# Modern Concepts of Heterogeneous Catalysis

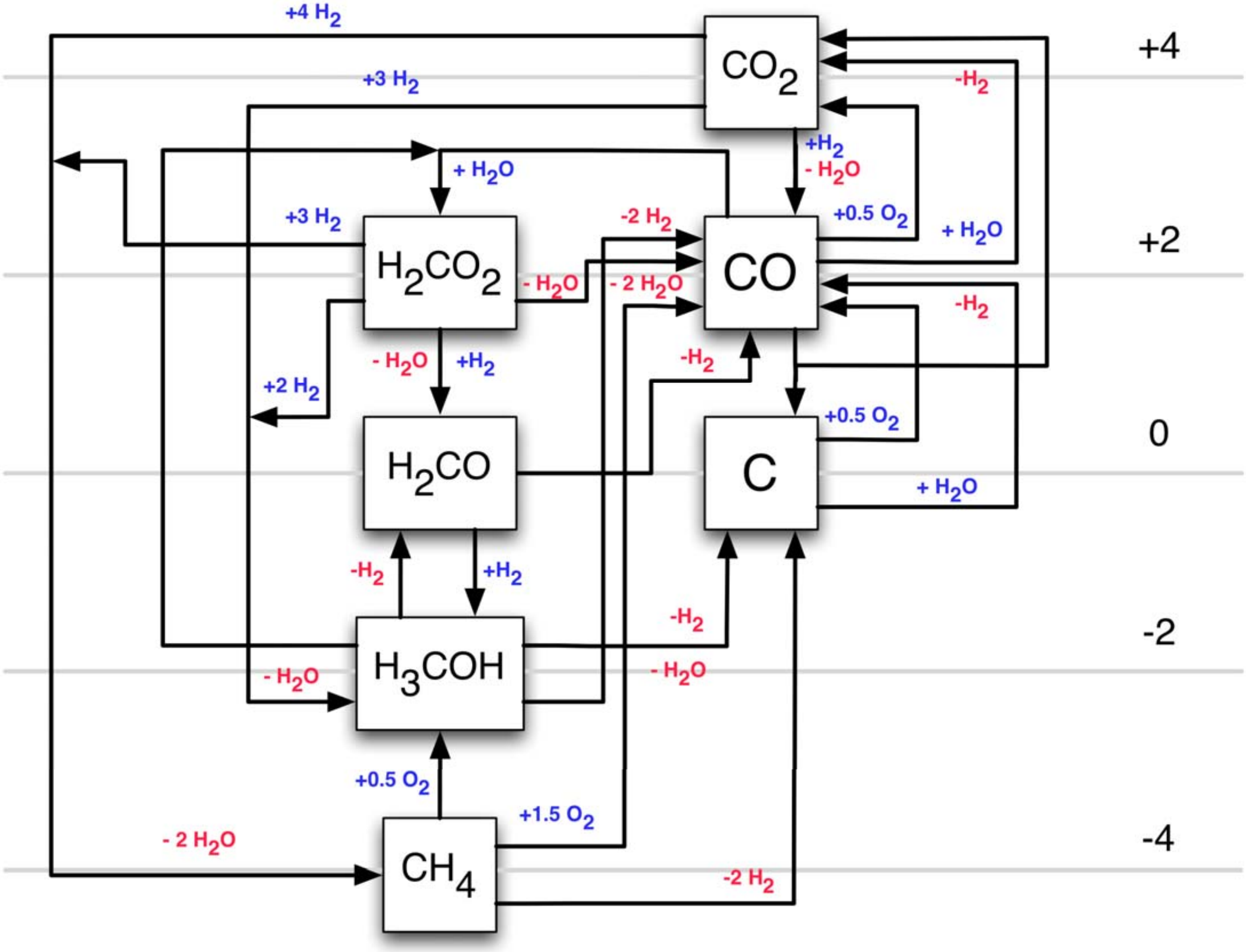
## Modern motivations

Robert Schlögl
www.fhi-berlin.mpg.de

# Modern

- Catalysis is since over a century an enabling science and technology.
- It emerges from synthetic chemistry (catalysts and new molecules) and from physical chemistry (course of a chemical reaction, quantum theory).
- More than 10 Nobel awards were devoted.
- As an independent science still problematic:
- Concepts, models, gaps, “real systems”

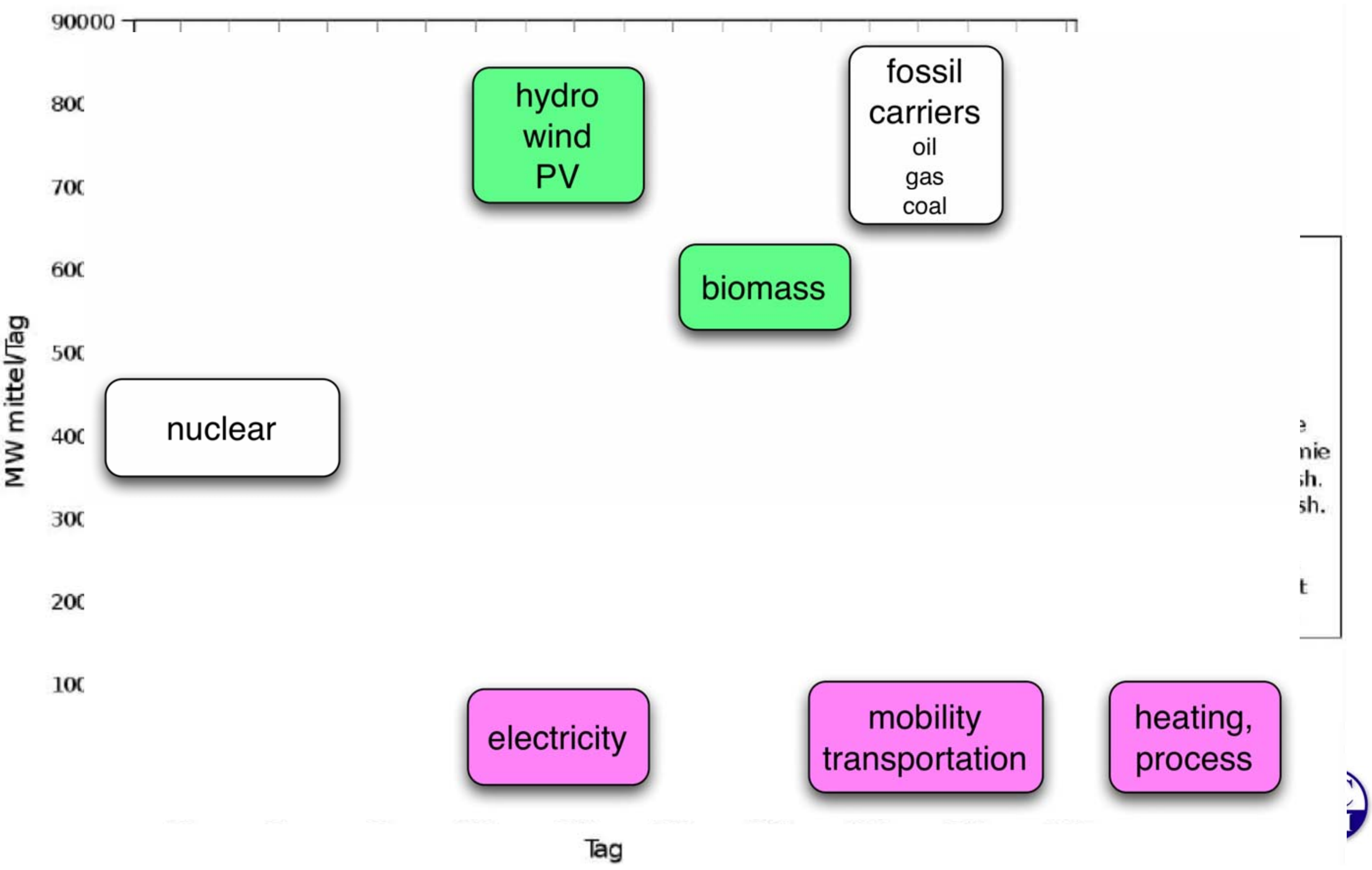
# Systems: C1 chemistry



# Motivation

- Despite its enabling role and several disciplinary attempts:
  - Chemical engineering
  - Surface science and theory
  - Combinatorial chemistry
- Catalysis is still an empirical science.
- Modern motivation: the energy challenge.
- Program:
  - The energy challenge
  - A review over concepts

# Structure of a challenge



nuclear

hydro
wind
PV

biomass

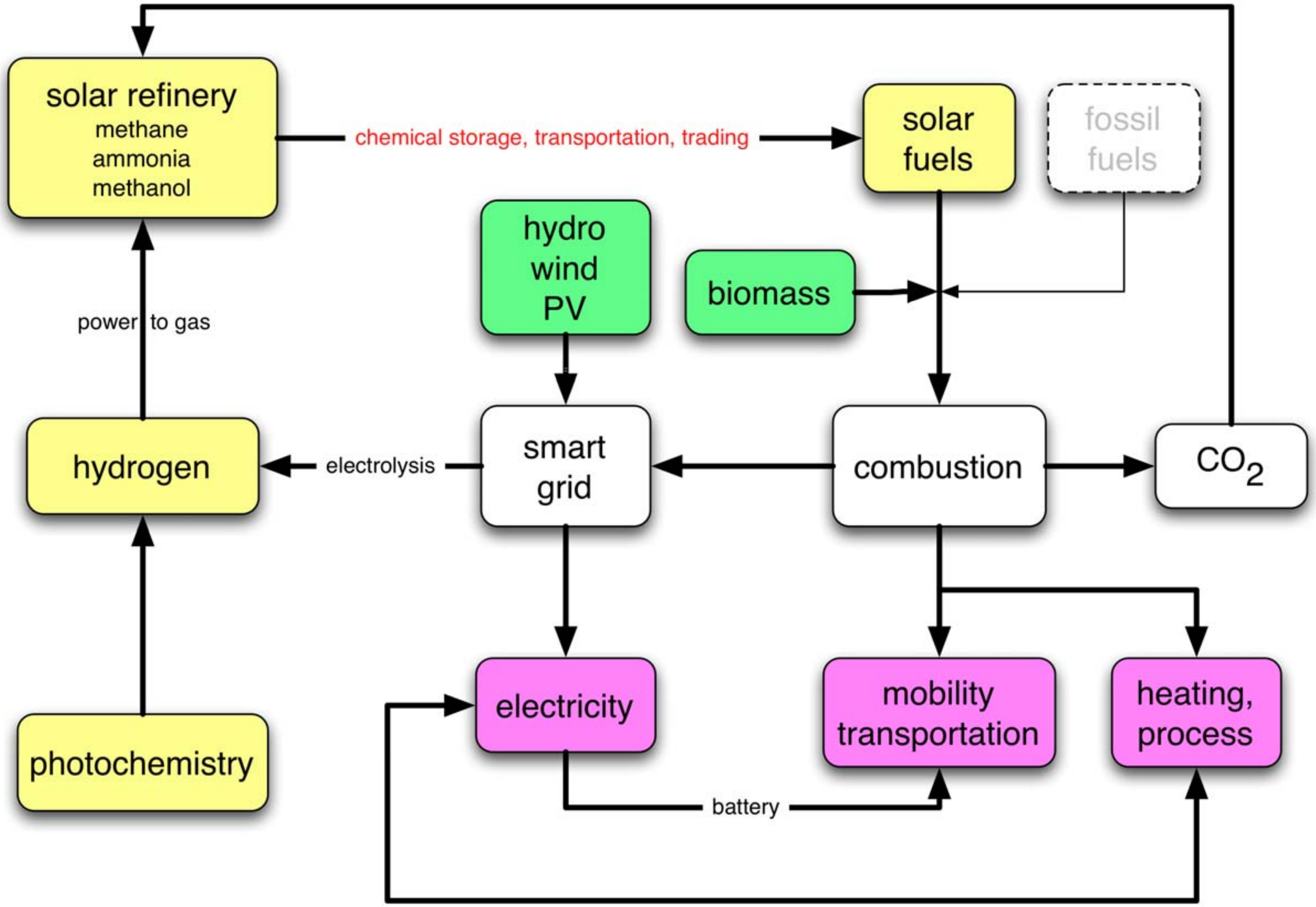
fossil
carriers
oil
gas
coal

electricity

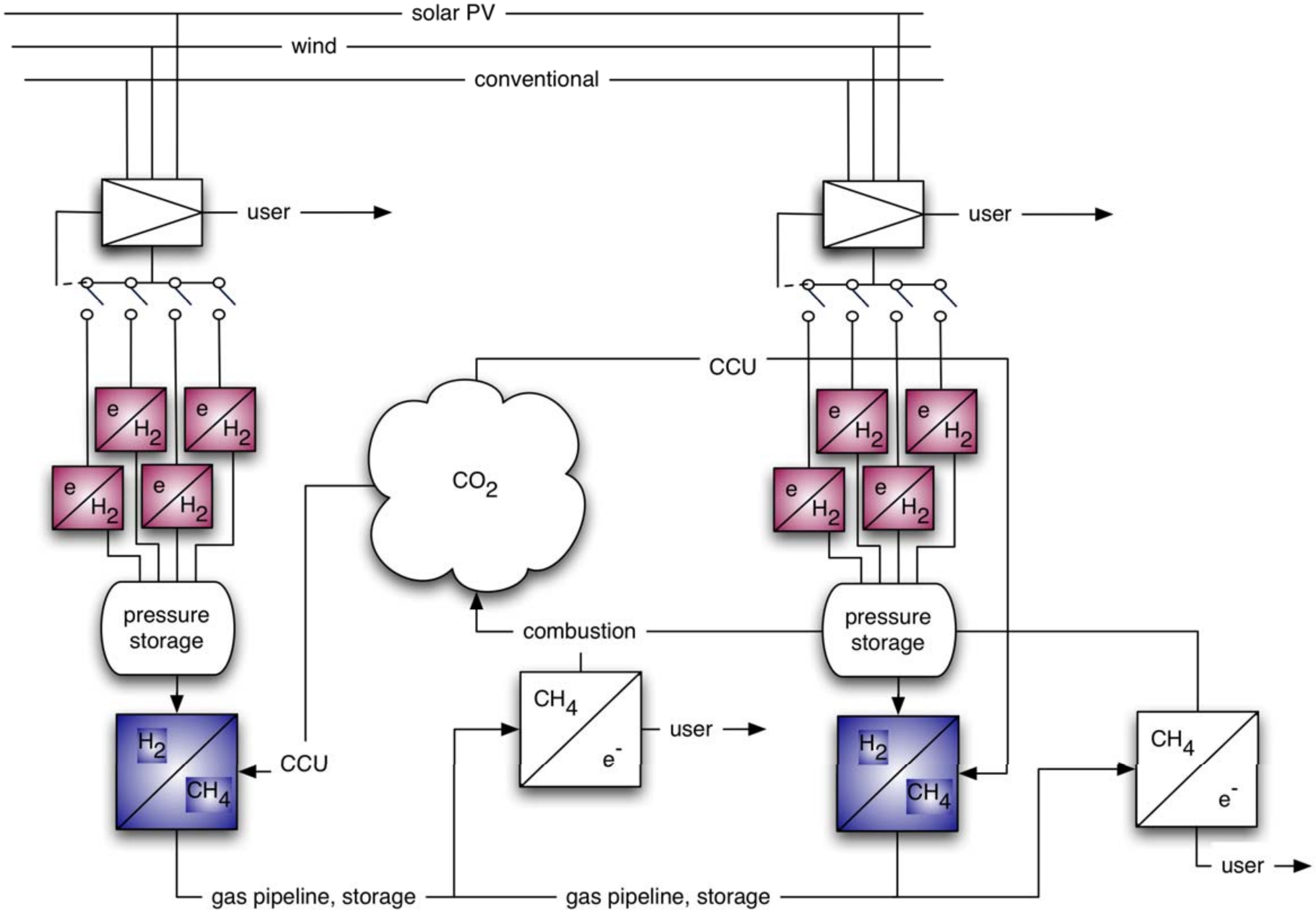
mobility
transportation

heating,
process

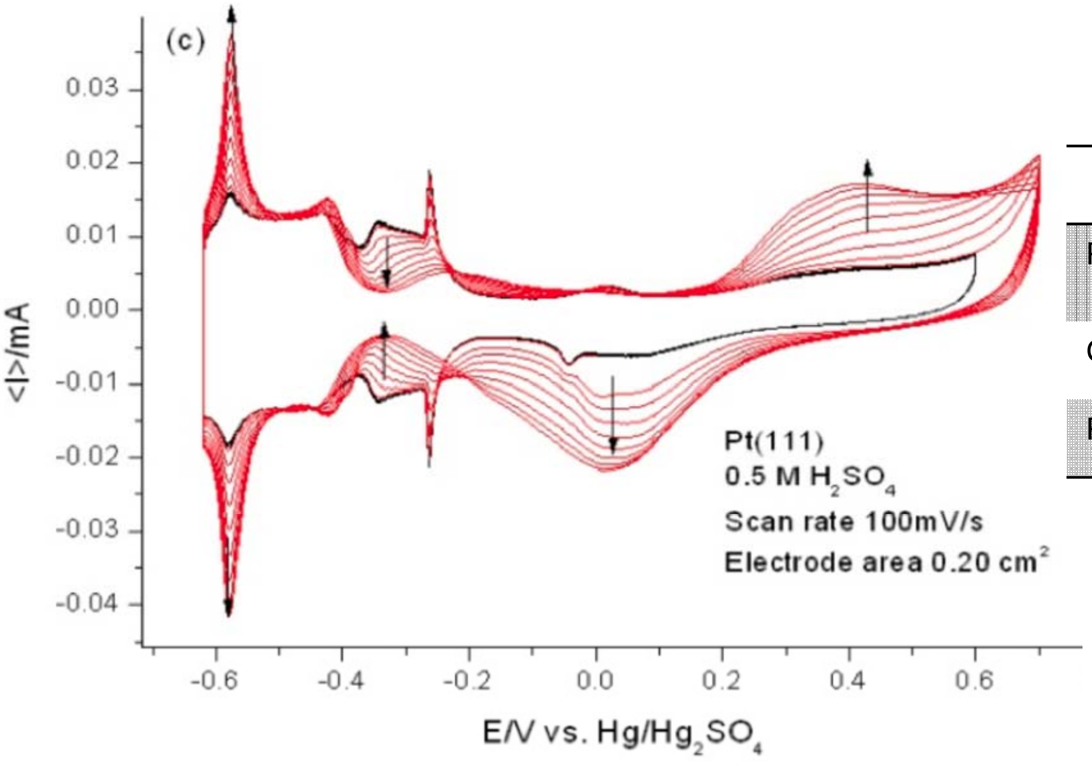
# A sustainable architecture with flexibility

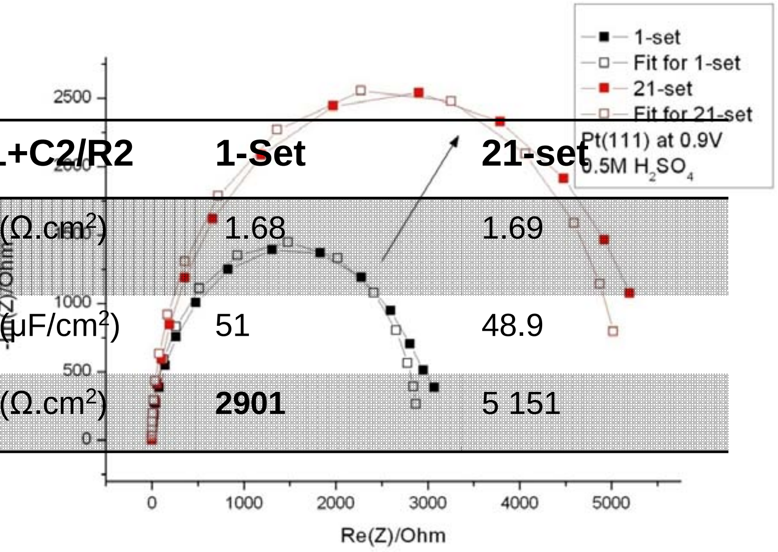


# Possible realization and critical elements

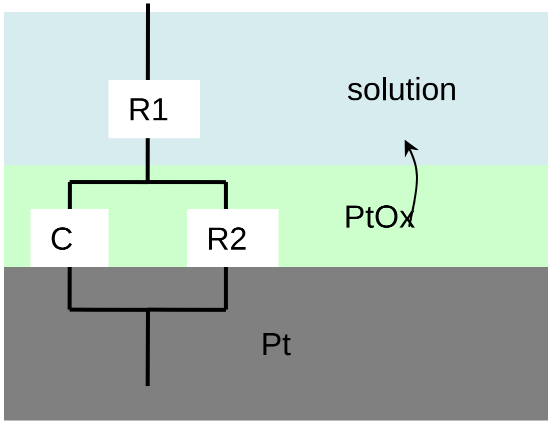


# Dynamics of Pt in OER



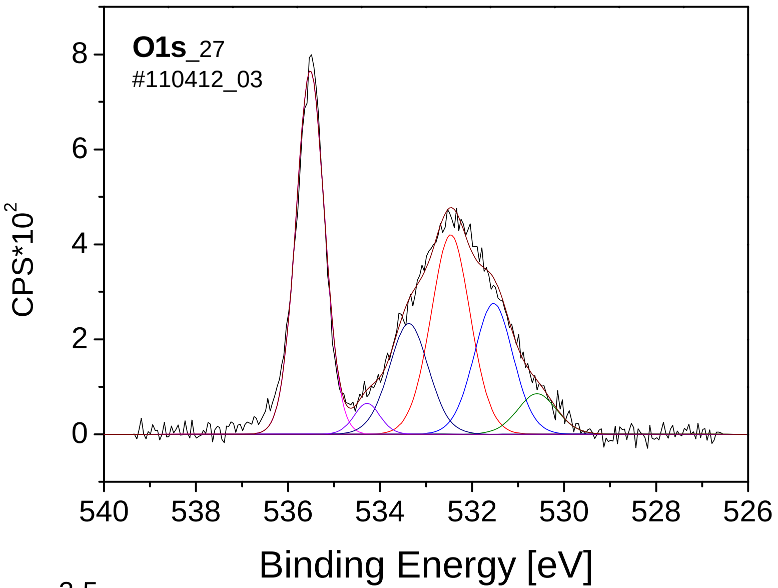


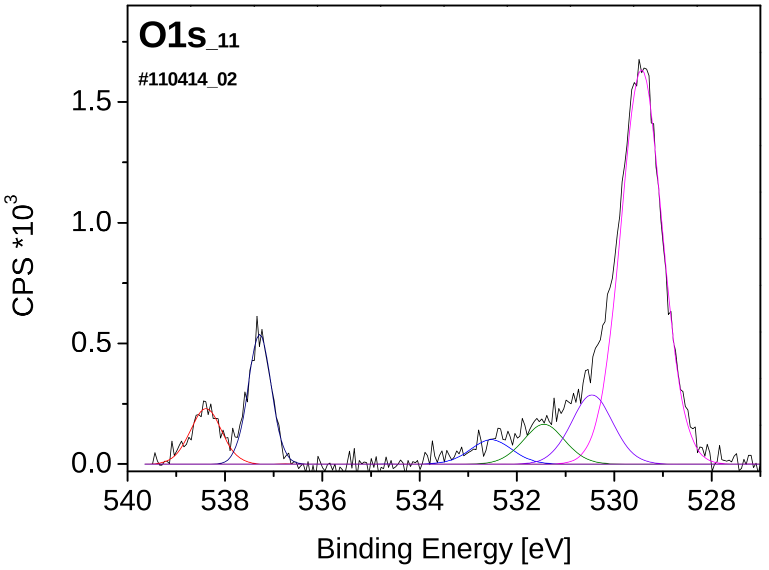
| R1+C2/R2 | 1-Set | 21-set |
|---|---|---|
| R1 (Ω.cm$^2$) | 1.68 | 1.69 |
| C2 (µF/cm$^2$) | 51 | 48.9 |
| R2 (Ω.cm$^2$) | **2901** | 5 151 |

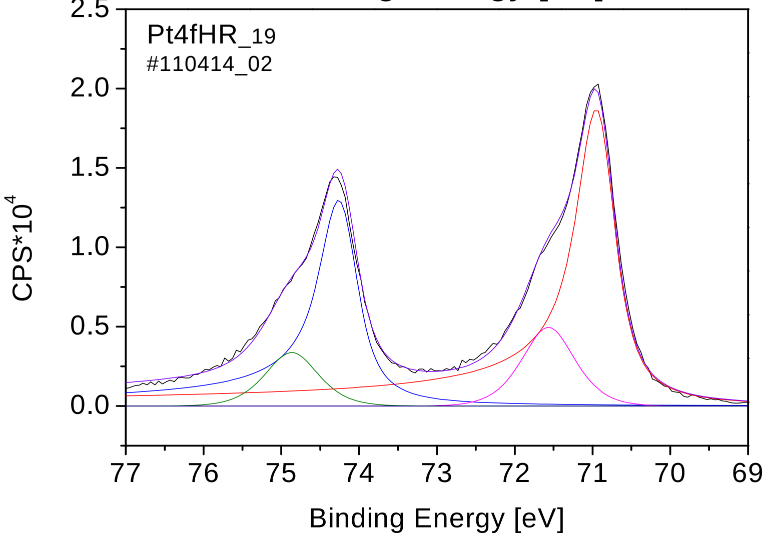


Irreversible roughening
Enhanced hydrogen production
Oxidic overlayer pre-requisite for OER

# Nature of the Pt “rust” film



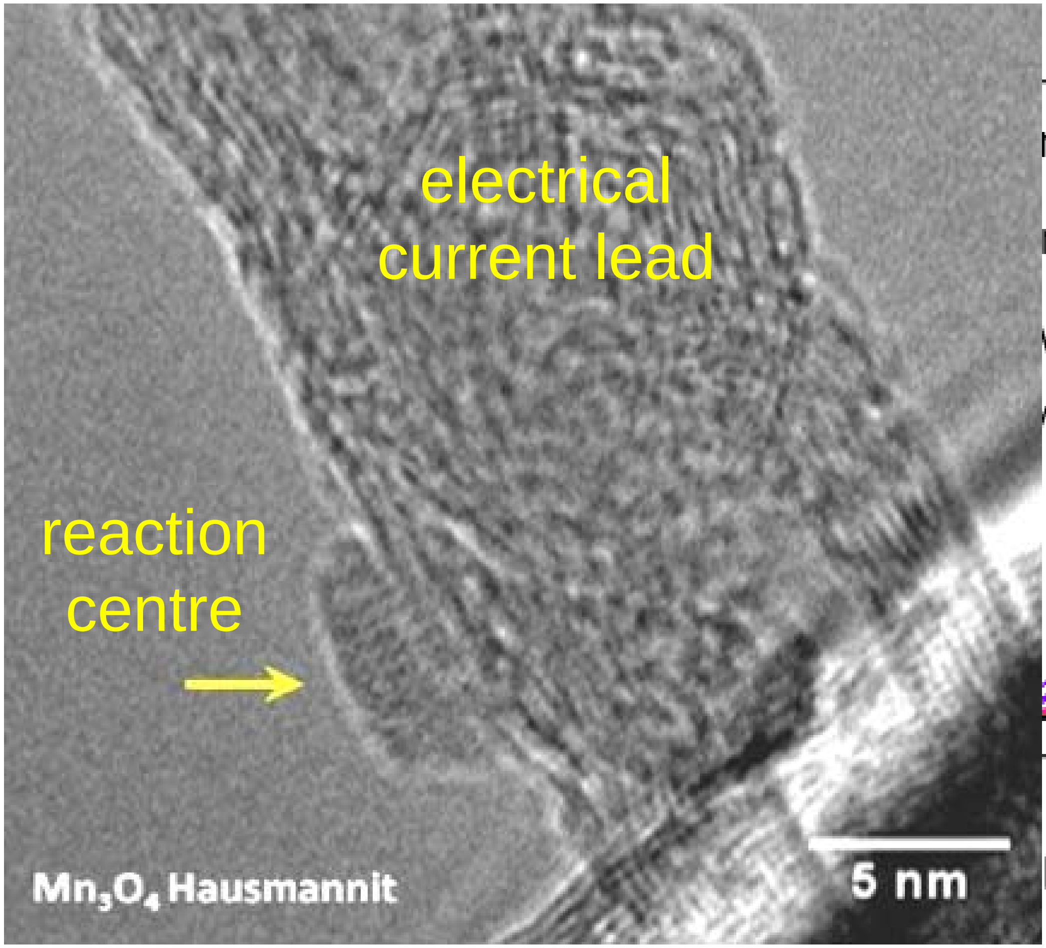


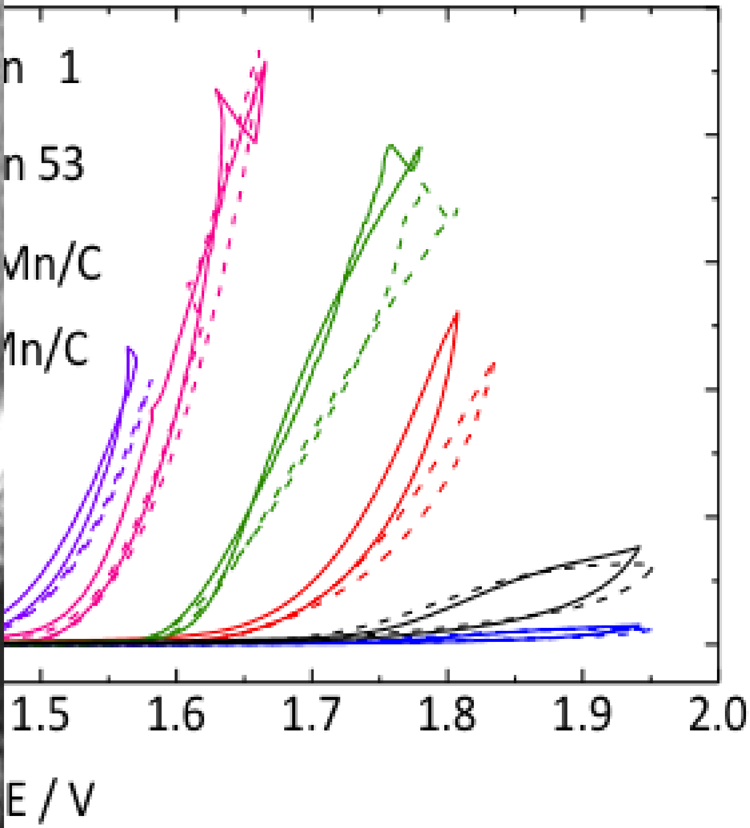


Ambient pressure XPS at very high resolution and extreme surface sensitivity:

Pt is covering with a one monolayer film of hydroxide in water leaving divalent Pt.

# Alternatives





# Summary electrolysis

- Problems with switching stability, over-potentials and use of non-sustainable materials.
- OER is the critical reaction.
- Electro-catalysts are dynamical and transform in-situ (learn from chlorine electrolysis).
- Stability and scalability are critical design parameters for second generation systems.
- Lack of solid fundamental understanding of electro-catalytic processes and their material requirements (empirical optimization less likely to be sufficient).

# Energy supply: a systemic challenge
# Catalysis is the core technology

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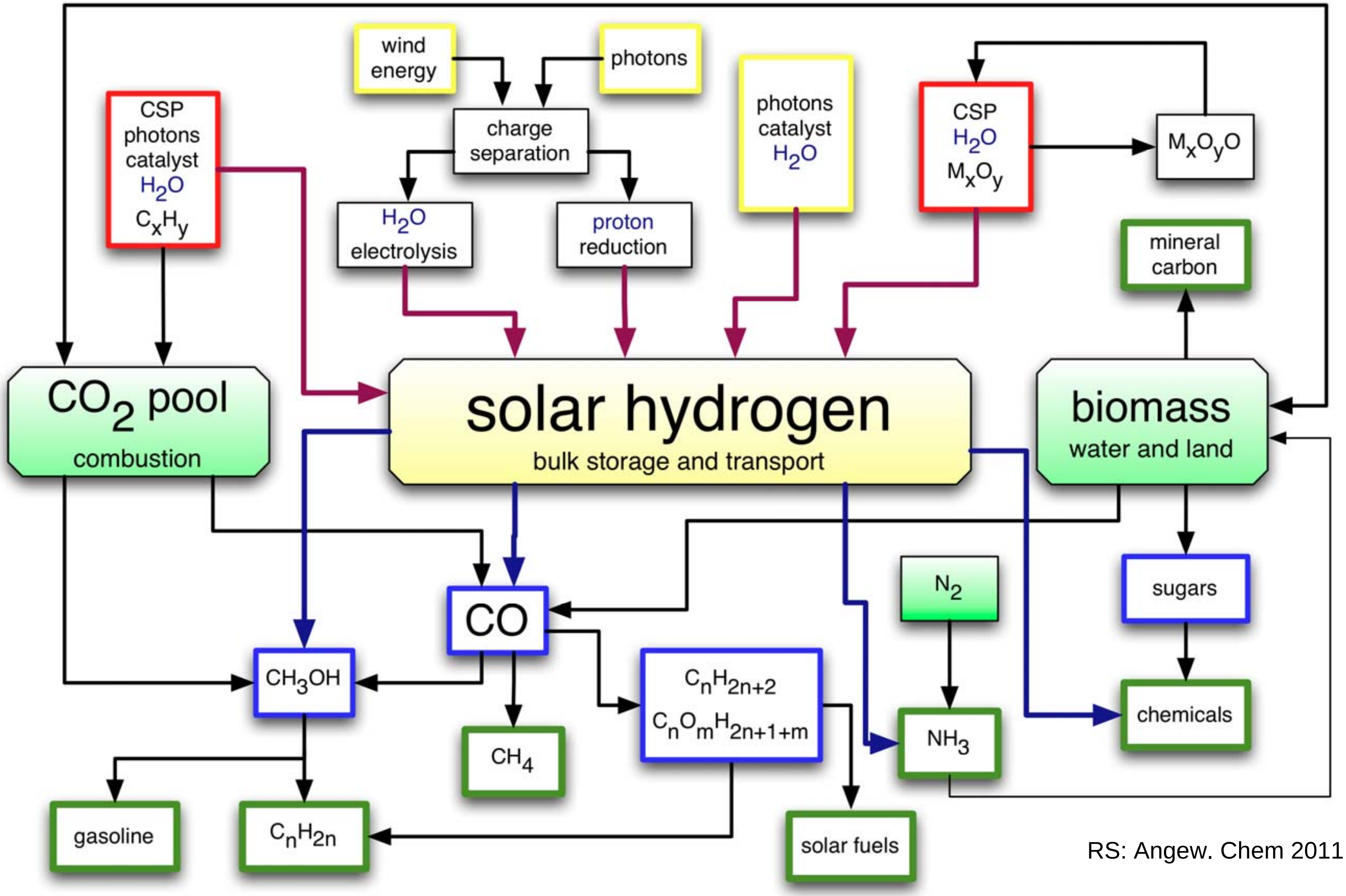

wind energy

photons

charge separation

$H_2O$ electrolysis

proton reduction

CSP photons catalyst $H_2O$ $C_xH_y$

photons catalyst $H_2O$

CSP $H_2O$ $M_xO_y$

$M_xO_yO$

mineral carbon

$CO_2$ pool
combustion

solar hydrogen
bulk storage and transport

biomass
water and land

CO

$N_2$

sugars

$CH_3OH$

$CH_4$

$C_nH_{2n+2}$
$C_nO_mH_{2n+1+m}$

$NH_3$

chemicals

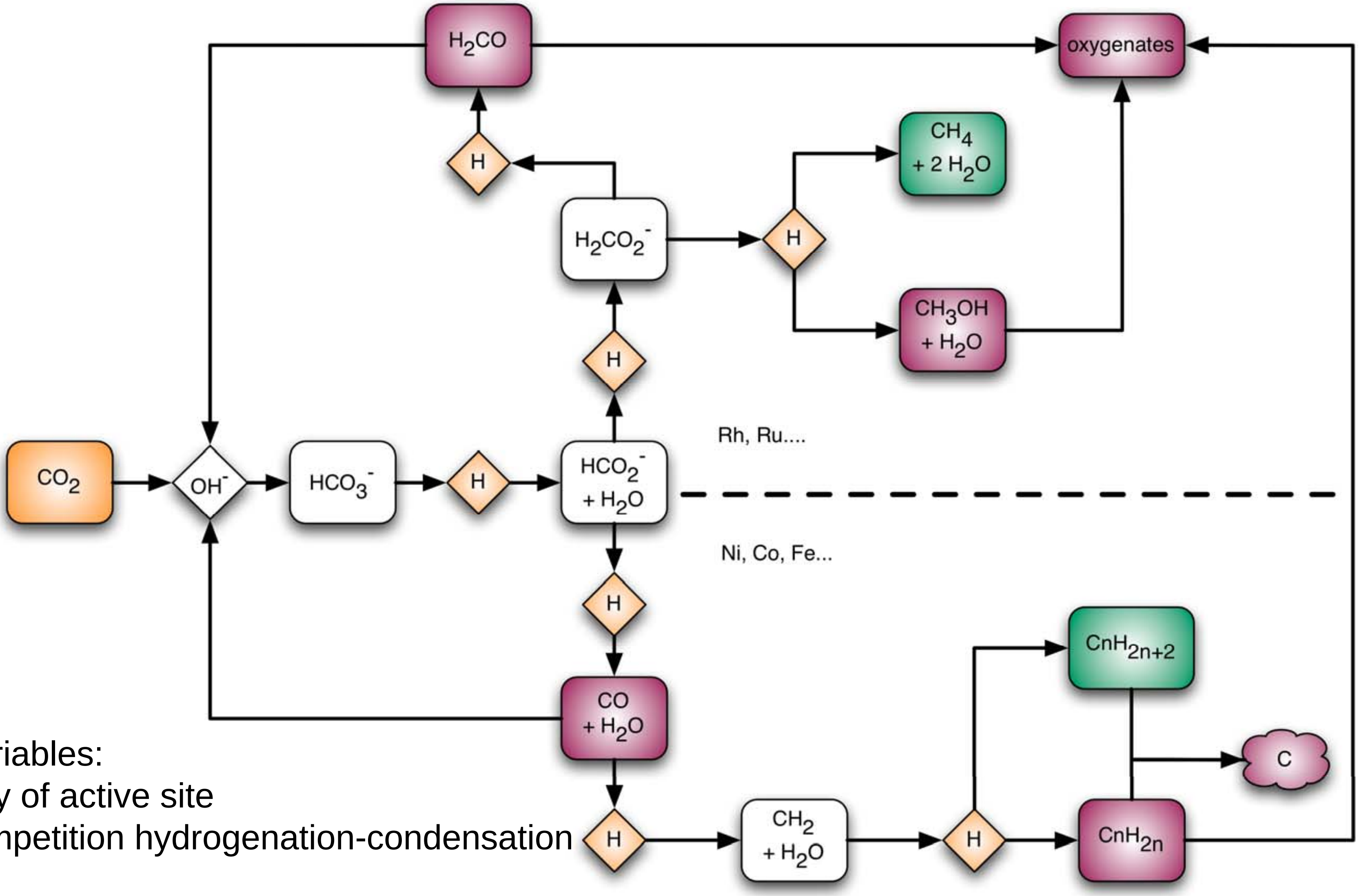
gasoline

$C_nH_{2n}$

solar fuels

RS: Angew. Chem 2011

# Power to gas:
# reaction network of a “simple” hydrogenation



Control variables:
Oxophilicity of active site
Kinetic competition hydrogenation-condensation

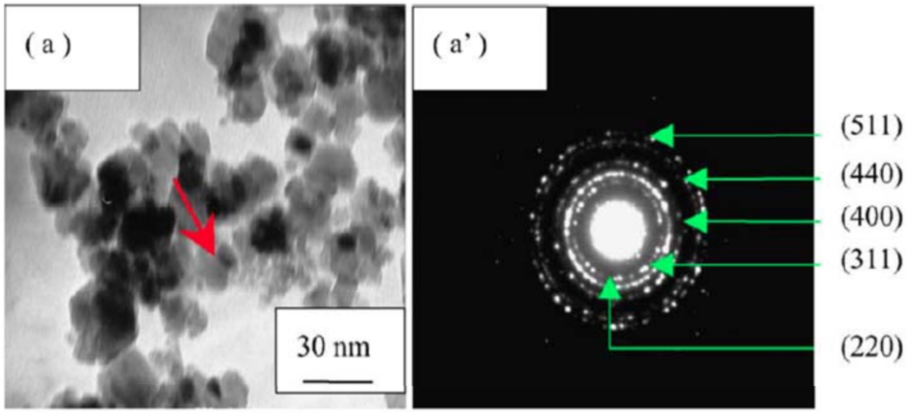
# Performance: Stable during test (!)

| Ref | Cat | $CO_2$ X | CO X |
|---|---|---|---|
| 1 | Ni | 0.8 | 1.0 |
| 1 | Ni/Ru | 14 | 1.8 |
| 1 | Ru | 9.5 | 0.7 |
| 2 | (Mn,Zn) FexO4 | 10 | n.d. |

1: Sezume et al., Faraday, I (1979)
2: Wang et al., J Mater. Chem., (2004)

- Complex NP can replace noble metals.
- Stability above 24 h is unknown.

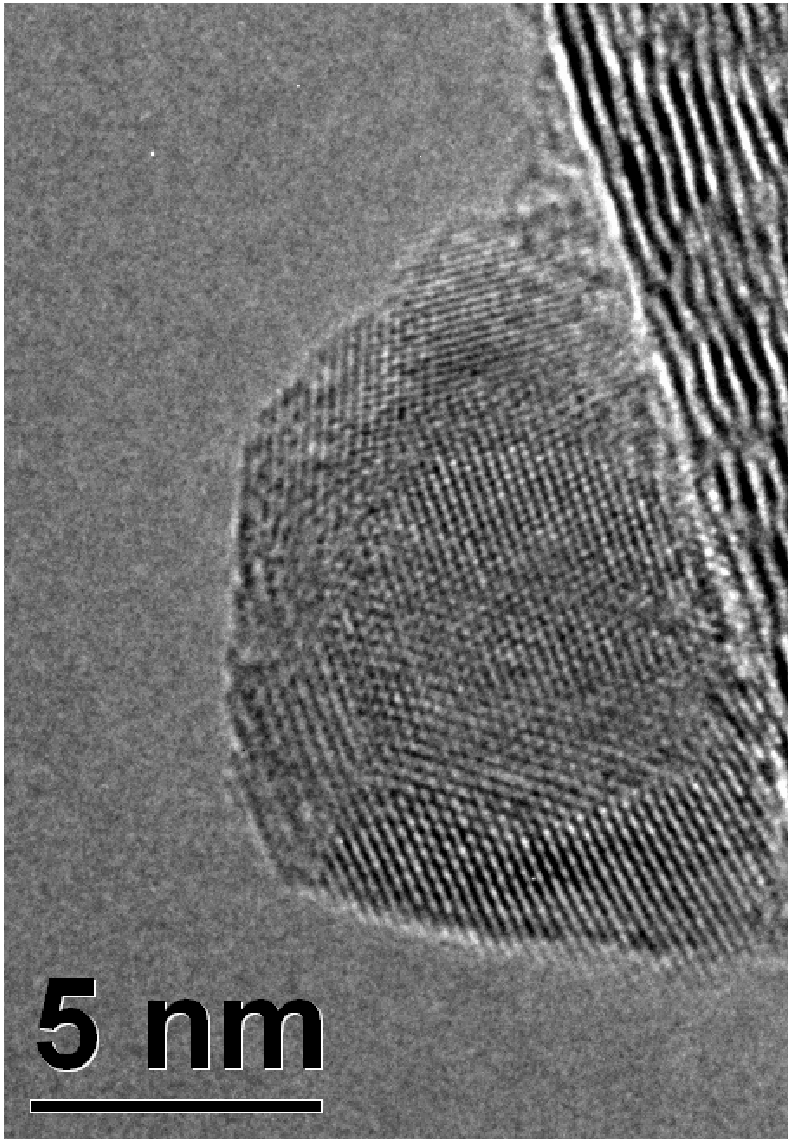
Performance is not facile,
No complete hydrogen conversion,
Side products unclear
Carbon deposition



# Carbon deposition as prime problem

Deposition of carbon limits catalyst performance: loss of active phase through CNT formation.

Protection through carbide formation: labile under reaction conditions: catalyst design allowing for facile carbon dissolution.



# Dynamics of Ni under hydrogenation conditions

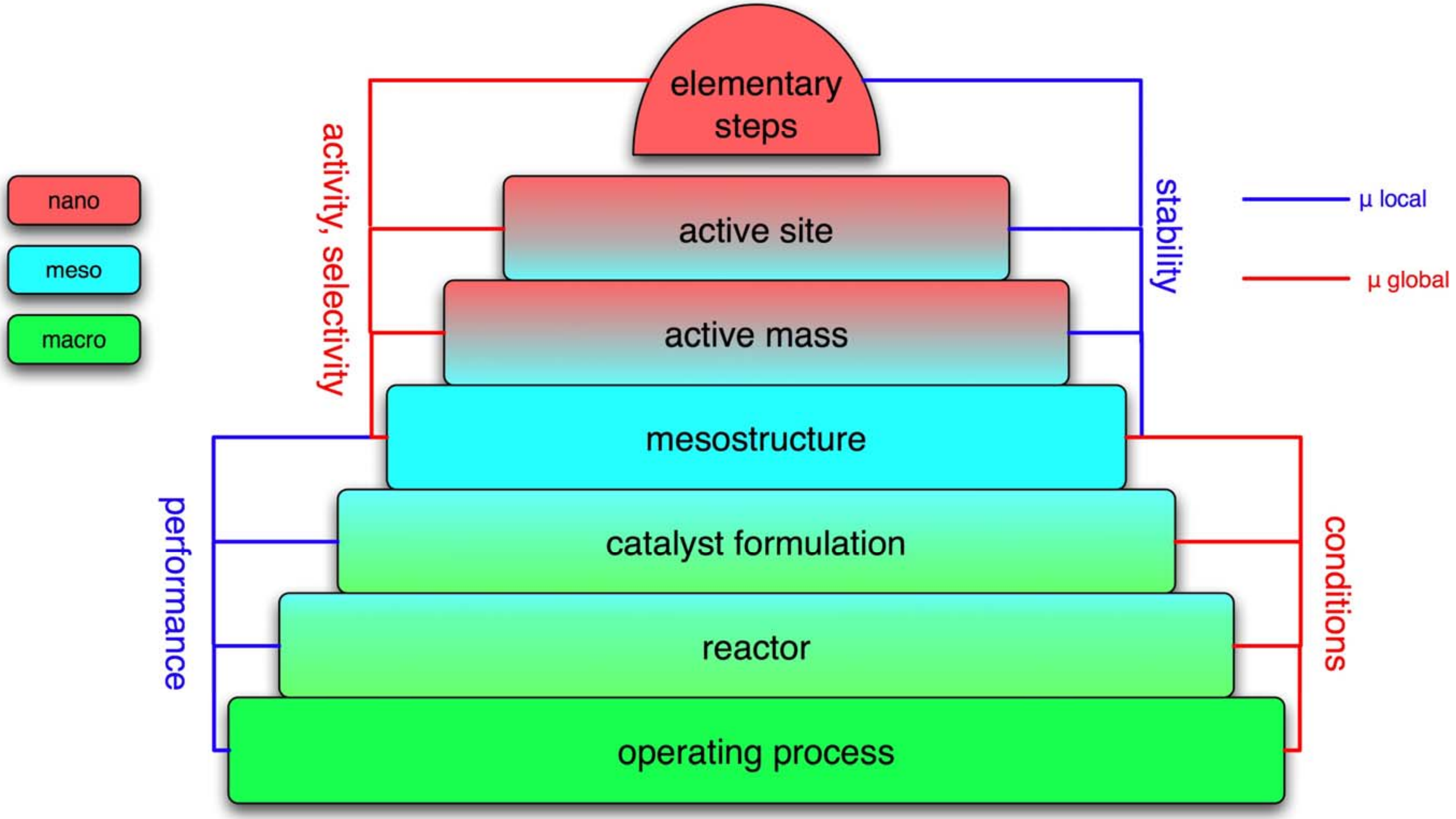
# Summary

- High performance systems contain non-sustainable noble metals.
- Base metal systems insufficient in stability and performance (mind educt purity: $CO_2$!).
- Complex material dynamics from reaction network activated.
- Gas purification for enduser gas distribution system despite high (90%) selectivity reduces efficiency and drives cost.
- Material and process development needed after verification of fundamental reaction understanding.

# 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.

# 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

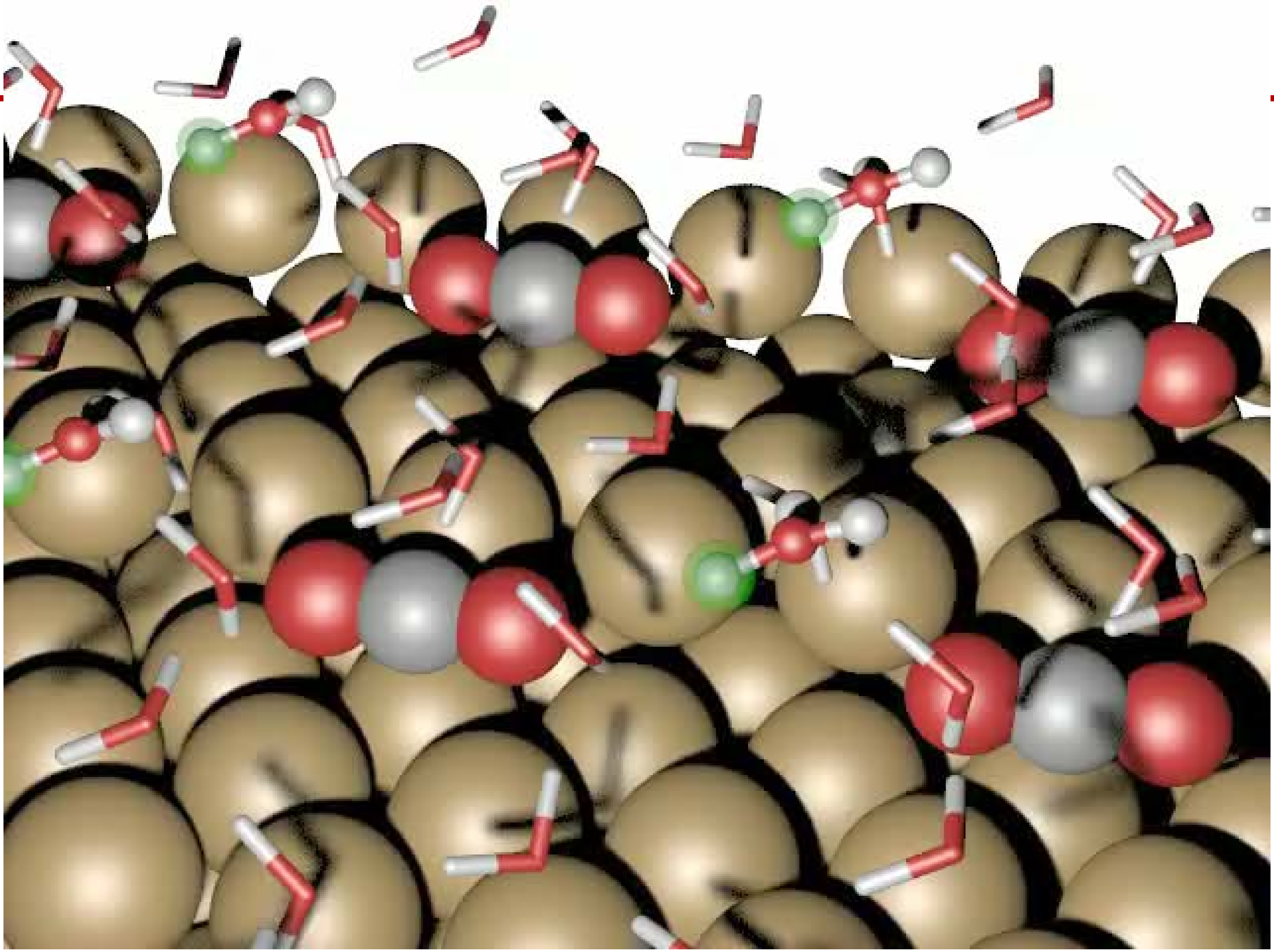
µ global

# Concepts

- The concepts developed differently in the disciplines of catalysis:
  - Homogeneous
  - Heterogeneous
  - Biological.
- Common to all: catalysis is a kinetic effect and cannot modify thermodynamic limits.
- Consequence: catalysts are non-equilibrium systems.
- They contain only few functional sites in a matrix of stabilizing species!

# 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”.



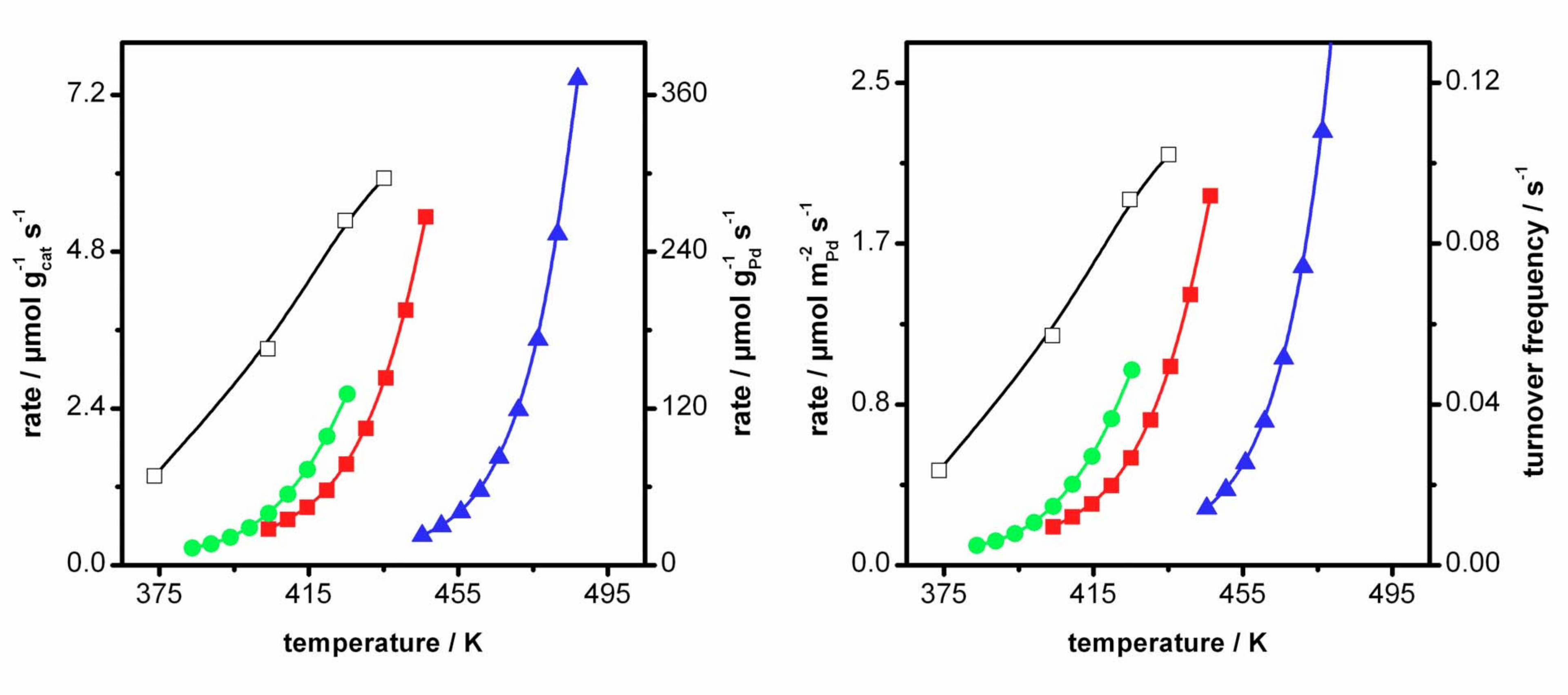
A. Peterson, Chris O’Grady

# 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.

# Catalytic activity in what units?

CO oxidation over 2% Pd/$Fe_2O_3$



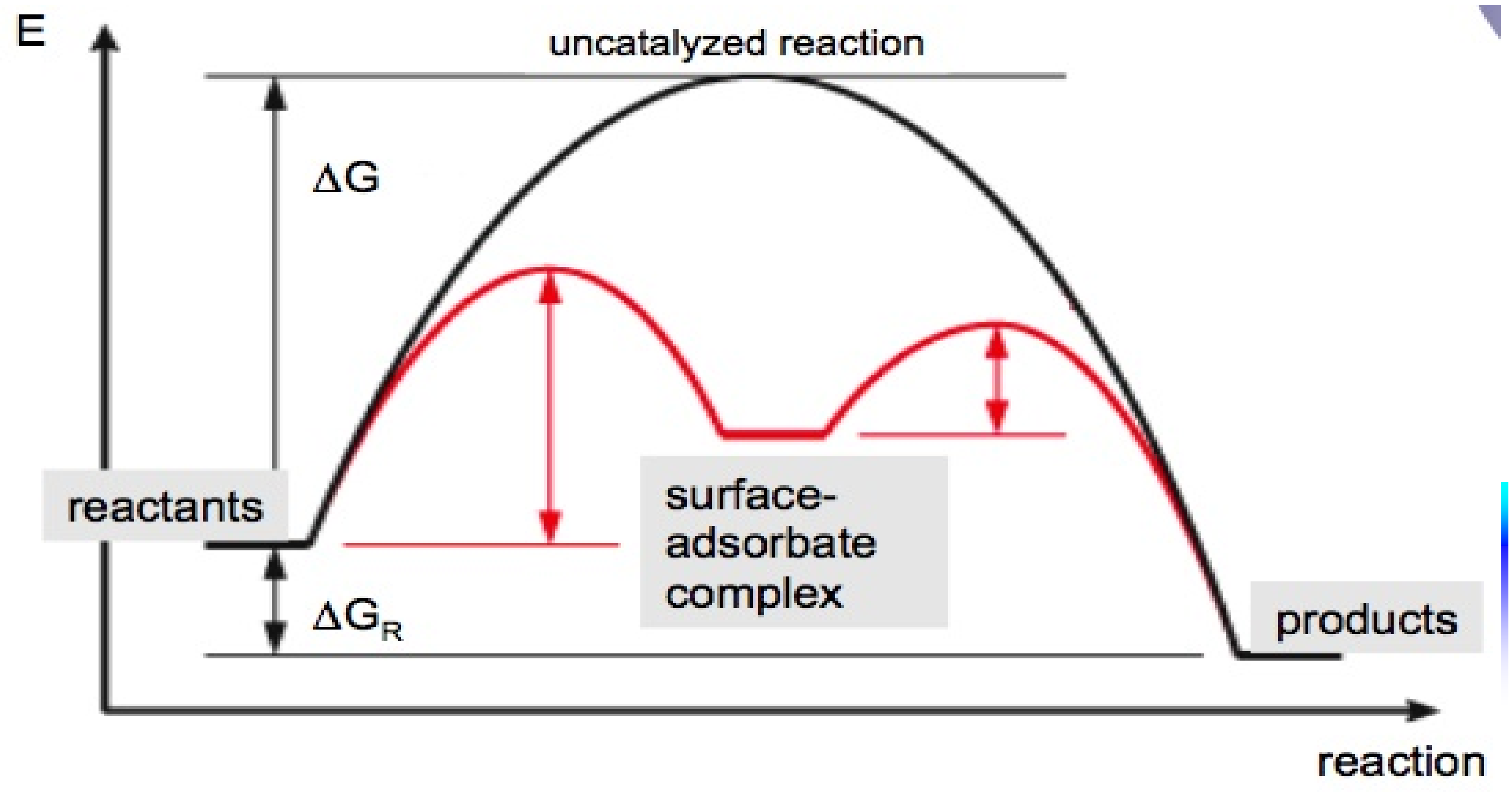
# Basic concepts

- 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.

# The standard model (Langmuir, Taylor, Ertl)

- A heterogeneous catalyst can be approximated by a single crystal surface.
- No compound of the catalyst with its reactants.
- 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.

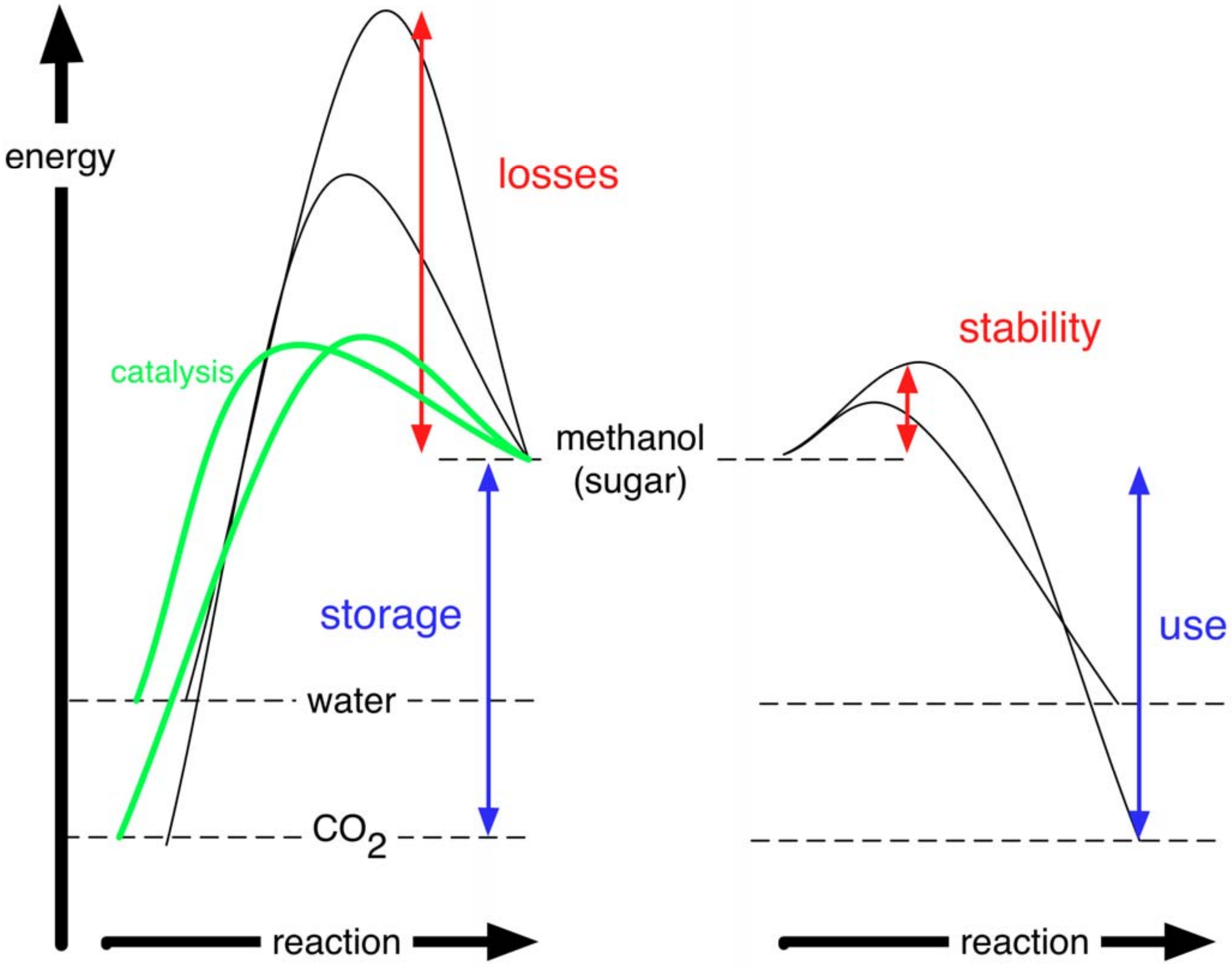
# Function of a catalyst: Static SM



Adsorbate structures dynamical (chemical waves)

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

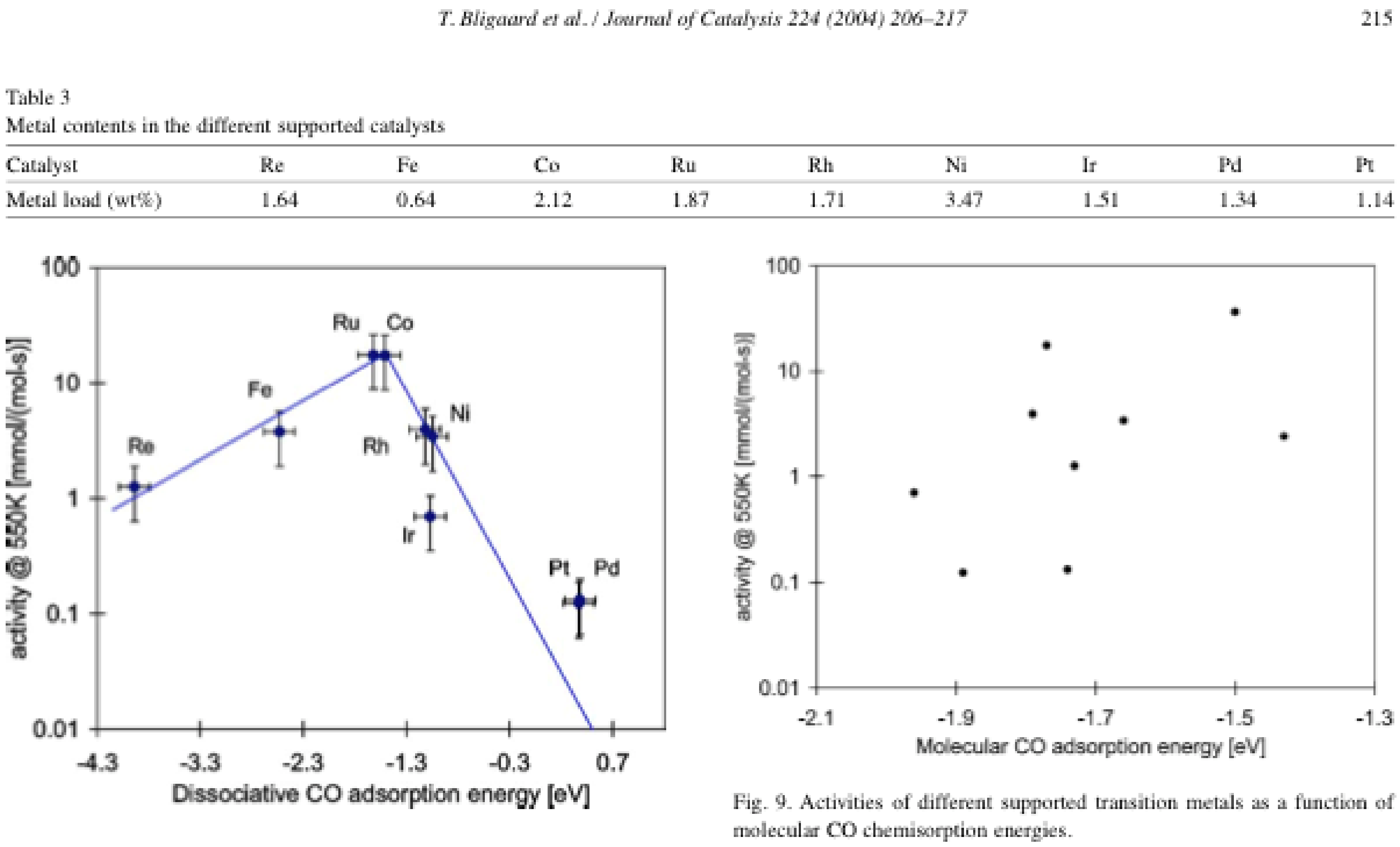
# Application: energy storage



# Modern concept (?): scaling relations

- A catalytic reaction is given by the ability of a catalyst to activate reactants:
- Optimum between strength of adsorption and heat of reaction: the Sabatier (Tamaru) principle.
- Modern version the “vulcano” trend.
- Concept allows predictions of catalytic reactivity from simplified theories.
- Offering the chance to “test” many catalysts by computation rather than by experimental screening.
- Reduction of the search space for potent catalysts.

# Example: CO methanation

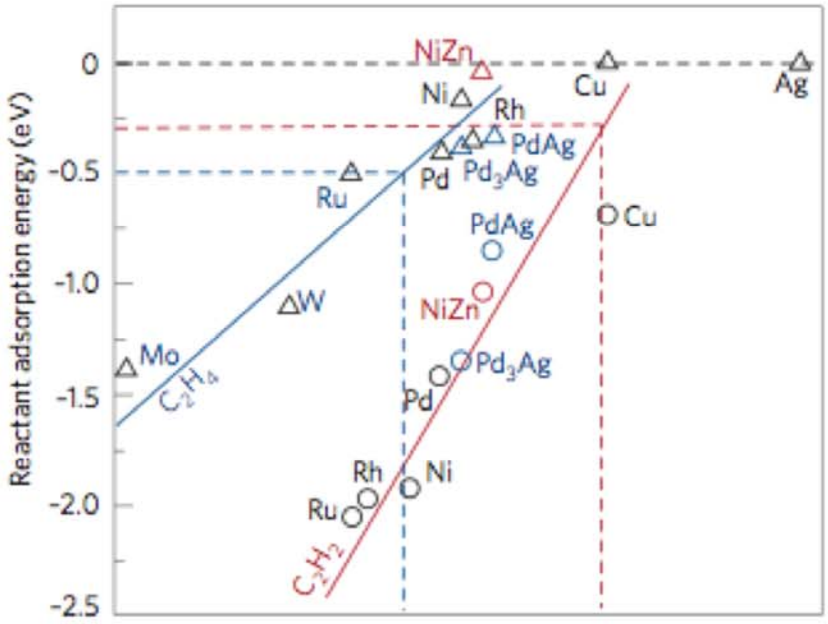


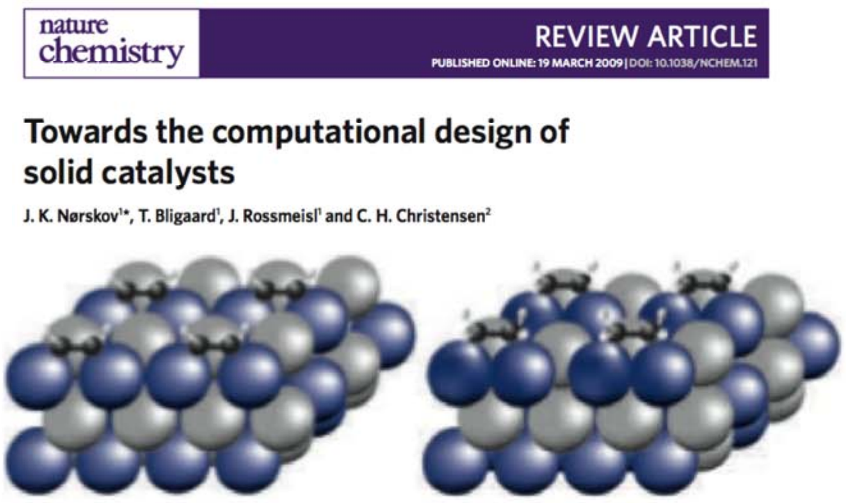
*T. Bligaard et al. / Journal of Catalysis 224 (2004) 206–217* 215

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.




nature chemistry

REVIEW ARTICLE

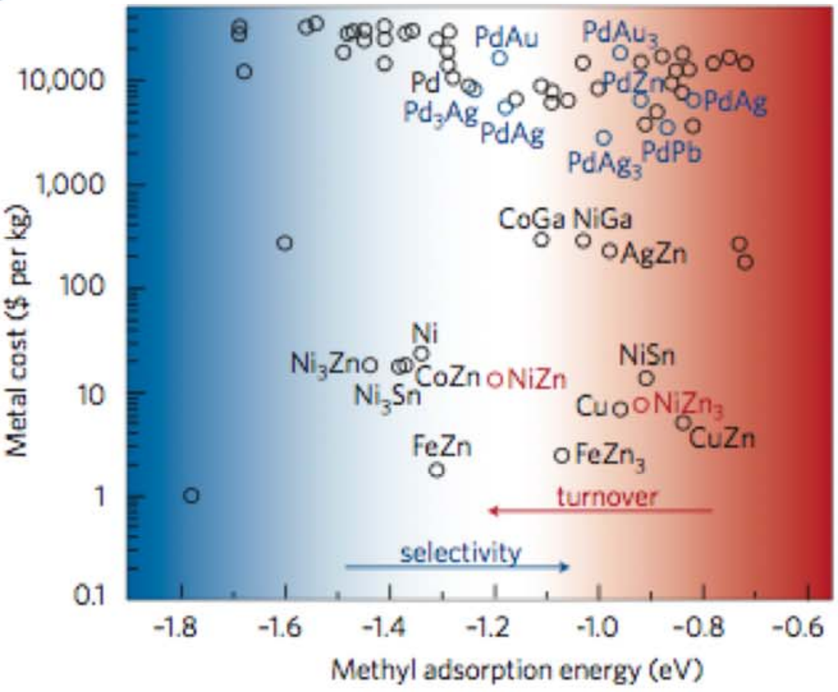
PUBLISHED ONLINE: 19 MARCH 2009 | DOI: 10.1038/NCHEM.121

Towards the computational design of solid catalysts

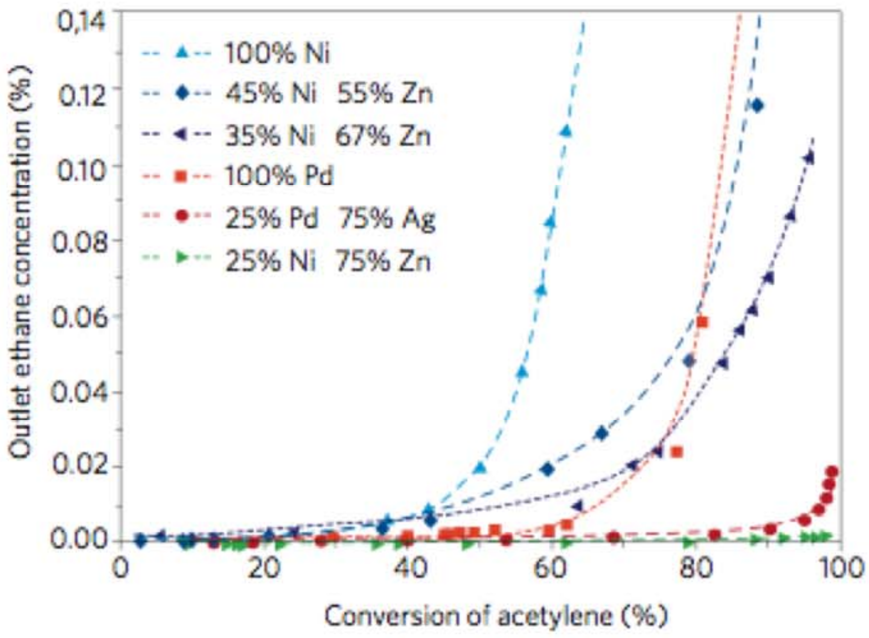
J. K. Nørskov[1]*, T. Bligaard[1], J. Rossmeisl[1] and C. H. Christensen[2]

Stability and decomposition kinetics

**b**



**d**



# Fundamental gap: complexity

- We consider individual mechanistic processes.
- Desire for single molecule spectroscopy (SPM).
- We observe $10^{17}$ ($10^{10}$ planets of humans) simultaneous events:
- Can there be a unique relation?
- Statistics: distribution of properties leads to distributions of reaction pathways:
- Beware of using the term “mechanism”.
- In homogeneous systems the distribution of properties is much narrower.

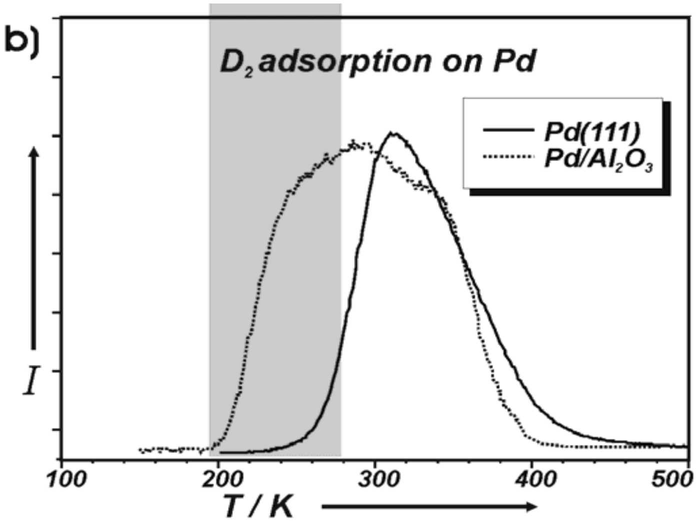
# Model systems

- are “real”  (contrast to high performance 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 interactions.
- are made to a maximum structural definition (equals minimal reactivity).

# Model reactions
# Structure effects

Pentenes to pentane

Hydrogenation
in the presence of
subsurface H
[Pd particles]



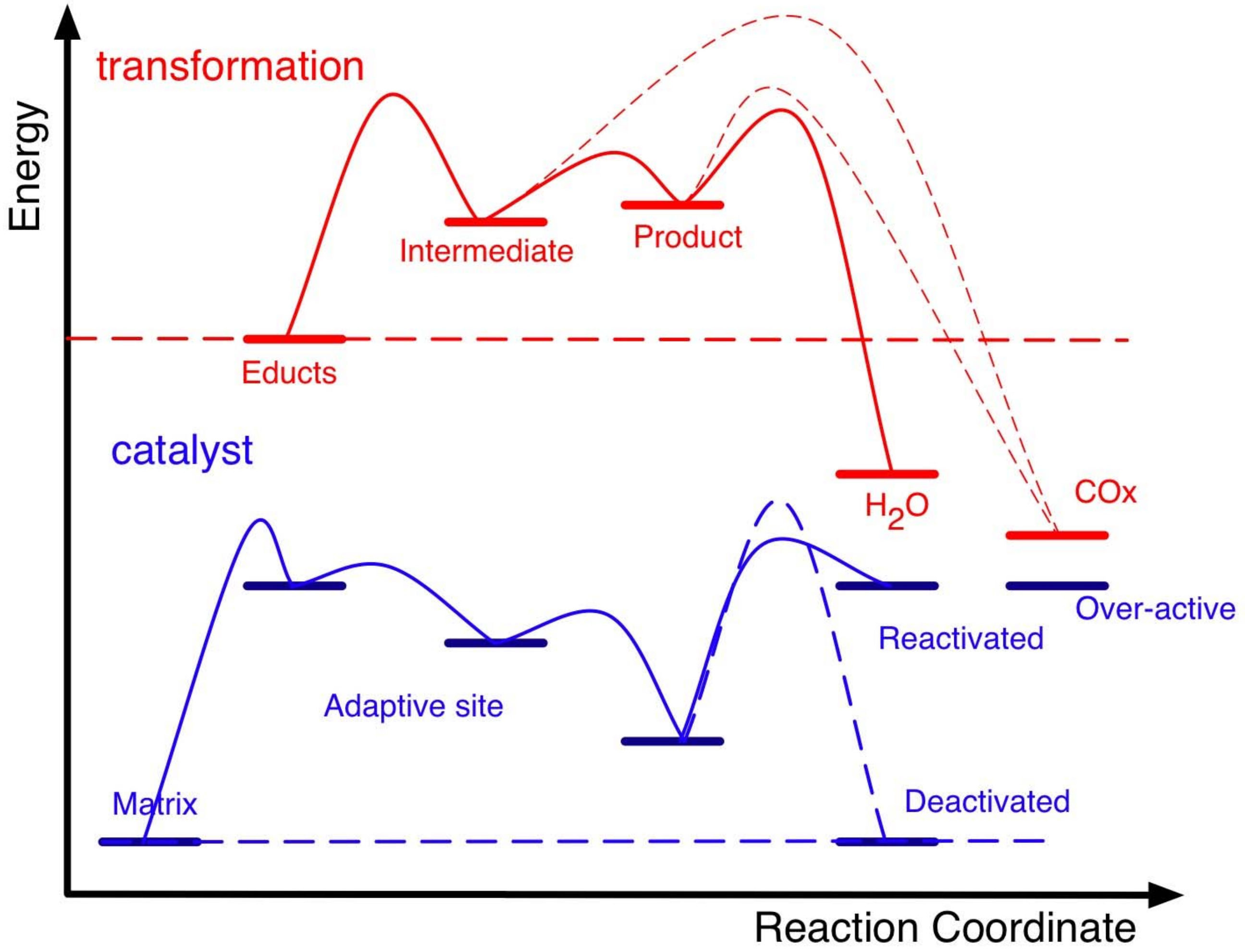
No hydrogenation
without
subsurface H
[Pd(111)]

Freund, Shaikhutdinov et al., Angew. Chem. 2003

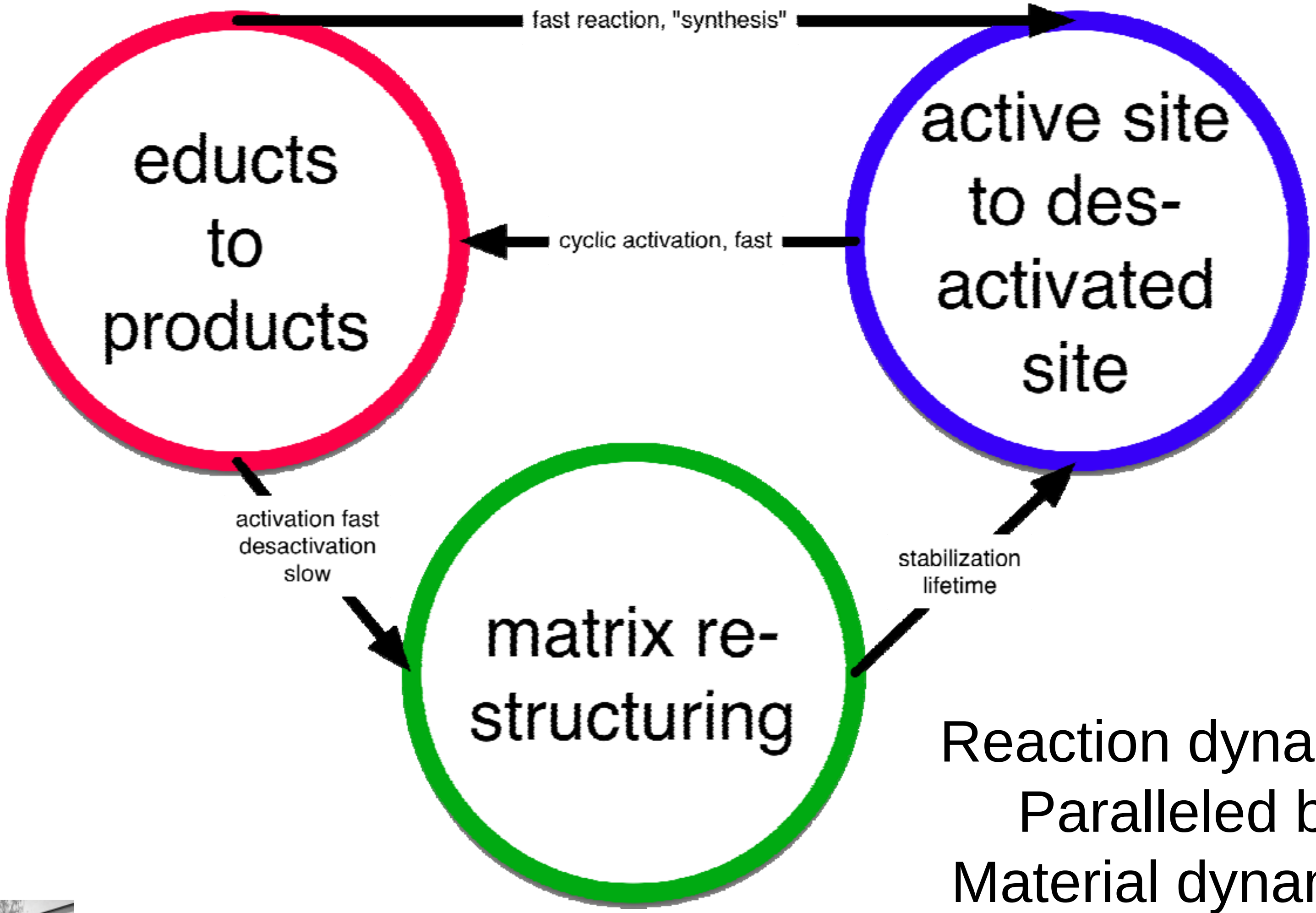
# Active sites

- 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

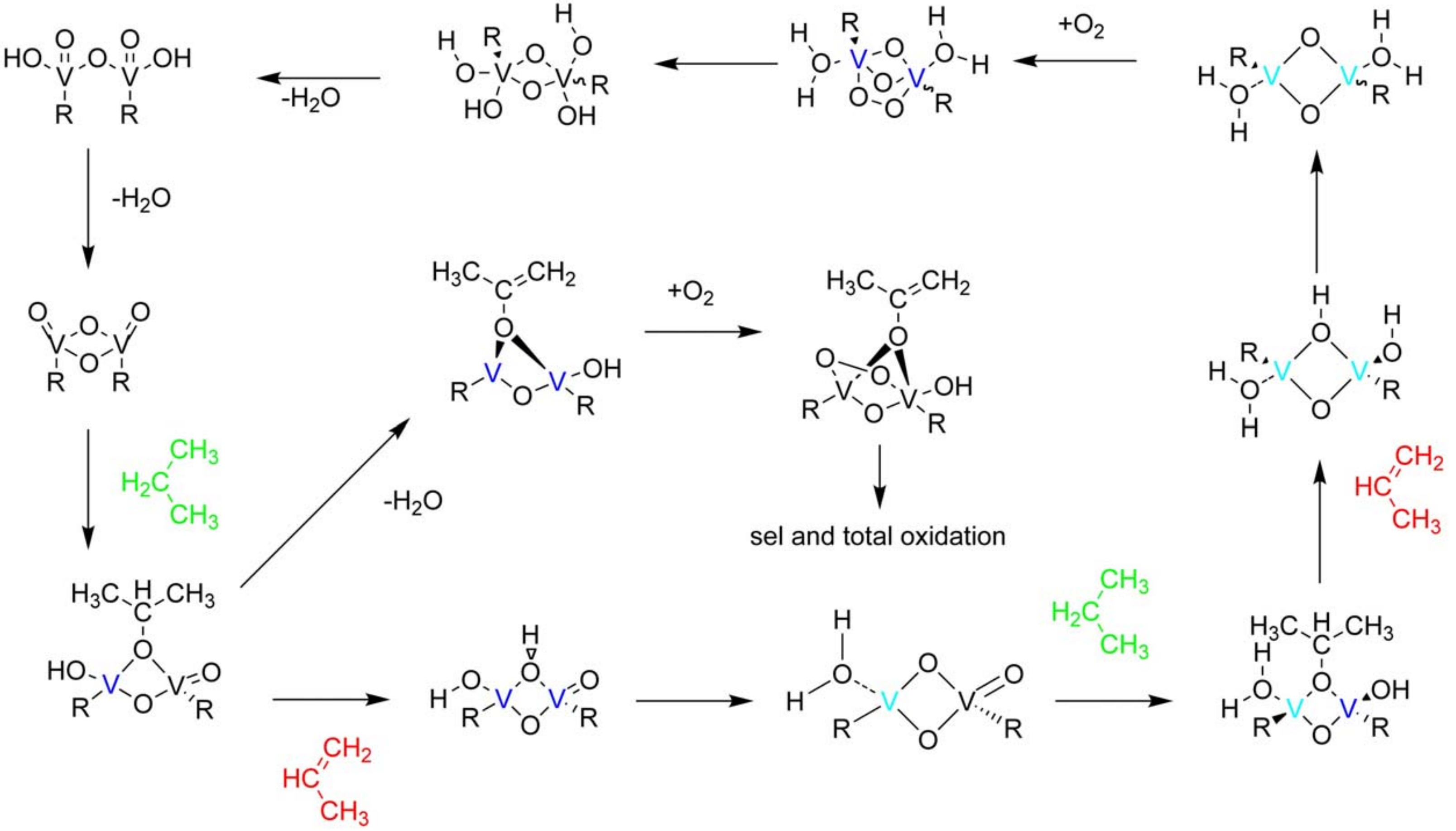


# It is inadequate to concentrate on the “reaction”



Reaction dynamics
Paralleled by
Material dynamics

# Reaction pathway catalyst



Dynamics and adaptation

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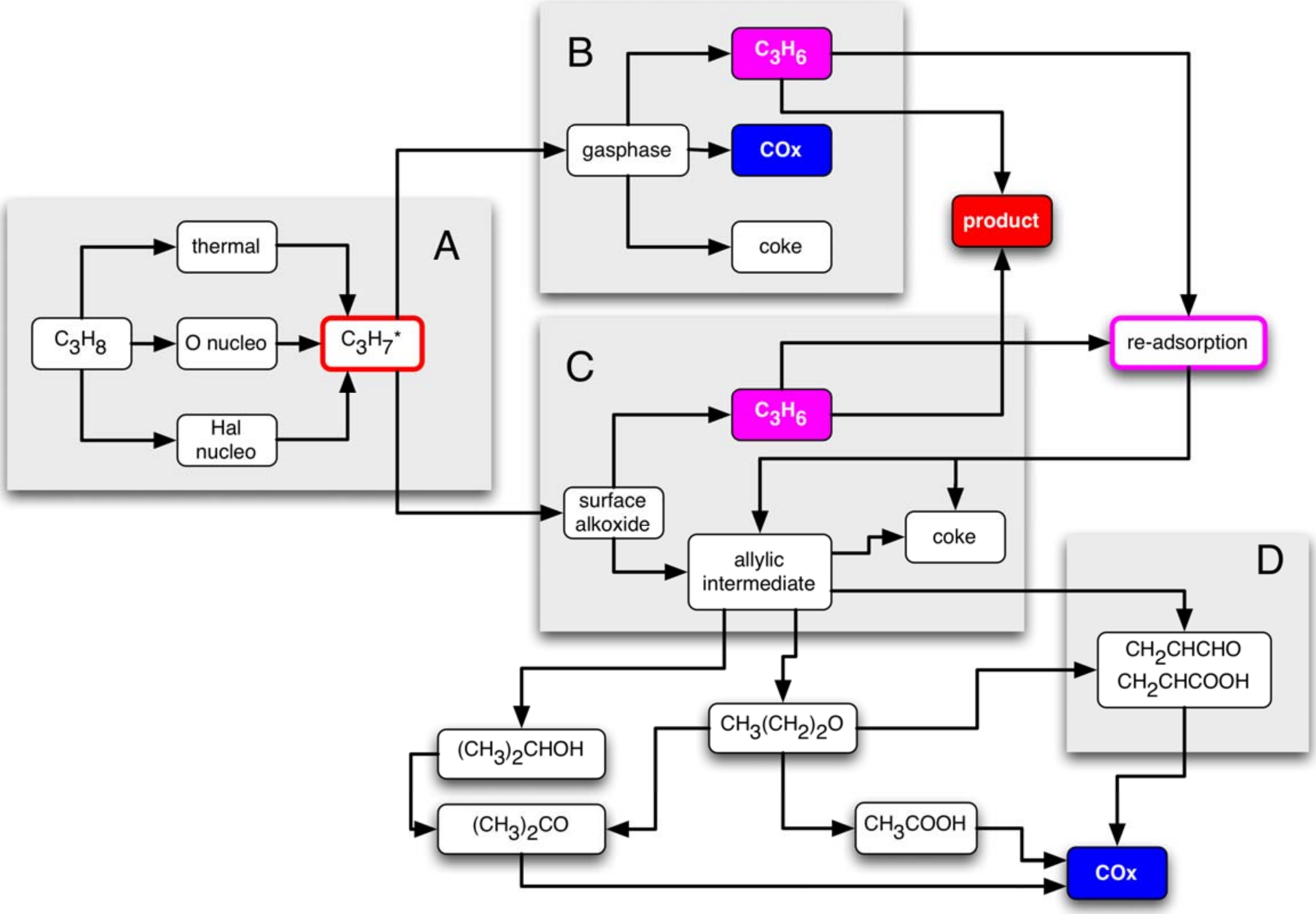
# Reaction networks:
# A catalyst activates it all!



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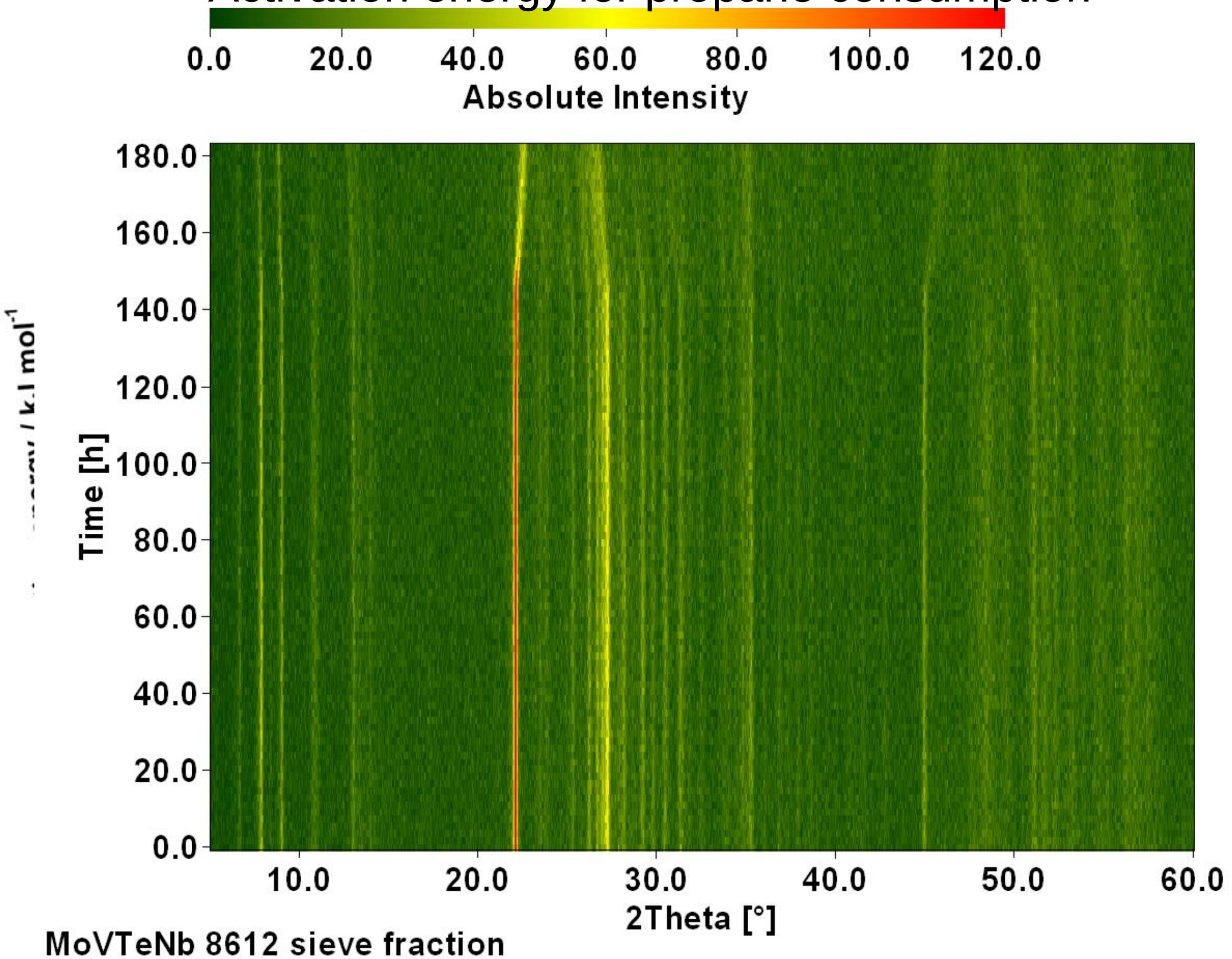
# Dynamics vs stability

Activation energy for propane consumption



**MoVTeNb 8612 sieve fraction**

$H_2O$ / $O_2$ / propane

0 / 0 / 3

5 / 0 / 3

5 / 12 / 3

0 / 12 / 3

GHSV=5000h$^{-1}$

T=673K

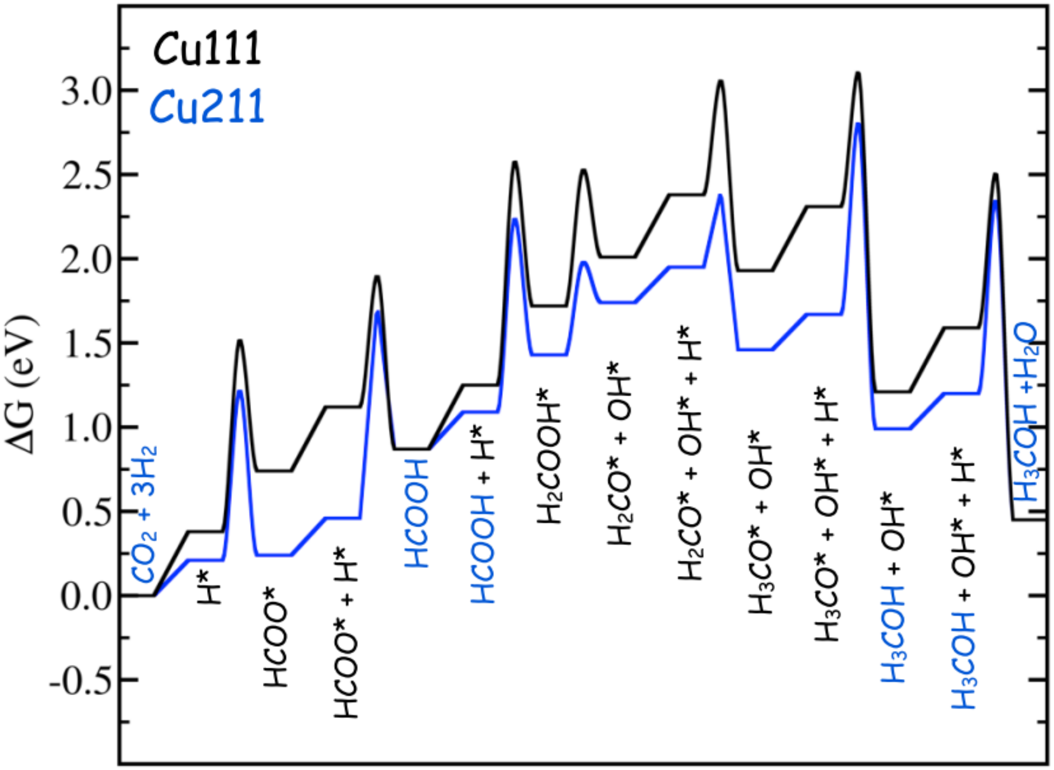
390°C

# Numerical models

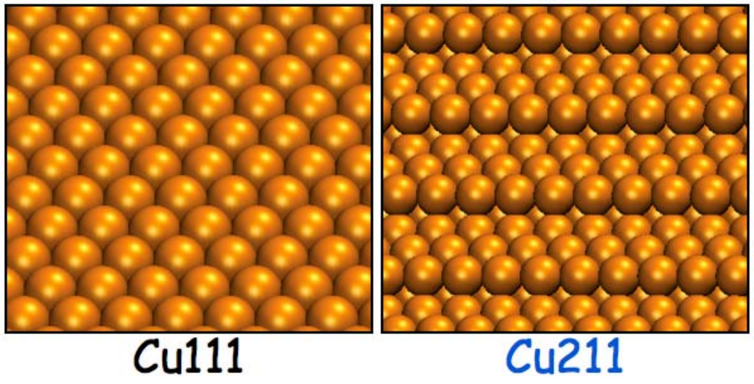
- Microkinetics with a set of elementary steps derived from surface science experiments
- Identification of the rds from energetics
- Ab-inito calculation of critical steps and their transition states
- Incorporation of experimental values from key steps (adsorption, activation)
- Prediction of rates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

# Reaction pathways: reagents

SUNCAT
CENTER FOR INTERFACE SCIENCE AND CATALYSIS

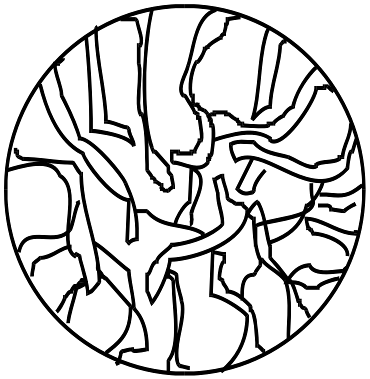


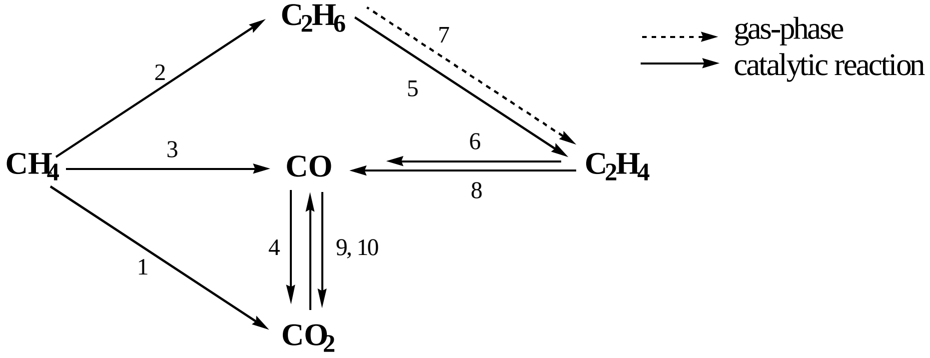
The mean field approximation is a upper bound for modelling active sites.



Courtesy of F. Studt and J. Nørskov, SLAC Standford

# Macrokinetic descriptions: transport and atomistic processes?





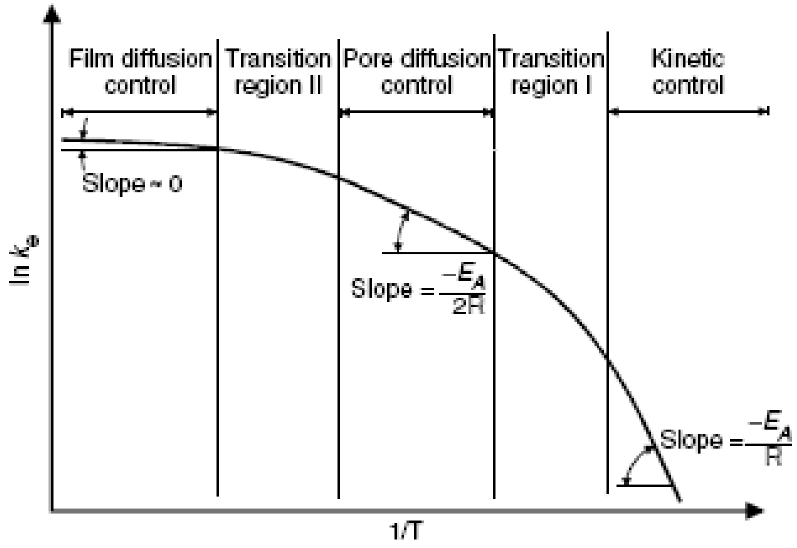
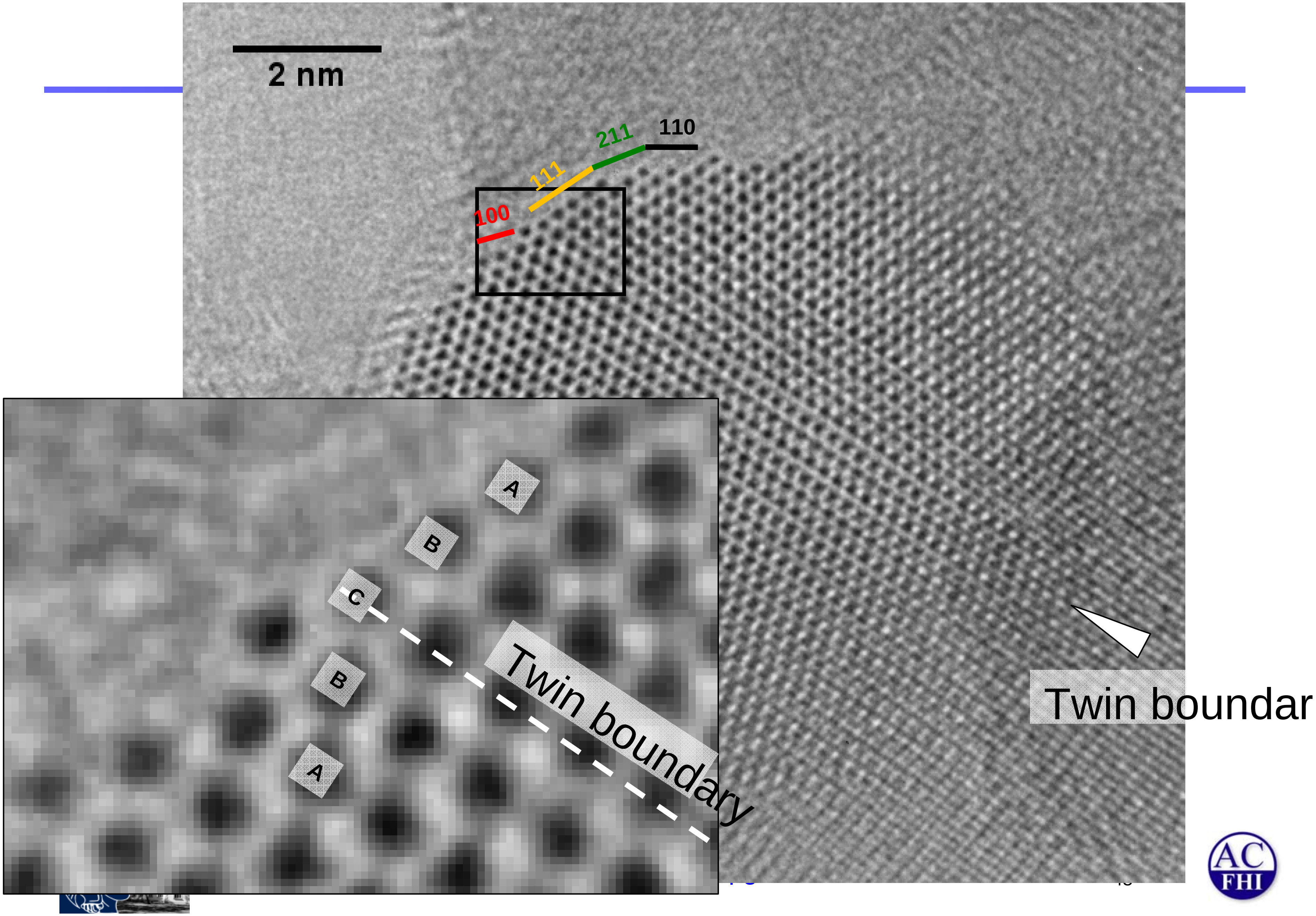


**Fig. 3** Transition from the kinetic regime to the diffusion-controlled regime of a heterogeneous catalytic fluid–solid reaction carried out on a porous catalyst.

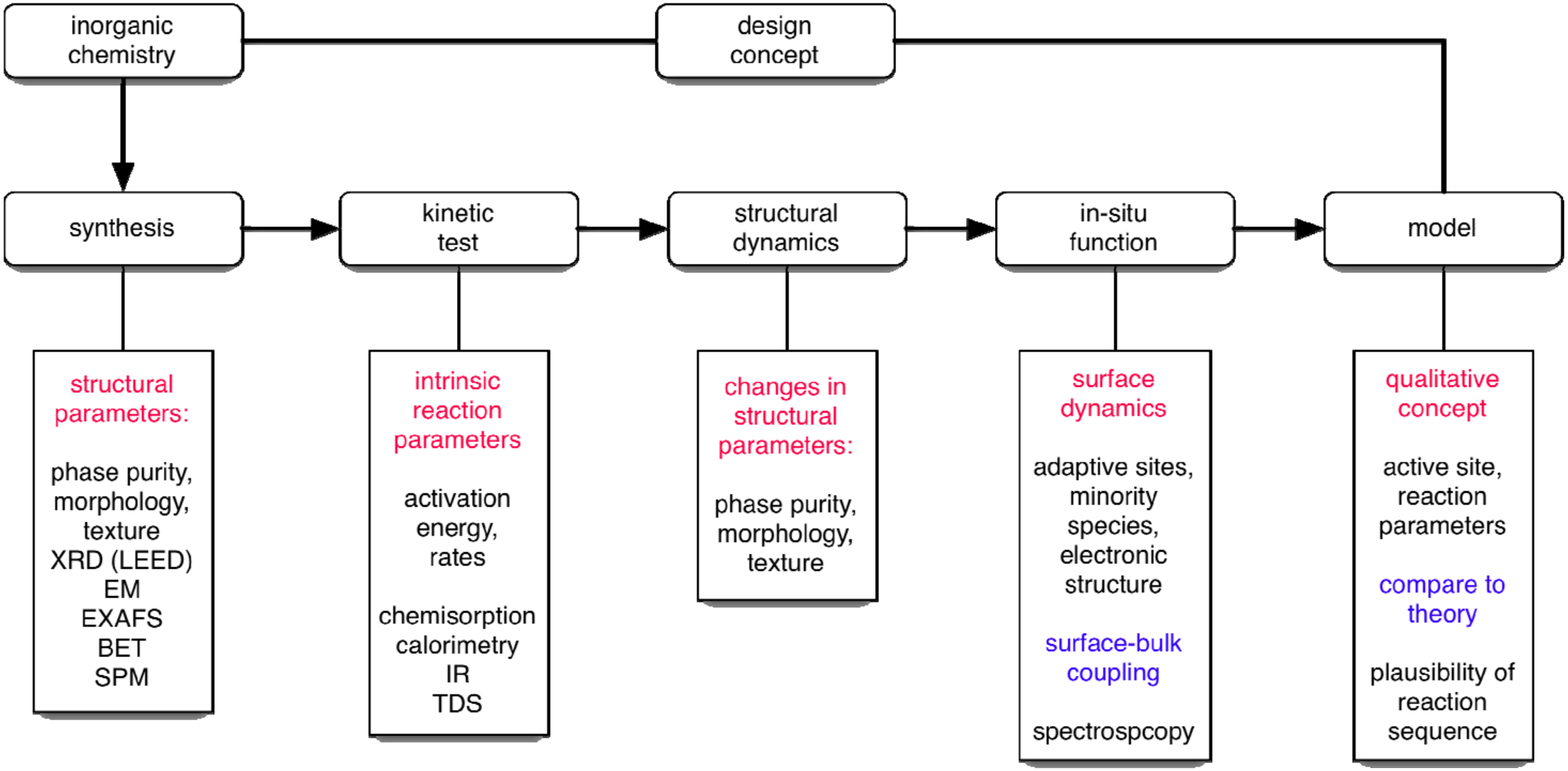
(1): $CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$
(2): $2\,CH_4 + 0{,}5\,O_2 \longrightarrow C_2H_6 + H_2O$
(3): $CH_4 + O_2 \longrightarrow CO + H_2O + H_2$
(4): $CO + 0{,}5\,O_2 \longrightarrow CO_2$
(5): $C_2H_6 + 0{,}5\,O_2 \longrightarrow C_2H_4 + H_2O$
(6): $C_2H_4 + 2\,O_2 \longrightarrow 2\,CO + 2\,H_2O$
(7): $C_2H_6 \longrightarrow C_2H_4 + H_2$
(8): $C_2H_4 + 2\,H_2O \longrightarrow 2\,CO + 4\,H_2$
(9): $CO + H_2O \longrightarrow CO_2 + H_2$
(10): $CO_2 + H_2 \longrightarrow CO + H_2O$

# Modern: The generic innovation

- We can follow the dynamics of catalysts.
- In-situ (not “operando”) spectroscopy.
- Precison structural analysis (high-energy sites).
- Allow catalysts to respond to the chemical potential of the reactants:
- Catalysts activate themselves!!
- Do not attempt to design active structures too reactive as activation will damage the system.


2 nm
211
110
111
100
A
B
C
B
A
Twin boundary
Twin boundar

# A research approach (both for models and high performance systems)



inorganic chemistry

design concept

synthesis

kinetic test

structural dynamics

in-situ function

model

structural parameters:

phase purity,
morphology,
texture
XRD (LEED)
EM
EXAFS
BET
SPM

intrinsic reaction parameters

activation energy,
rates

chemisorption
calorimetry
IR
TDS

changes in structural parameters:

phase purity,
morphology,
texture

surface dynamics

adaptive sites,
minority species,
electronic structure

surface-bulk coupling

spectrospcopy

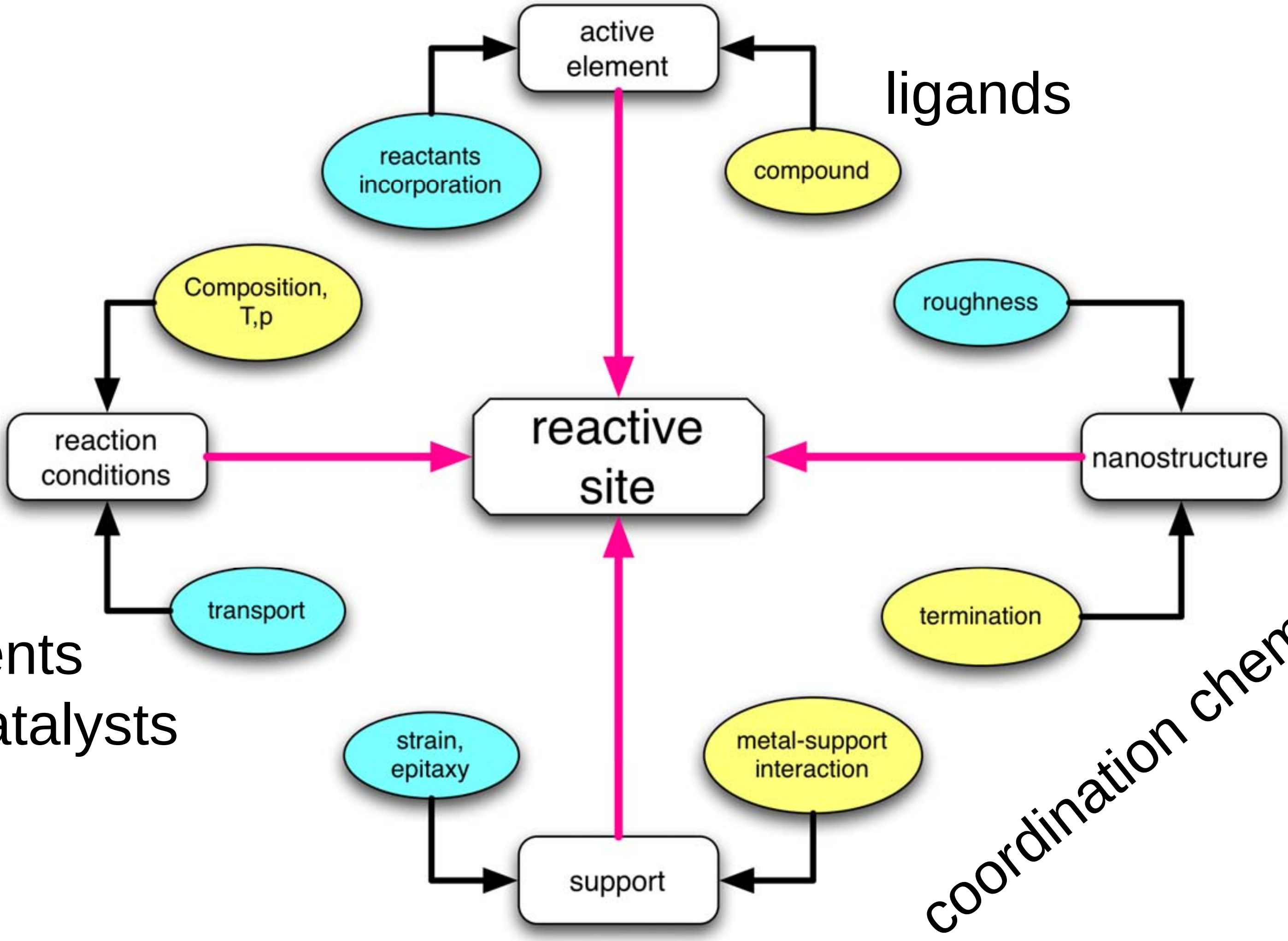
qualitative concept

active site,
reaction parameters

compare to theory

plausibility of reaction sequence

# Summary



active element

reactants incorporation

compound

Composition, T,p

roughness

reaction conditions

reactive site

nanostructure

transport

termination

strain, epitaxy

metal-support interaction

support

ligands

solvents
co-catalysts

coordination chemistry

# Conclusions

- 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 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.

Dem Anwenden muss das Erkennen vorausgehen

Max Planck

# Thank You