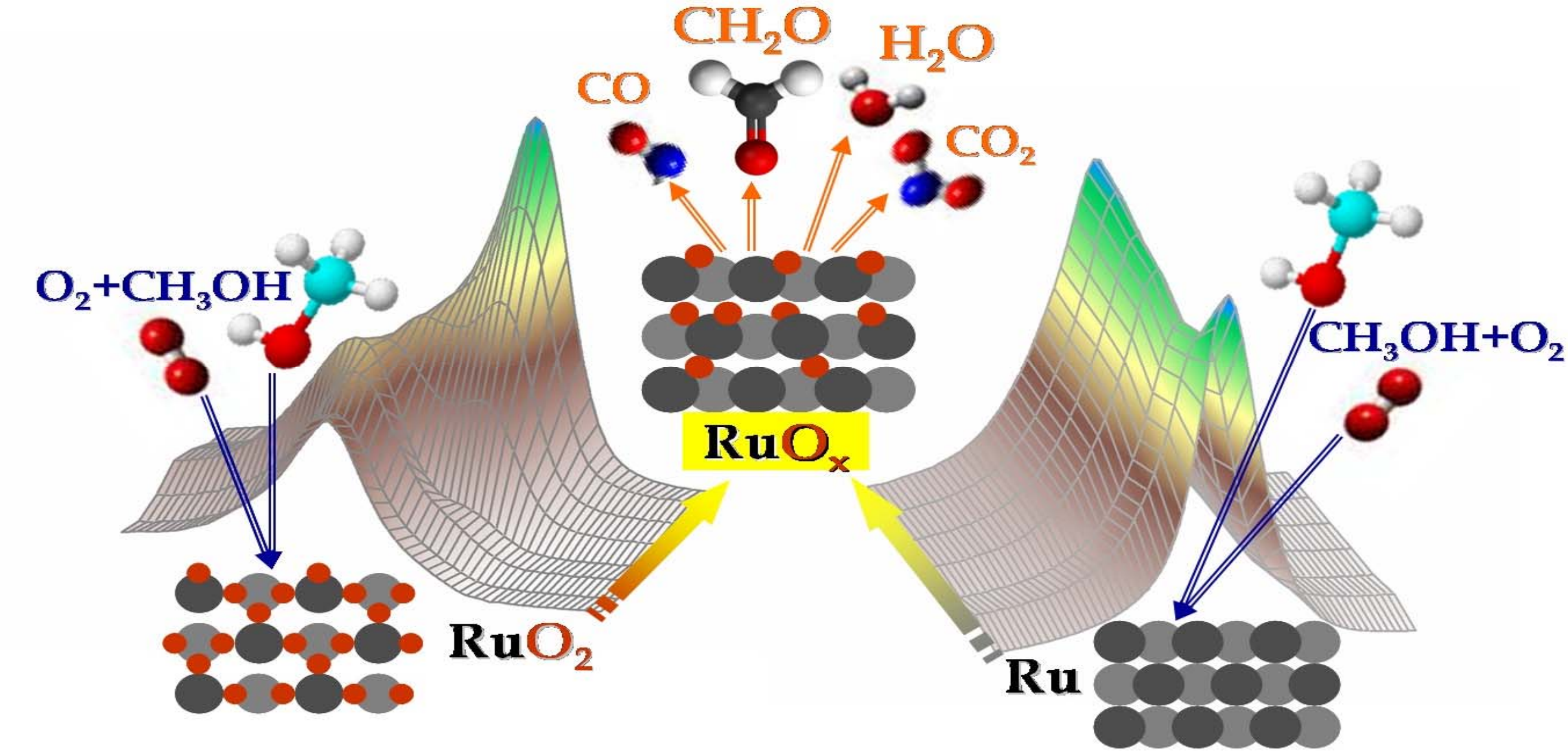
MeOH oxidation: material dynamics

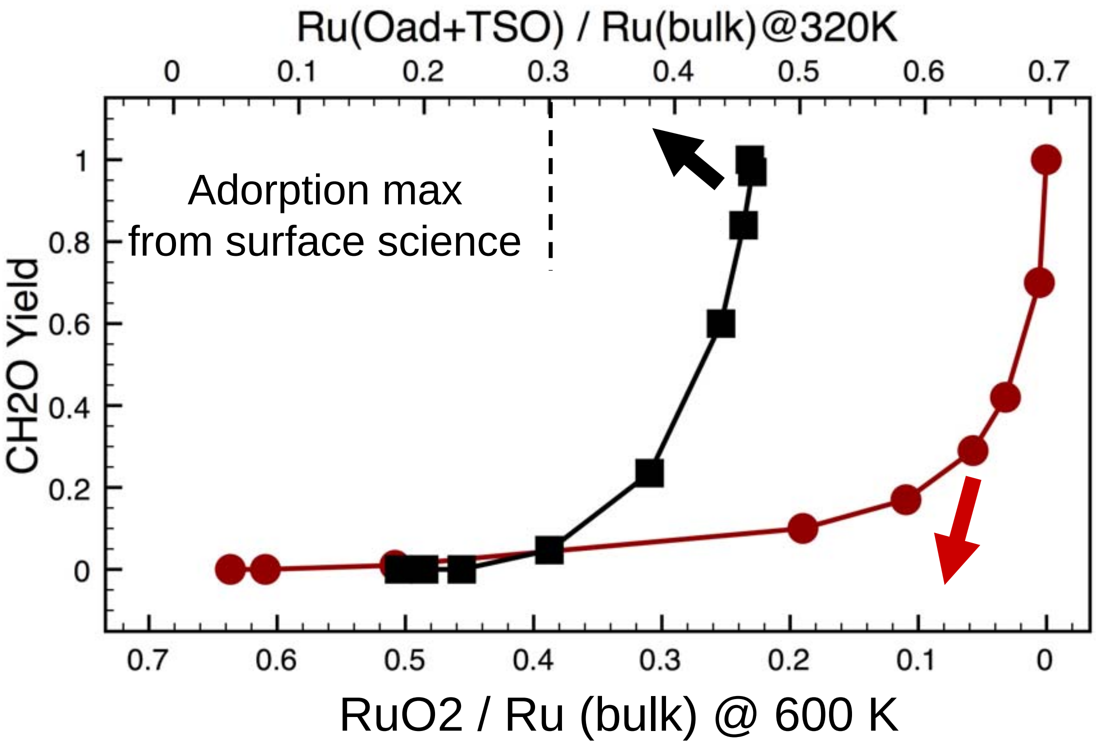


Ru3d: metallic "TSO" for both pre-catalysts at reaction conditions:
Selectivity controlled by electrophilicity of O ad

Structure-function relation with Ru: MeOH oxidation

Accumulation of Ru(TSO)

metallic pre-catalyst
p_{CH3OH} / p_{O2}=1.5

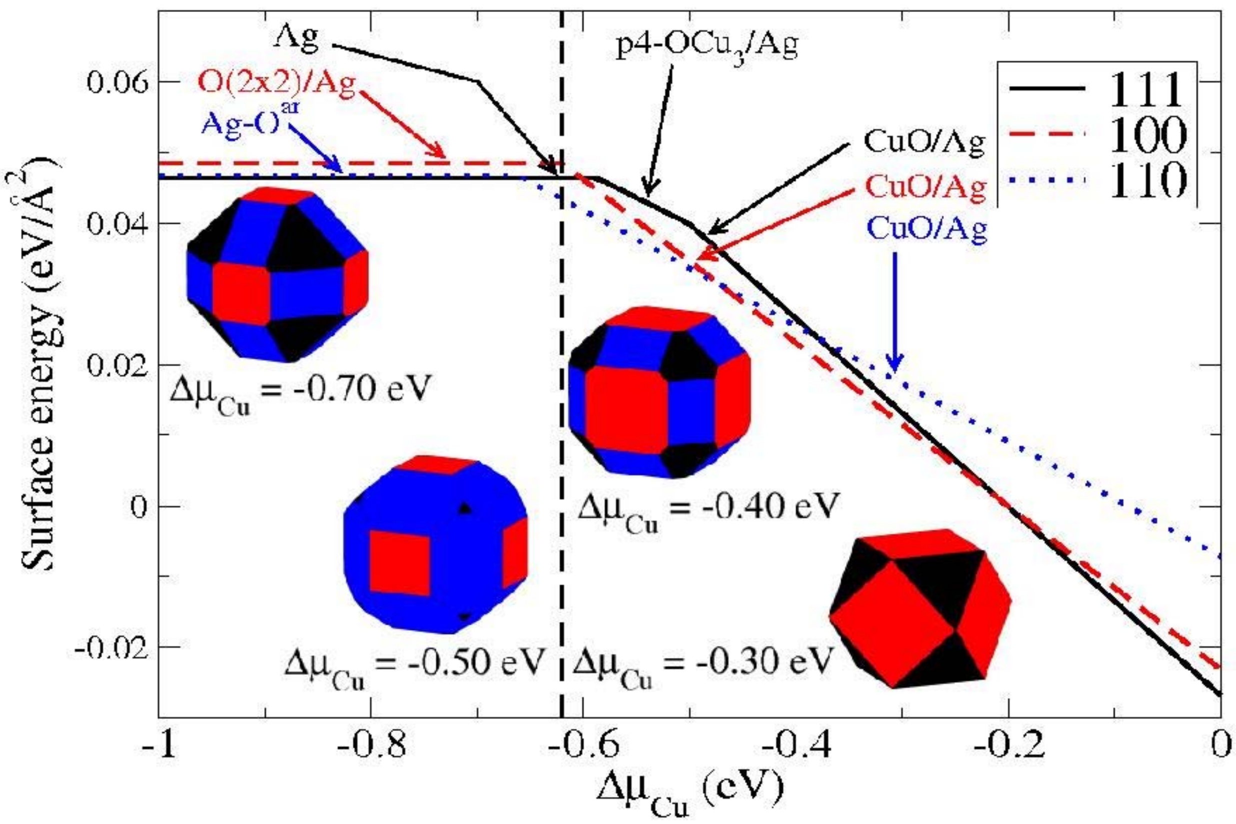


Reduction of oxide phase

Correlation between the formation of RuO_x transient surface oxide (TSO) and CH_2O production

Theory: stability of CuxO/Ag

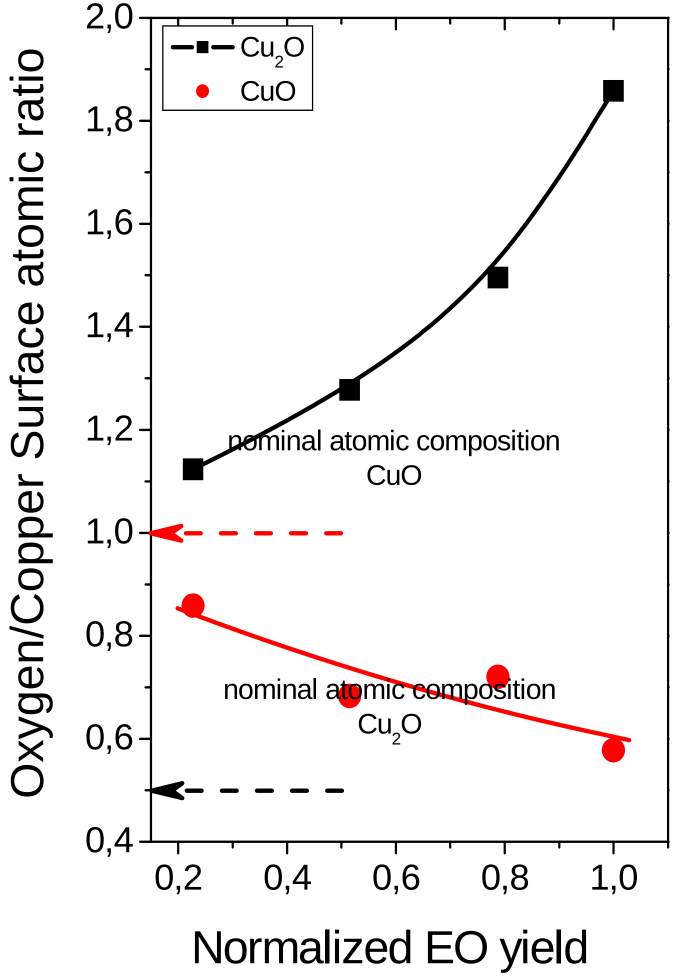
Fixed $\Delta\mu_{O=}$-0.61 eV (T=600K, $p(O_2)$ = 1atm)

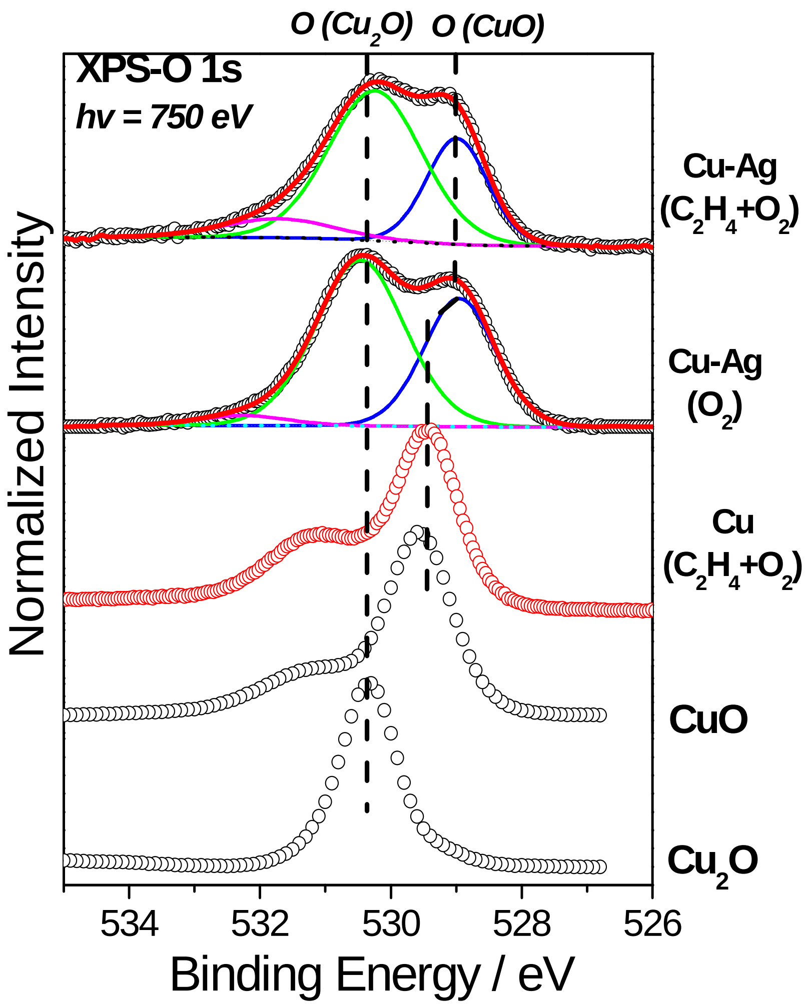


M. Scheffler et al.

- 2D Ag-Cu surface alloy is not predicted to be stable on any facet
- Increasing $\Delta\mu_{Cu}$, (110) is the first facet to accommodate Cu, followed by the (100) and the (111)
- Up to Θ (Cu)<1 ML, the most likely structures are:
  CuO/Ag(110)
  CuO/Ag(100)
  p4-OCu$_3$ or p2/Ag(111)
- The (111) facet does not have the largest surface area, at variance with pure Ag

Experiment: max yield at max surface oxide





Methanol oxidation to formaldehyde

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Reductionism

- The single crystal approach
  - Removes chemical complexity (additives, contaminants)
  - Removes structural complexity (ordering)
  - Removes transport perturbations except surface transport
- This allows
  - To determine elementary step kinetic parameters
  - To find geometries and atomic coordinates of adsorbates
  - To couple experiment and high-level (ab-initio) theory

The standard model

- Catalysis operates through spatio-temporal decoupling of elementary steps (ES).
- ES are changes in reaction coordinates:
  - adsorption and desorption (coordinates between catalyst and reactant)
  - reaction (coordinates between atoms within reactants).
- Control variables:
  - interaction energies
  - chemical potential
  - transport