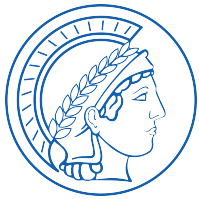


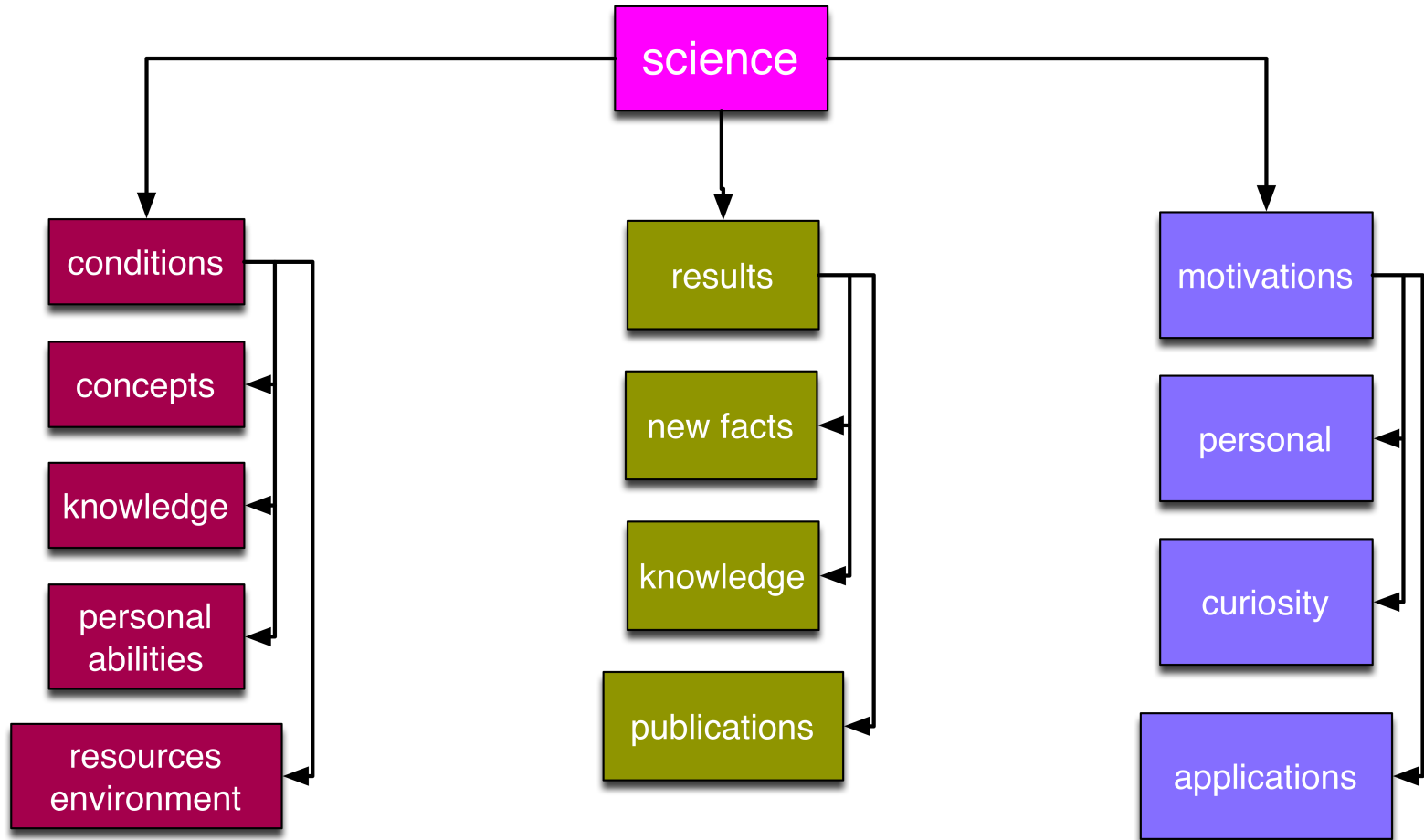
Ethics in science

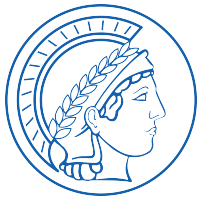
An incomplete account with practical consequences

Robert Schlögl



What it takes for science

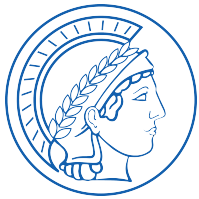




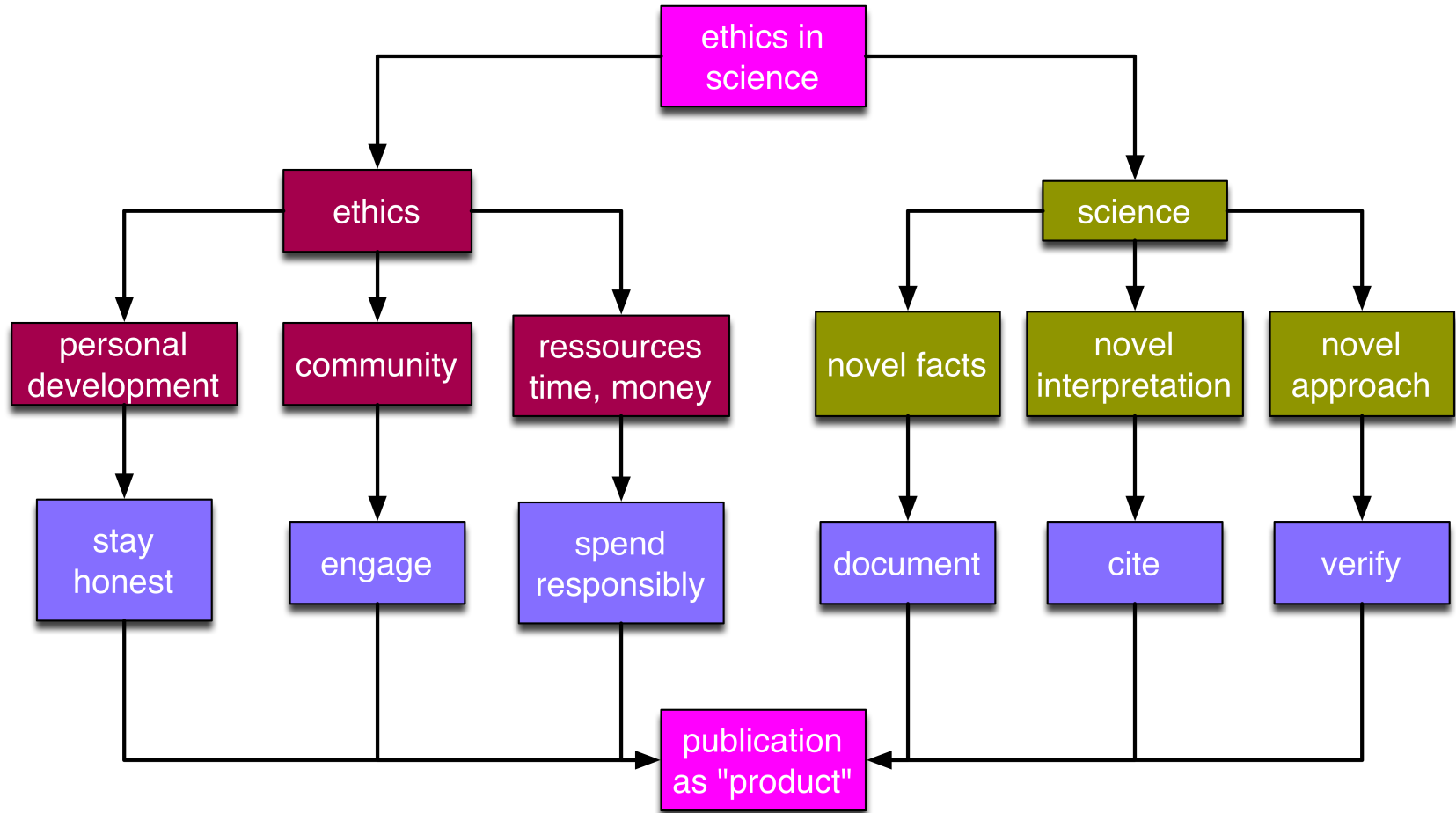
Ethics in science

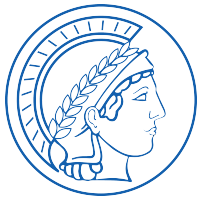
- Science is no sports!
 - Speed is a minor parameter (limits of doctoral time periods in your interest!)
 - Correctness and originality are crucial
 - Responsibility for resources lies with you when planning and executing work.
- We do not do science to produce publications.
- Science is also no soap opera!
- We do science to learn and understand.
- We publish to document and to induce discussion.
- The use of publications and their citations are secondary quality metrics! We should not work for rankings!!
- First come correctness and originality.





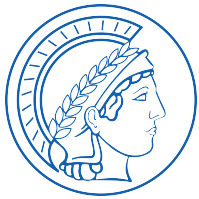
The imperative!





Fraud and „Plagiat“

- German science ethics requires proof for the following:
- Data base of experiments (original data, experiment, plausibility) 10 years of documentation.
- Authorship (only and exclusively contributors, gray lines for support and funding).
- Publication ethics (no multiple publication of same results).
- Citation practice: no stealing of ideas or results, also not from own work. (data and concepts count, not wording!)
- Issues: all these points are obvious but have borderline cases when it comes to practical applications.
- The MPG and the DFG have issued guidelines for good scientific practice, many journals try to verify the authors relations to the work submitted and even request original data.

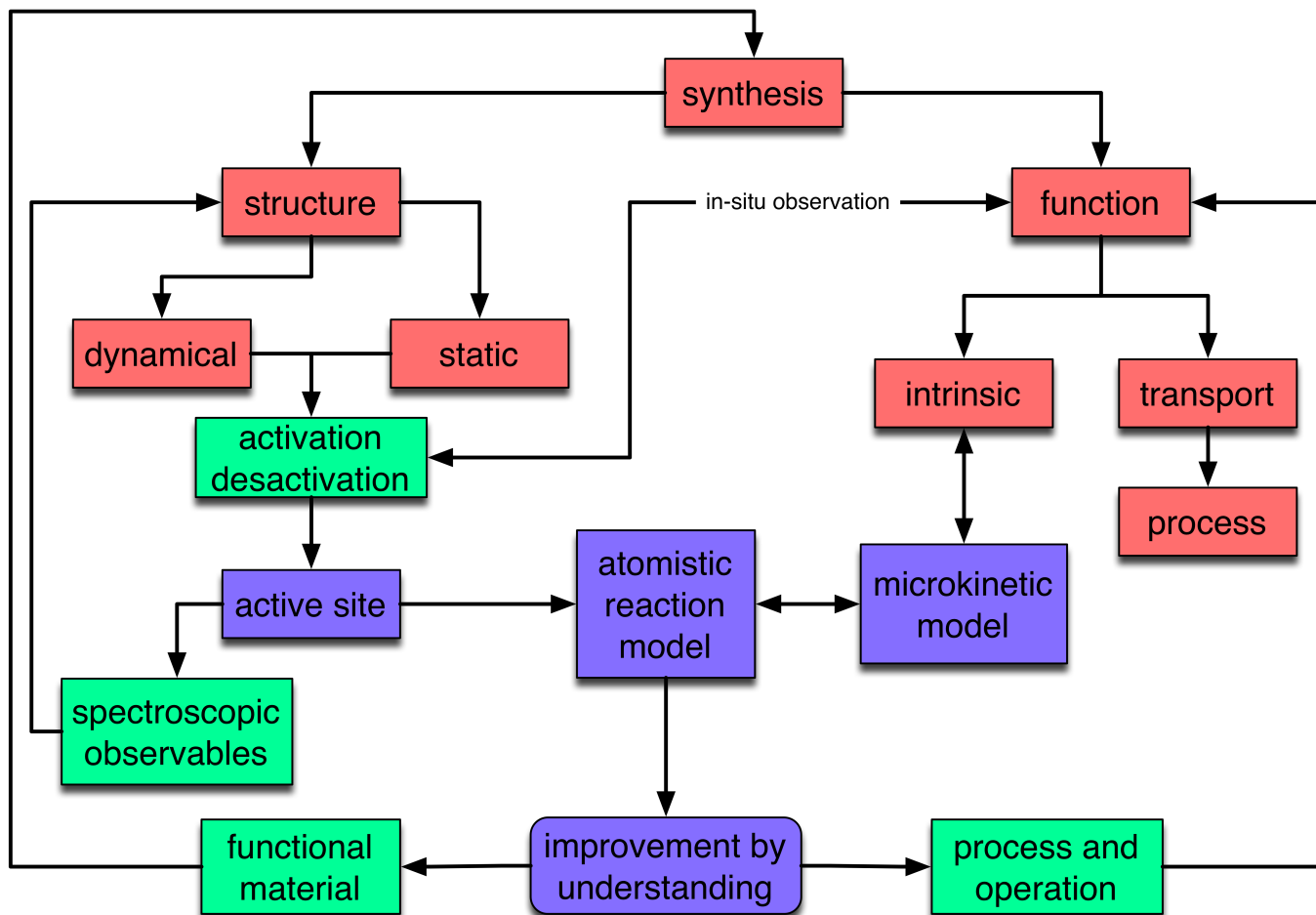


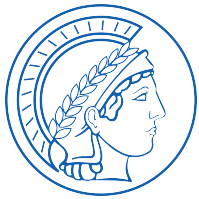
Department AC consequences

- The director is in general responsible for compliance with all German and International rules. (At AC, the group leaders represent the director!).
- We document all results of experiments that are used in publications together with the drafted publication in the AC database. (your obligation!).
- The data are owned by the MPG!, you own the authorship for the data.
- We document the history of publications in a FHI-wide workflow and provide as many results as possible open access as we are tax-payer financed. We never conduct secret (also against your colleagues) science!! (temporary occlusion for IP purposes are ok).
- We practice collaborative research: multiple author work is the rule, single author papers are the exception. We decide on the authors only after finishing work on a paper, the director has the final word.
- Significant neglect of these rules or publications without „workflow“ are cause for immediate disciplinary consequences and dismissal from the FHI!



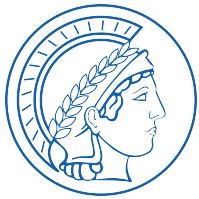
A perfect workplan for catalysis research (is this really possible?)





Recommendations

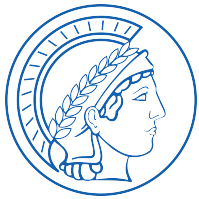
- Use critical literature studies ahead of experiments.
- Plan your experiments in families of well-chosen parameters; reproduction and error estimates.
- Analyse your results immediately when obtained : database entries (weekly!!!).
- Discuss your results frequently with your colleagues (plausibility!).
- Do never hide results also when unpleasant or unexpected („cosmetics“).
- Avoid extensive waste of experiment time due to misplaced parameters.
- Create a working hypothesis as soon as possible and discuss with supervisor.
- Document your research concept (introduction) and your working hypothesis.
- Always have a running presentation of your key results ready (monthly) and save previous versions for seeing the evolution of insight.



Practical points

- Synthesis is not preparation: understand what you do and pre-determine as many parameters as possible:
 - Titration of precipitation
 - IEP before adsorption
 - TG/MS before calcination
 - Never use Muffle furnaces (gas kinetics) even for drying!
- Synthesize sufficient sample and think about sample collection database
- Fill in sample database with as many details as possible, may be good for you when you need reproduction!
- Always analyze for elemental composition! Always analyze post-reaction.
- Use chemical probe reactions as much as possible (probe the interesting part of a catalyst).
- Verify in proven facts the absence of transport limitations!
- Never try to interpret data without consulting experts, become one!





Why this lecture? Catalysis

- Intellectual challenge in physical chemistry.
- “Everything is interesting, only little is relevant” (John Thomas)
- Catalysis is 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).
- As an independent science still problematic:
- Concepts, models, gaps, “real systems”
- Is there a chance to arrive at a genuine understanding as basis for the challenges of catalysis enabling renewable energy systems?

Heterogeneous Catalysis

Some introductory views beyond the textbook.....

Advances in Catal. Vol 50-52

J-W. Niemantsverdriet:
Spectroscopy in Catalysis

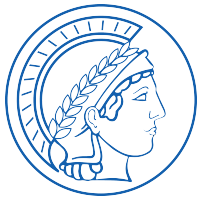
Lecture series:
Modern Methods in Heterogeneous Catalysis
FHI every winter term (fridays 9.00-12.00)

Robert Schlögl

Fritz-Haber-Institut der MPG

Max-Planck- Institut für Chemische Energiekonversion Mülheim (MPI CEC)

www.fhi-berlin.mpg.de

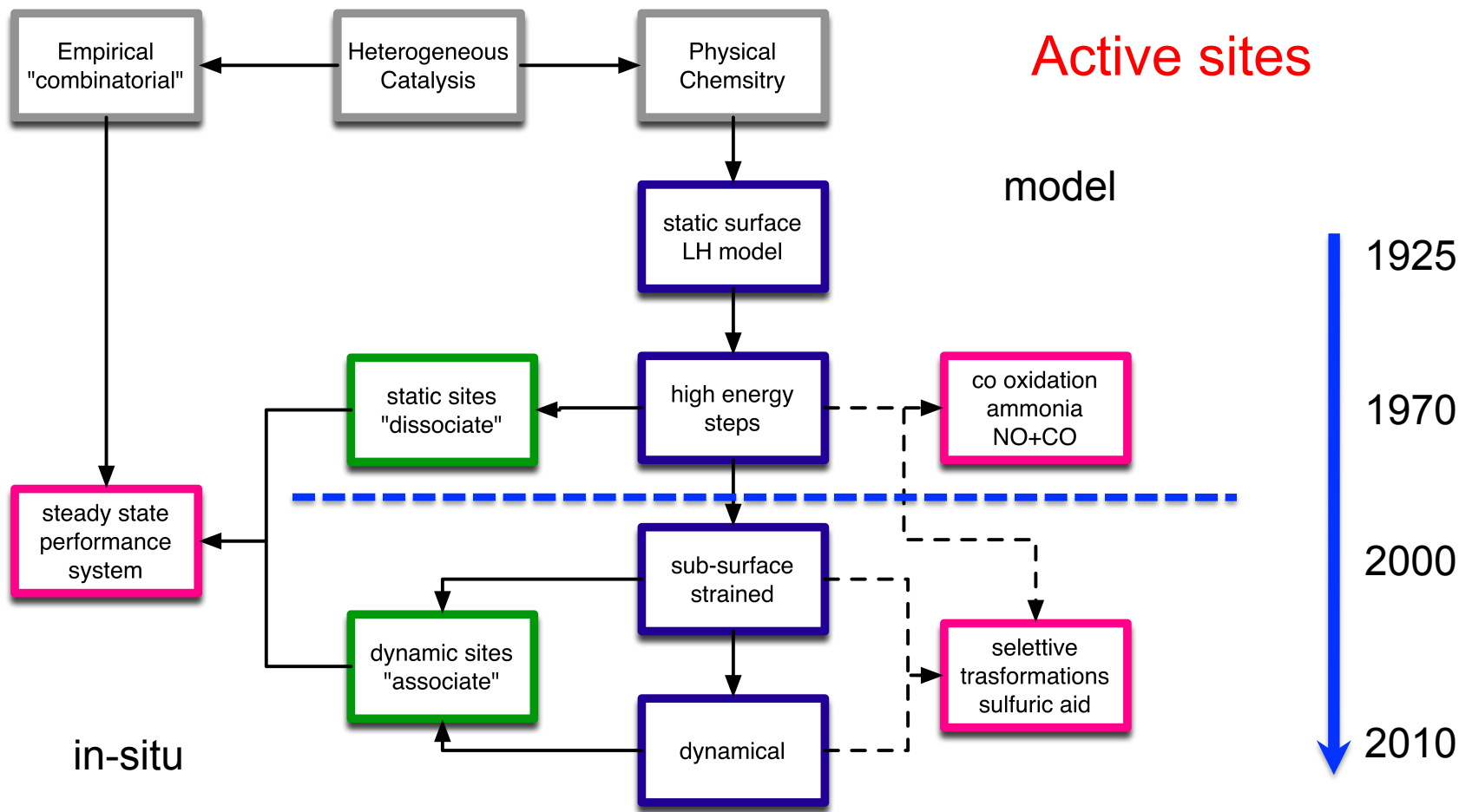


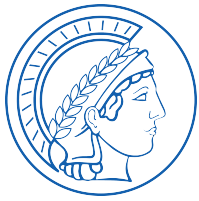
Active sites

- 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. How does this work? Deterministic against thermodynamics?
- Adaptivity required as mostly the reaction product is more reactive than the starting species: selectivity through autogenous partial deactivation.

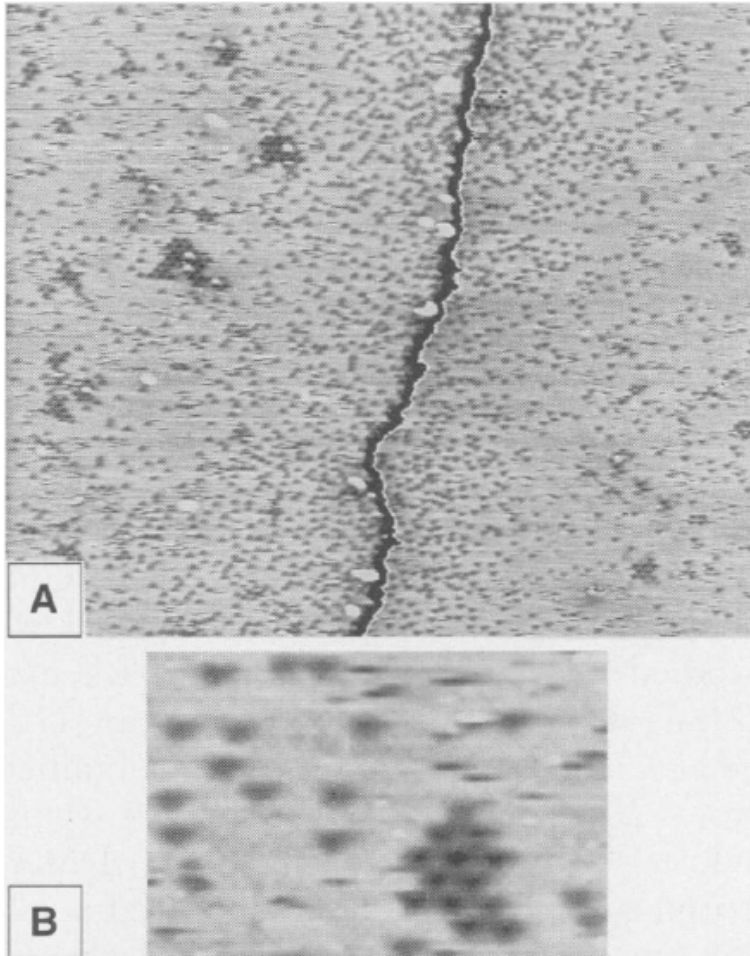


Heterogeneous catalysts: an evolutionary success story





Steps



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

Evidence that “defects” are important for reactivity.

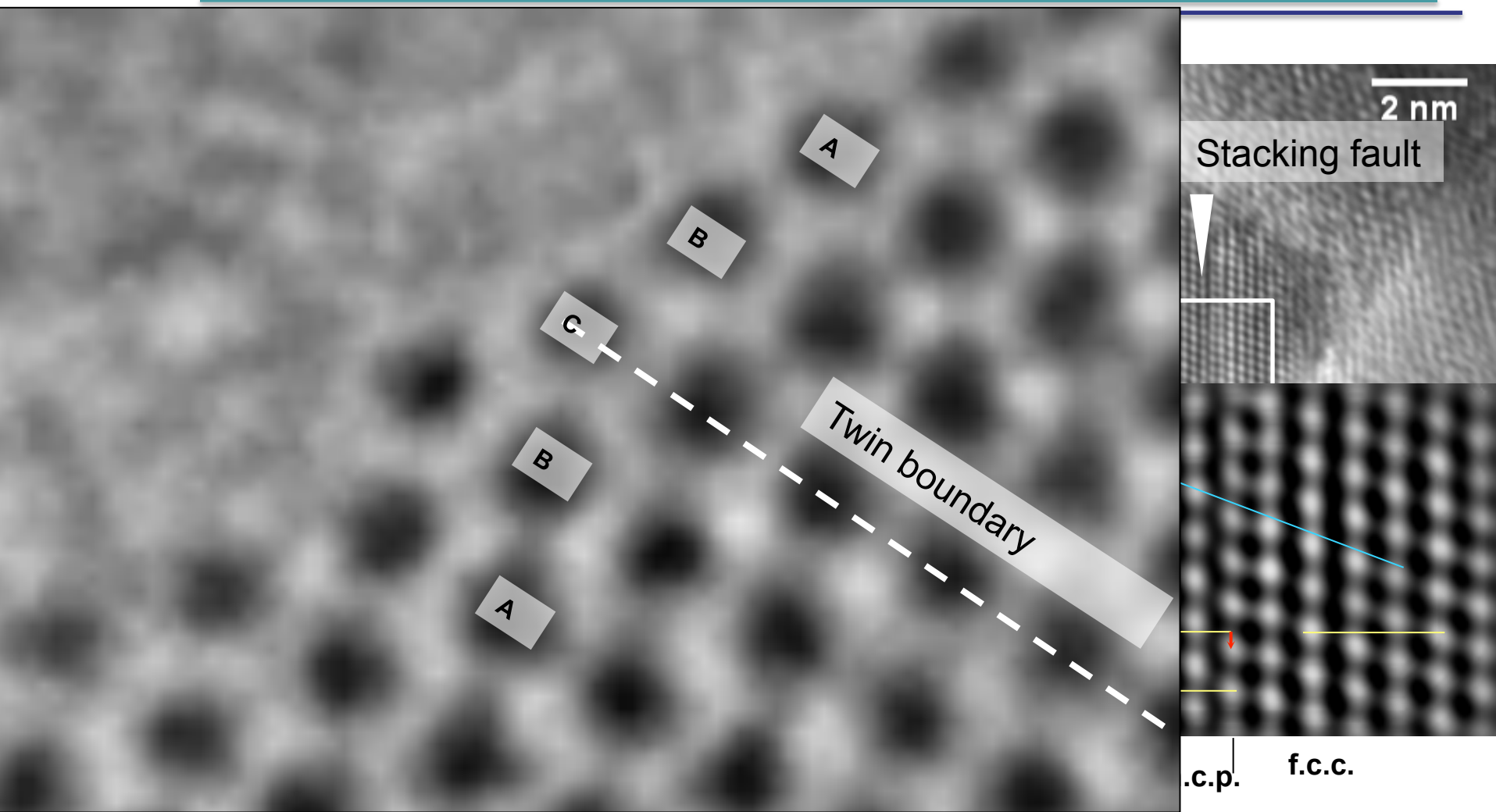
Was also found by Somorjai earlier indirectly during hydrocarbon conversions on Pt and Pd single crystals (selectivity control).

Ertl, Wintterlin, science 1989

Ru (0001) and NO



Methanol synthesis over Cu: high energy sites from synthesis of metal NP



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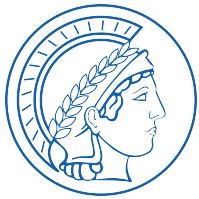
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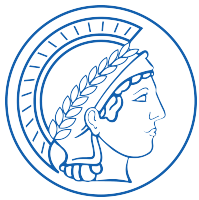
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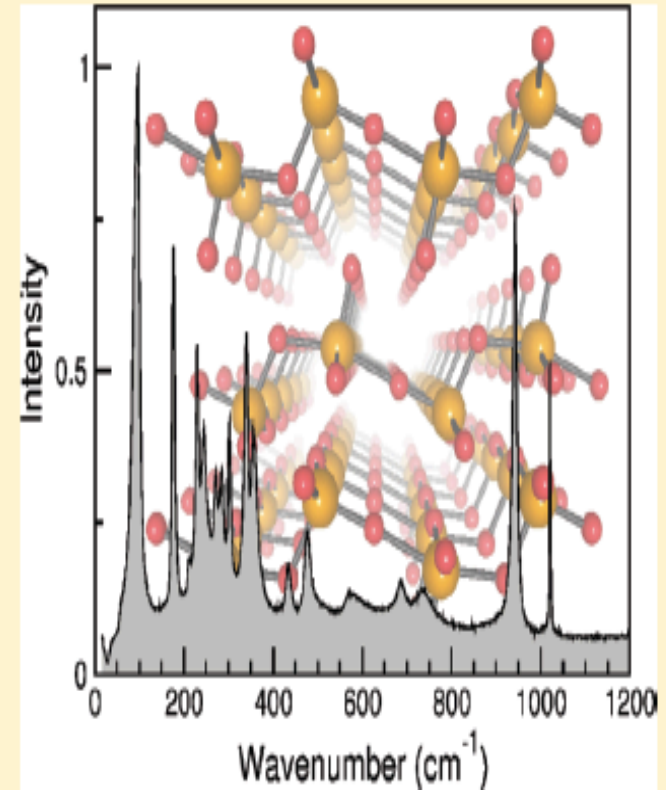
Dynamics

- Temporal evolution of a system on microscopic scales without external forcing.
- Occurs while system at larger scales is in steady state or equilibrium.
- Kinetics requires external forcing (min: transport).
- Dynamics in catalysis occurs on multiple scales.
- Term is used equivalent for reactions between the catalyst and reactants unintentional during catalytic transformation.
- Requires “activation” and is dependent on reaction conditions.



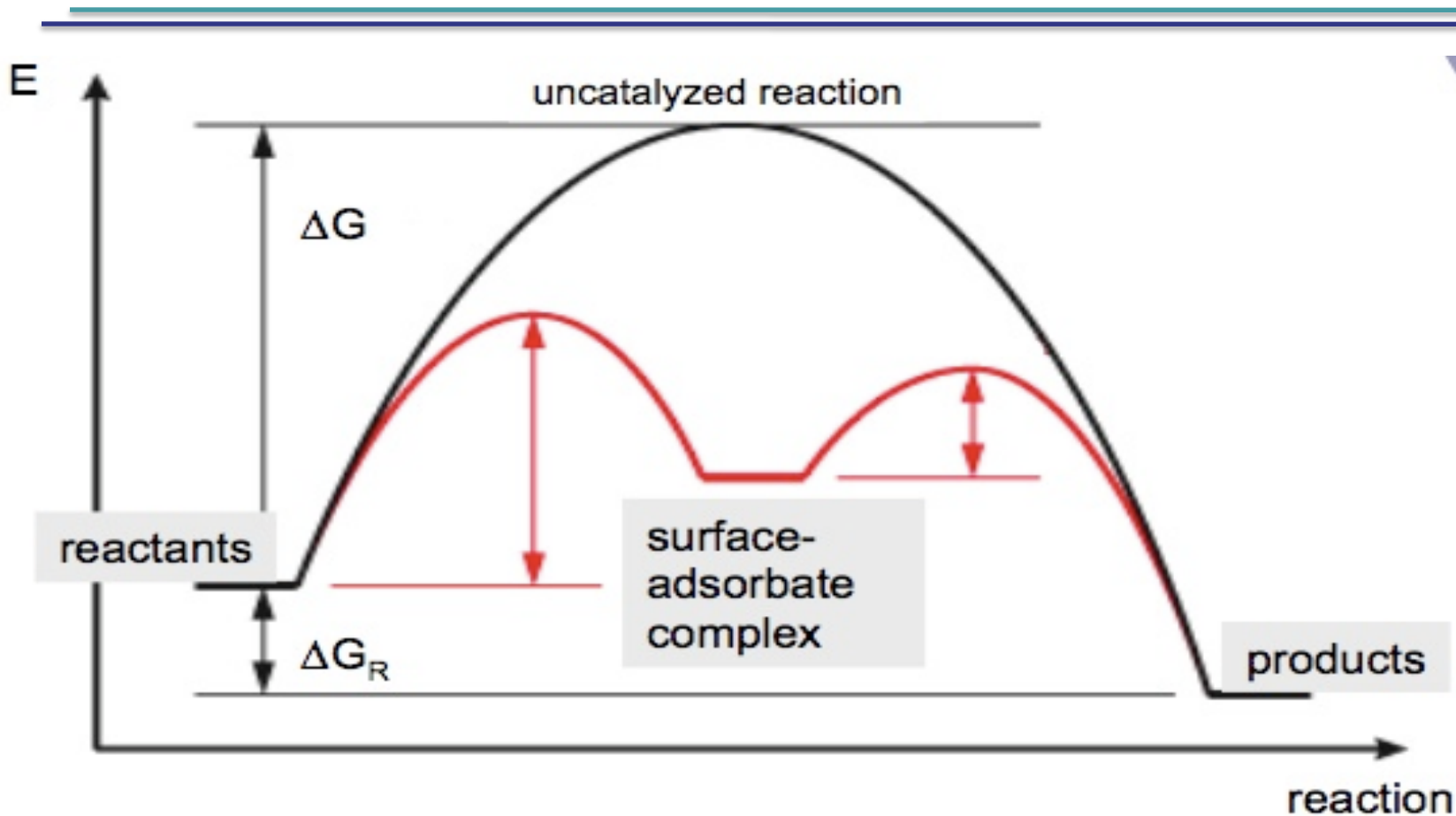
Dynamics is a term with multiple meanings in catalysis

ABSTRACT: We report here the Raman spectrum and lattice dynamics study of a well-crystallized β - V_2O_5 material prepared via a high-temperature/high-pressure (HT/HP) route, using α - V_2O_5 as the precursor. Periodic quantum-chemical density functional theory calculations show good agreement with the experimental results and allow one to assign the observed spectral features to specific vibrational modes in the β - V_2O_5 polymorph. Key structure–spectrum relationships are extracted from comparative analysis of the vibrational states of the β - V_2O_5 and α - V_2O_5 structures, and spectral patterns specific to the basic units of the two V_2O_5 phases are proposed for the first time. Such results open the way for the use of Raman spectroscopy for the structural characterization of vanadium oxide-based host lattices of interest in the field of lithium batteries and help us to greatly understand the atomistic mechanism involved in the α -to- β phase transition of vanadium pentoxide.





Function of a catalyst: Static SM



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



Many relevant reaction profiles are more complex



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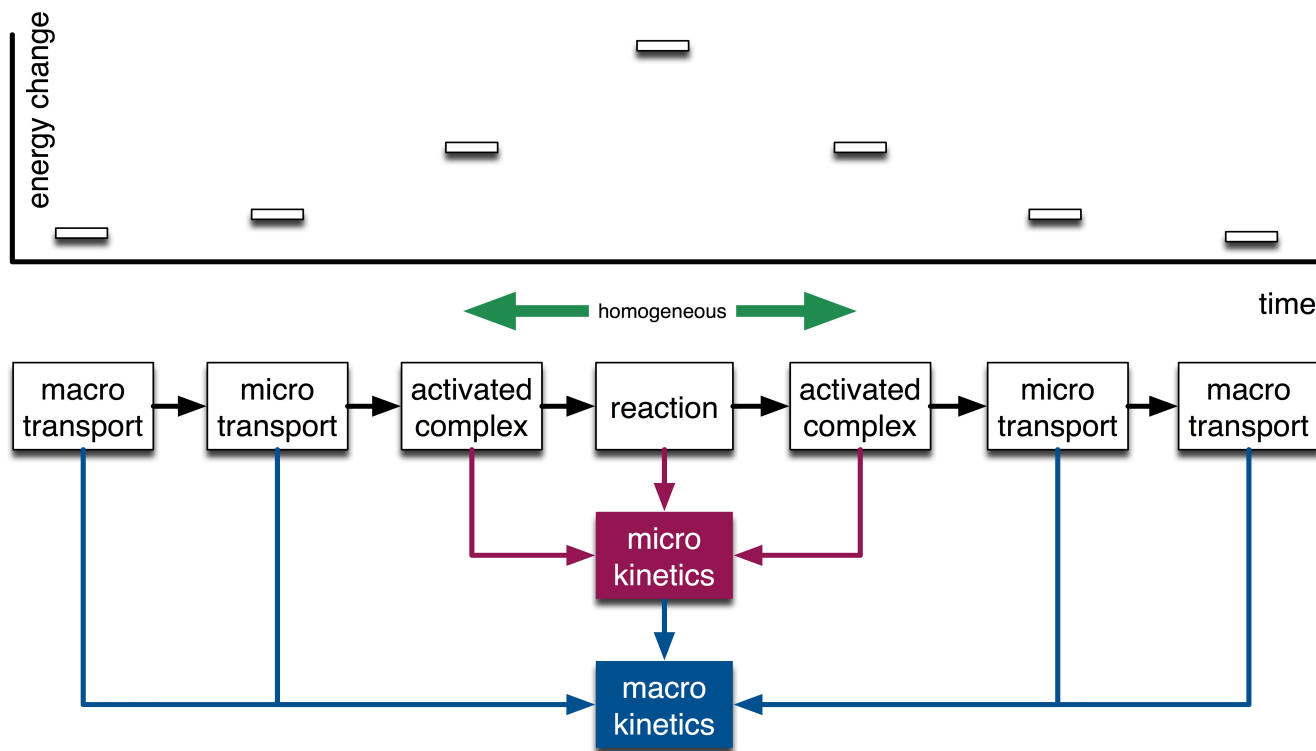


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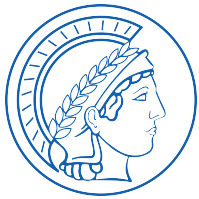


Catalysis - a multi-scale process: how to conclude about active sites from observation?



Several steps have to occur that a catalytic process can operate

Chemistry scales to the dimension of 10^{23} :
Molecular insight is only part of the story

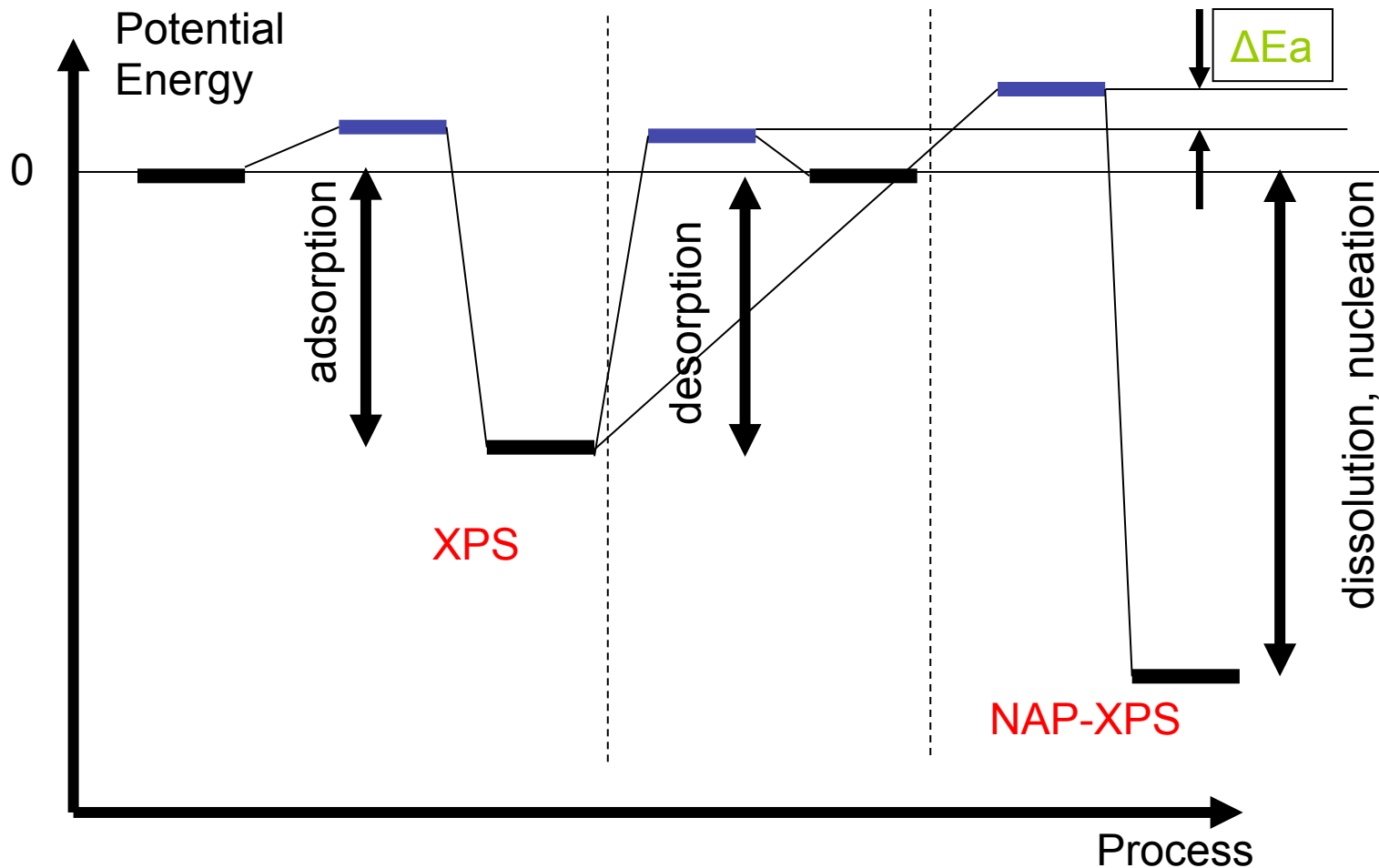


Catalysts: on the way from a challenge to a designer material

- Heterogeneous Catalysis cannot be described in general by concept of static catalysts (single crystals, models, pre-defined systems).
- The exceptions are systems in which activated adsorption is sufficient for the reaction: total hydrogenations and some oxidations.
- For selective reactions the concept of active sites needs a new element:
- Chemical dynamics
- In this concept catalysts are not static but react with the reagents according to their chemical potential.



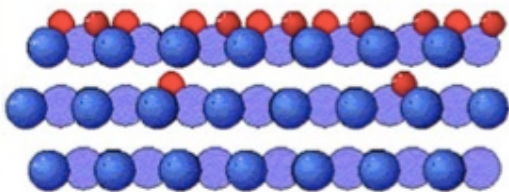
Chemical dynamics and energetics: one example is sub-surface reactivity



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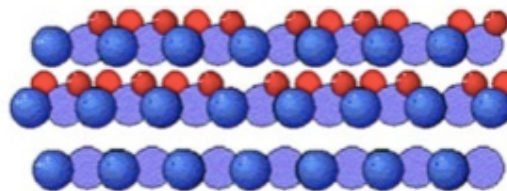
Surface and sub-surface species



A

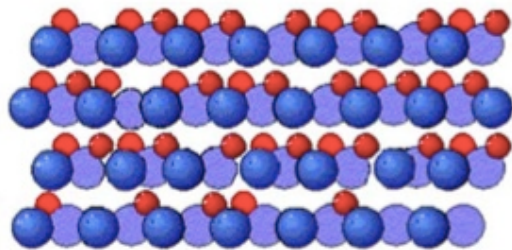
At low potential: metal plus dissolved species (“dirt”)

At slightly elevated potential:
“trilayer” (theory)



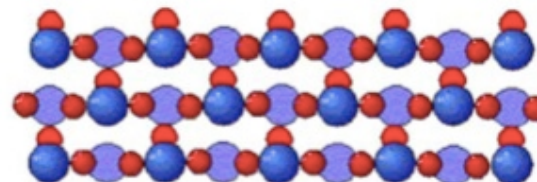
B

At potentials beyond the
“pressure gap”: sub-surface compounds
(transient)



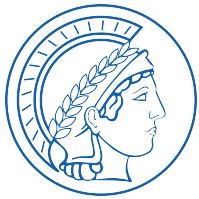
C

At high potential: compound; when defective:
nucleo- and electrophilic



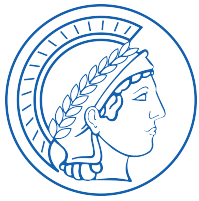
D

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The tool to design a catalyst

- One may expect to understand catalysts by studying the performance: arrive at the „structure-function relation“
- This is complex as we have no „active site spectroscopy“
- 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!!
- Similar ambiguities hold for the structure analysis: which is the active part that is relevant?



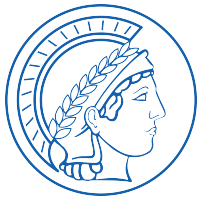
Active sites: both types may co-exist

- **Static sites**

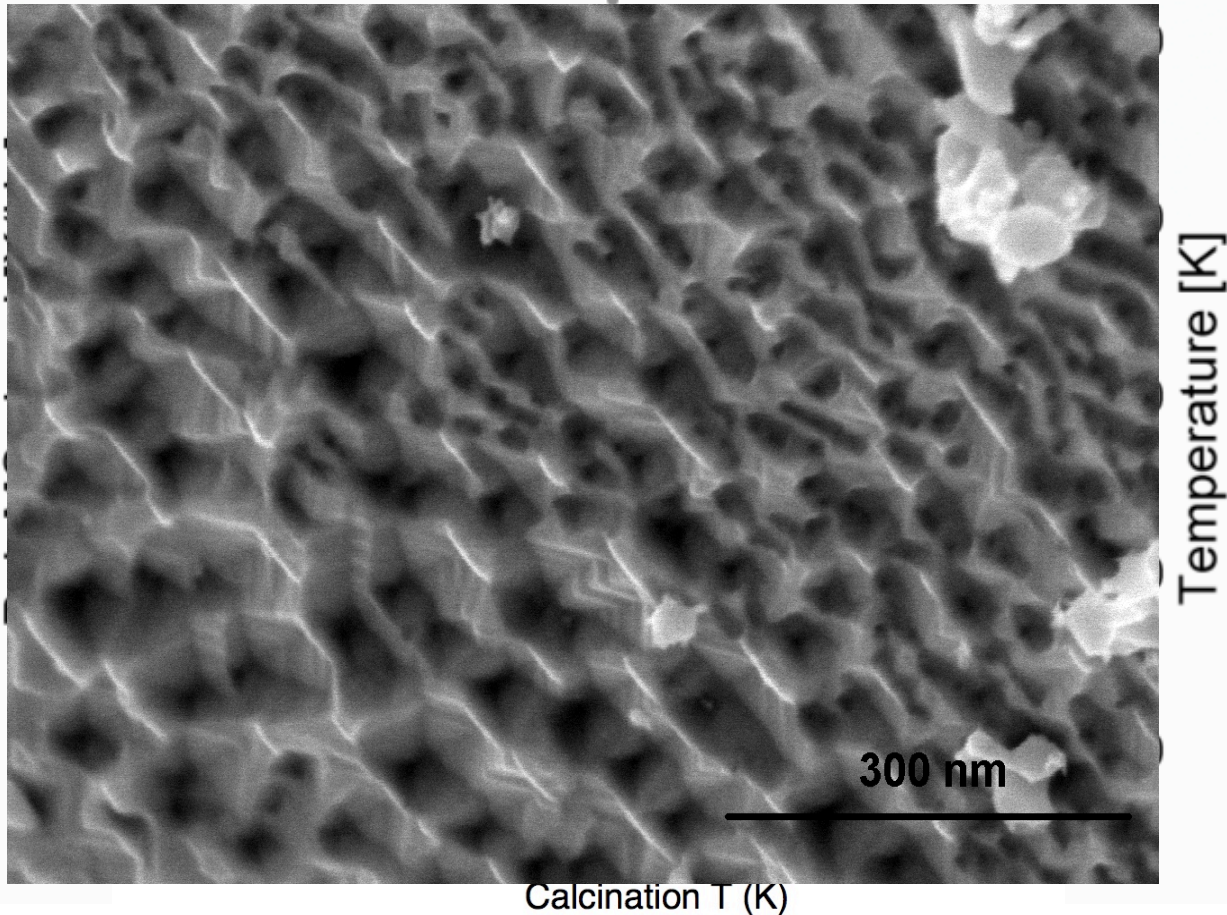
1. Stable high energy sites
2. Require no activation for operation
3. Part of the bulk phase
4. Rigidly attached to the bulk phase
5. Active in dissociation reactions
6. Steps and edges

- **Dynamical sites**

1. Stochastic high energy sites
2. Require activation through reactants
3. No part of the active structure
4. Low-dimensional termination layers
5. Active in substitution reactions
6. Segregates, sub-surface compounds



Oscillatory dynamics

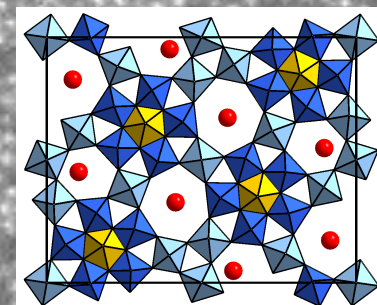


Only in oxidizing feed
and after prolonged
activation in
stoichiometric feed:

Under other
combinations of
conditions and at
shorter times only
ignition from a
low-temperature weakly
active state

Reactivity an extrinsic property of phase

5 nm



Dem Anwenden muss das Erkennen vorausgehen

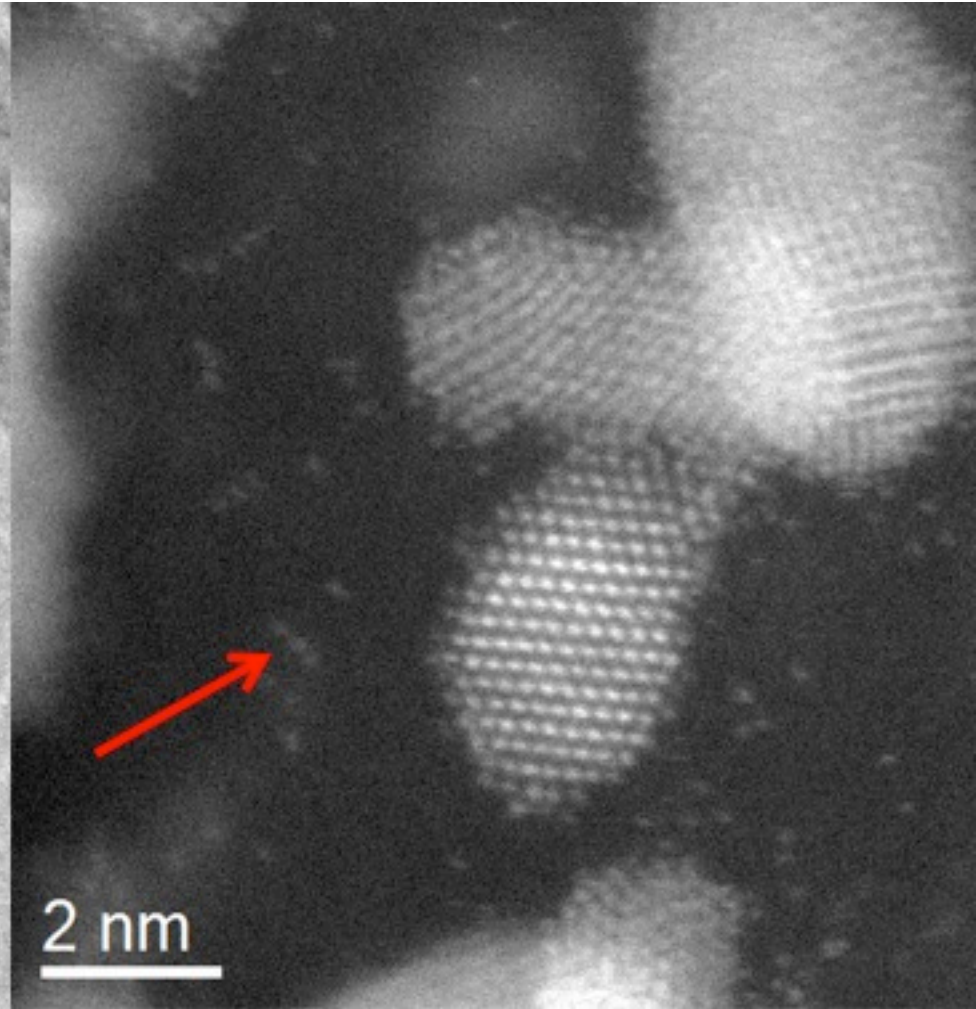
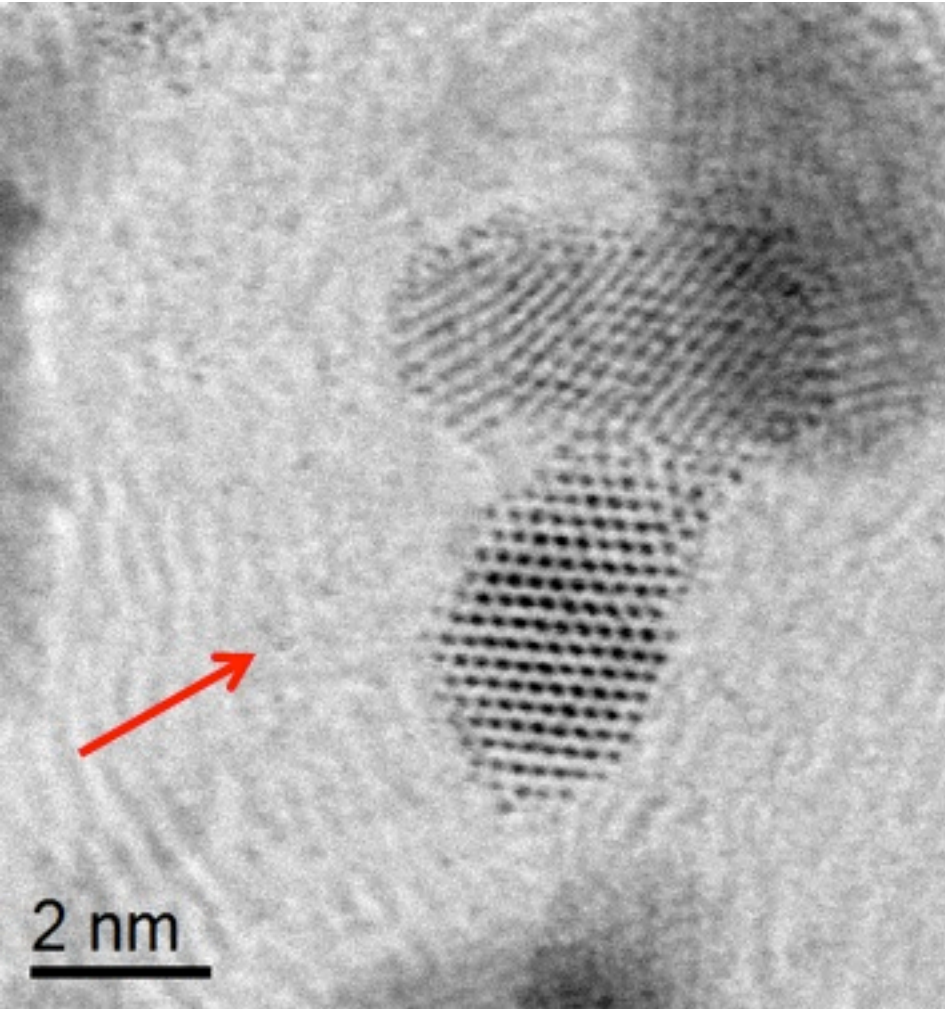
Max Planck



Thank You

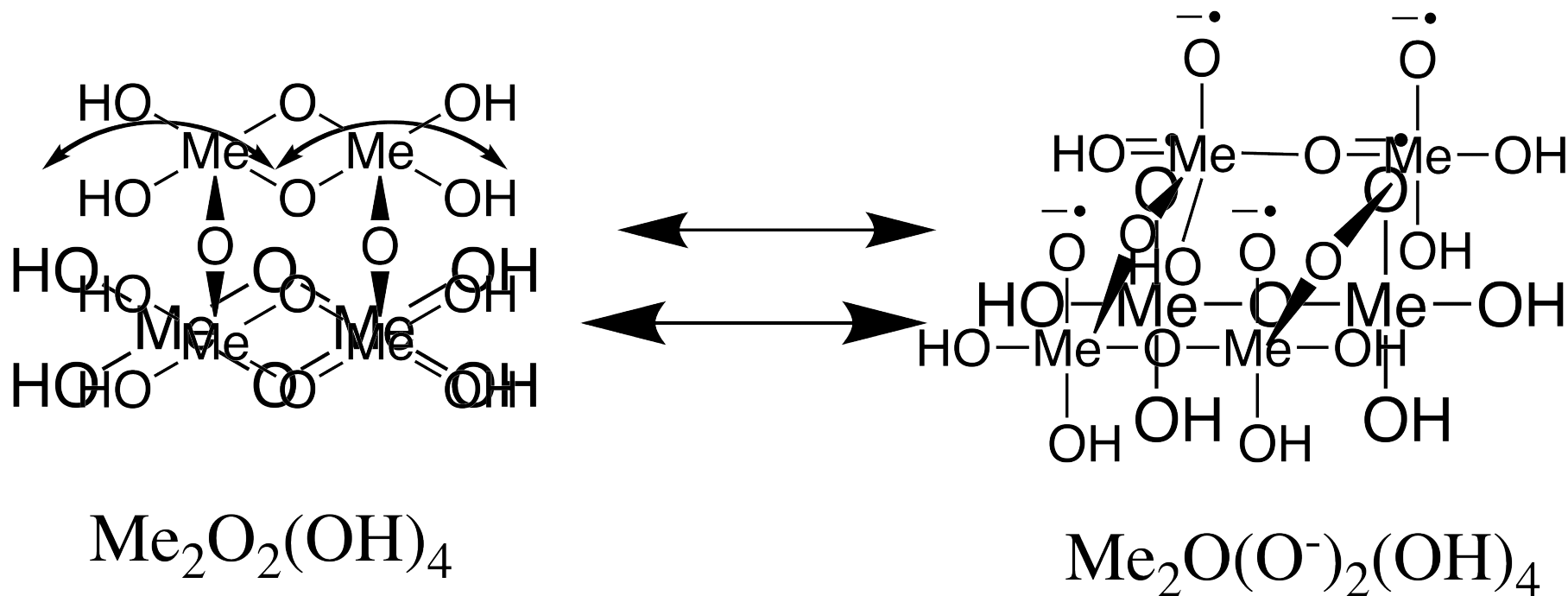


Dynamical catalysts create active sites “on the fly”





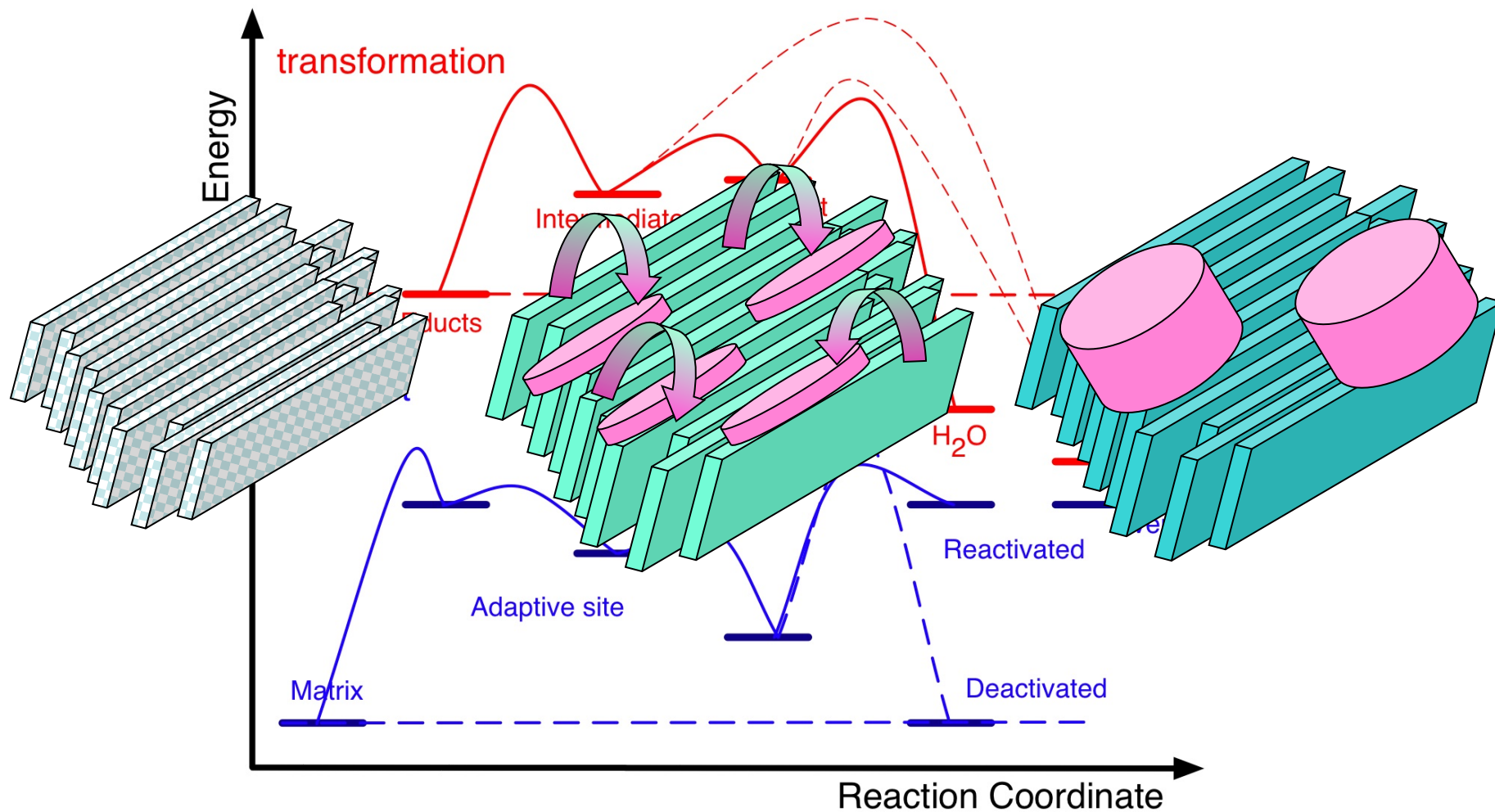
Chemical dynamics decouples oxidation of substrates and reduction of oxygen



A facile concept to exchange one electron pair:
Challenge: the activation of di-oxygen requires 4 electrons:
Larger site or stable intermediate involving two processes



Selective oxidation: Coupling of transformation and material



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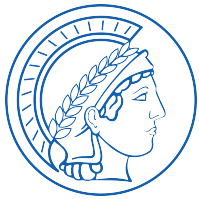
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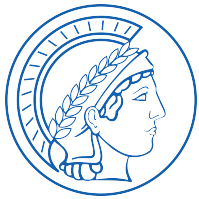




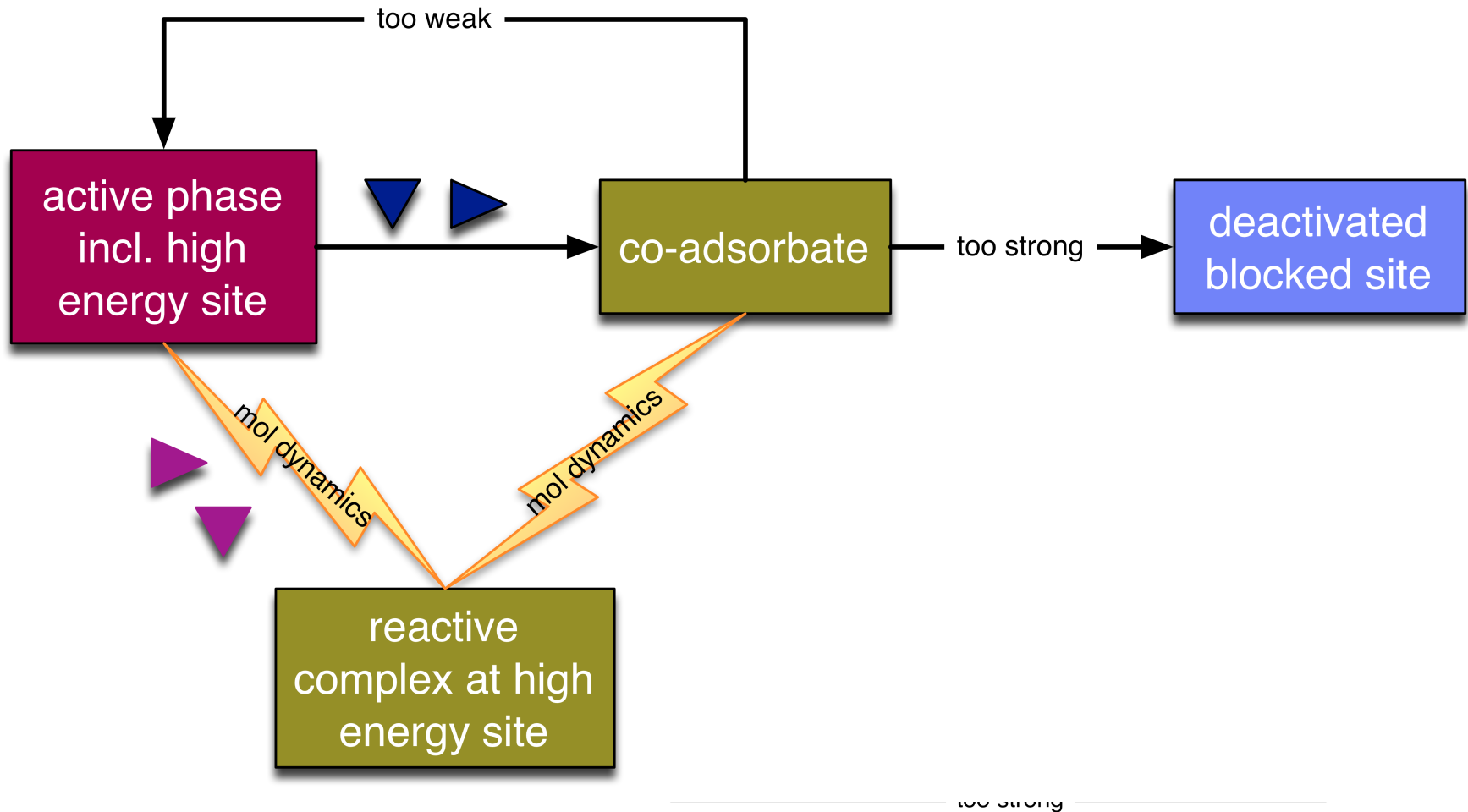
To take with you

- Let us assume that the unifying concept between all sorts of catalysis is the notion of a dynamical active site.
- It forms only in situ and requires sufficient flexibility of the matrix material: nanostructuring and high temperatures, addition of water or other co-catalysts.
- In solids restructuring, sub-surface chemistry or segregation.
- The resulting active phase (complex) fluctuates always around a stable mean structure and brings about for short times configurations that react with stable substrate molecules: activation.
- In solids this may also be achieved for very stable educts by static step structures with suitable modifications when the resulting product does not block the static site. (otherwise adaptive site required with “ligand” exchange or change in local electronic structure).
- The catalyst regeneration is only on average a cyclic process and occurs through dynamics acting also on the deactivated site.





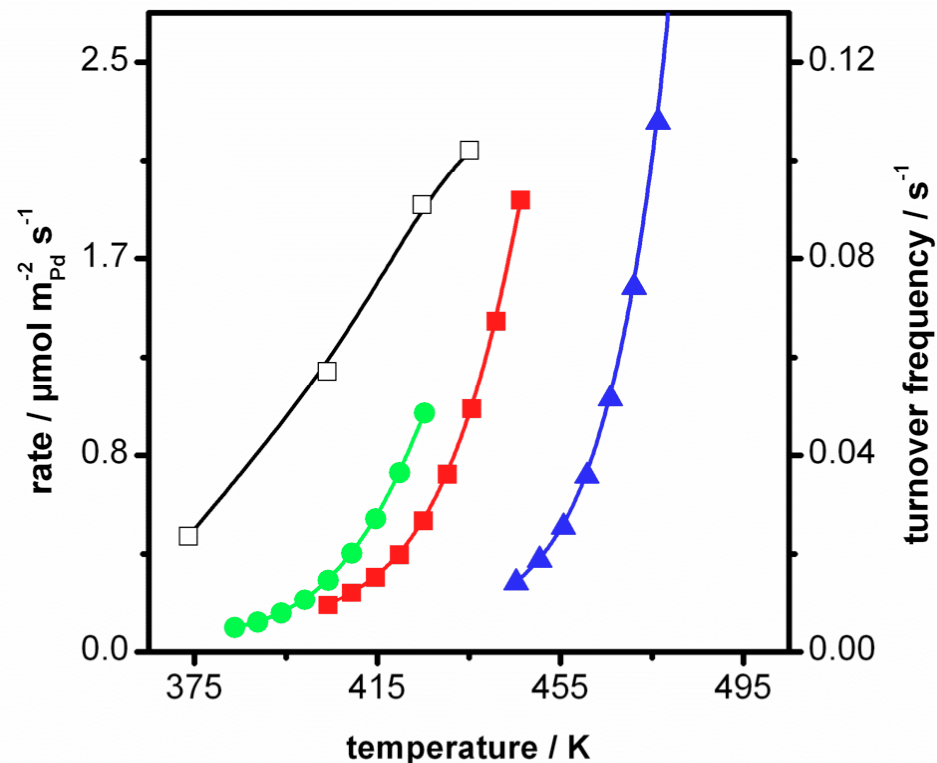
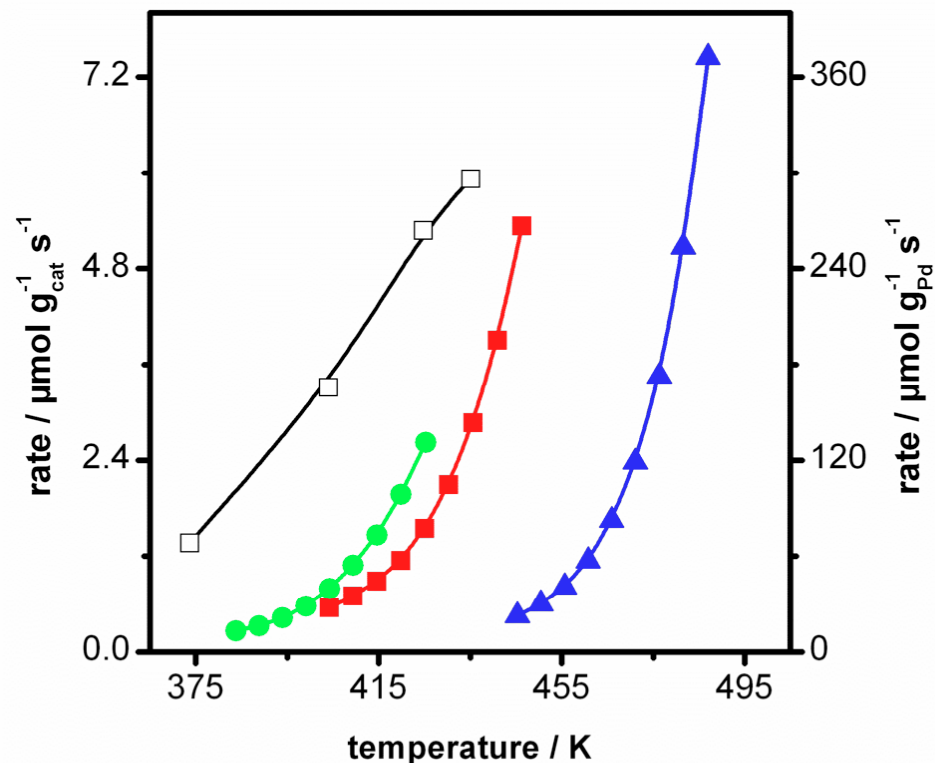
What a catalyst does beyond elementary reaction steps

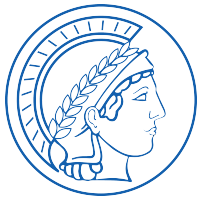




Catalytic activity in what units?

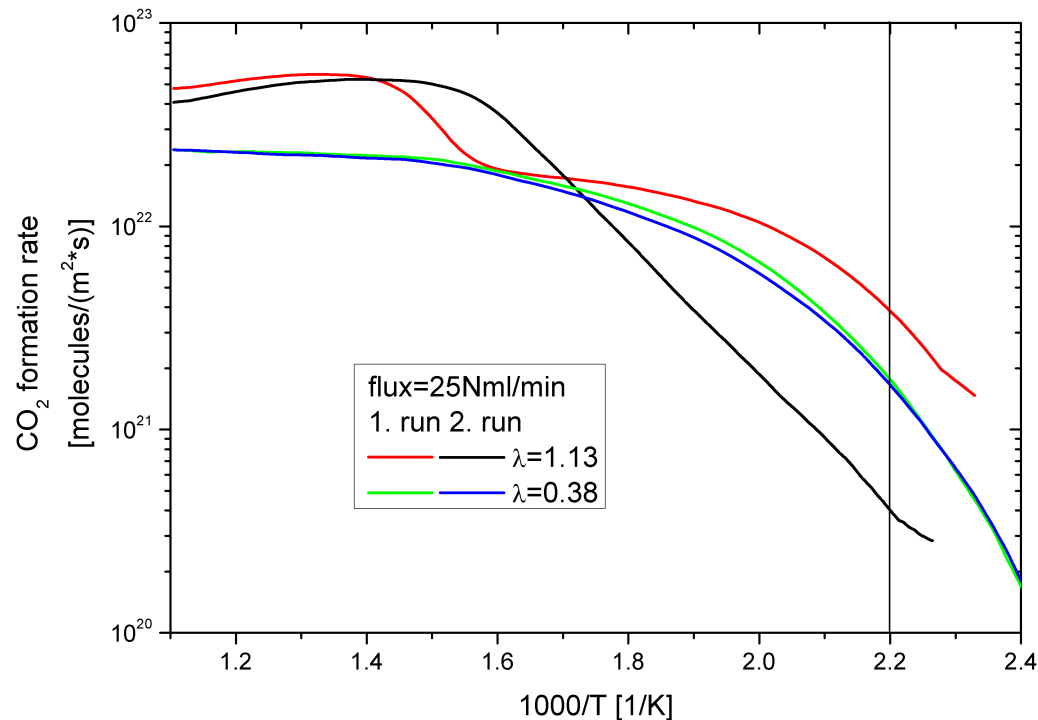
CO oxidation over 2% Pd/Fe₂O₃





CO oxidation: a test reaction

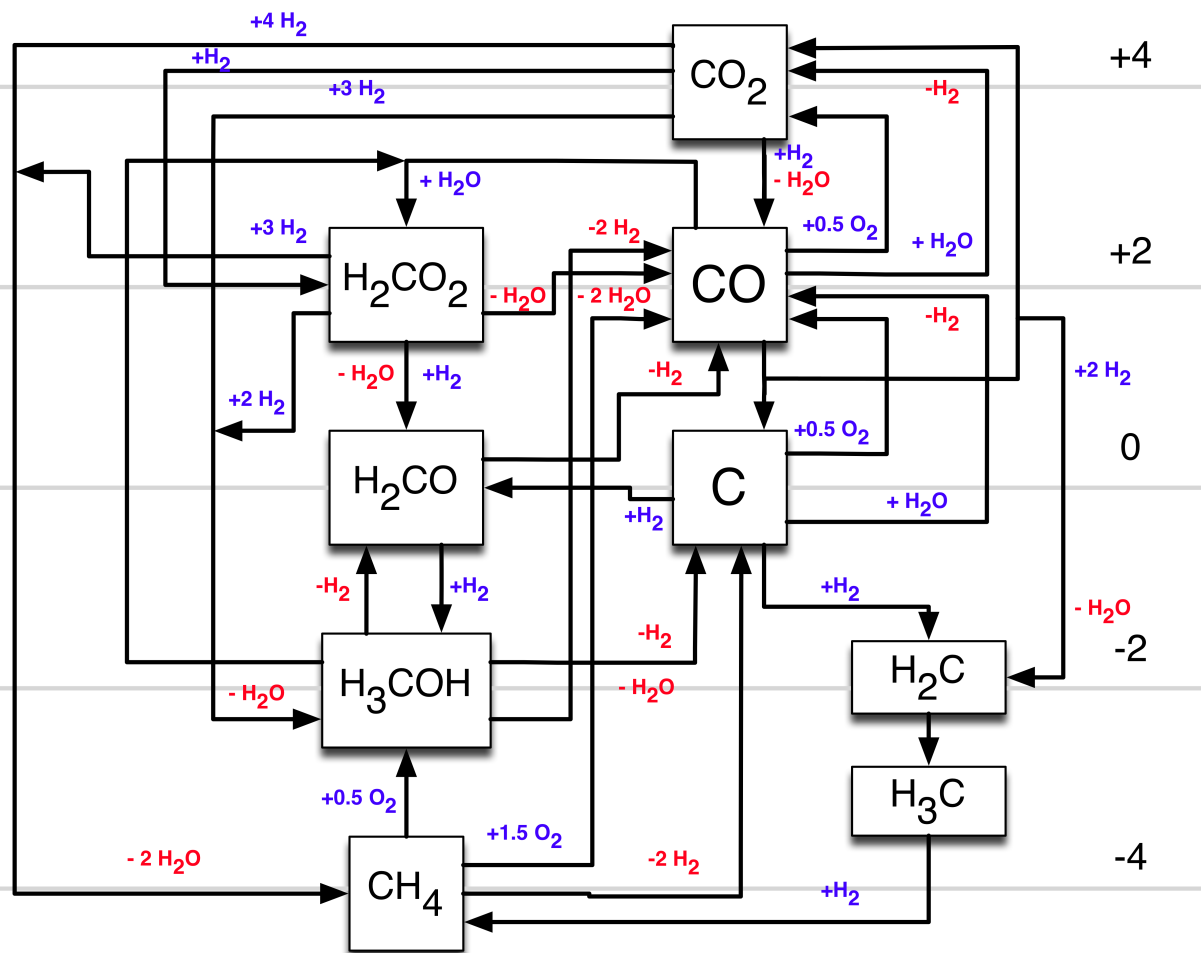
TPO of CO,
1% CO. 0.5% O₂. 100 Sccm. 25 mg catalyzt



Careful execution
of experiment
for isothermal
and non-
transport limited
performance



CO: system chemistry



Activation of a molecule opens up many reaction pathways:

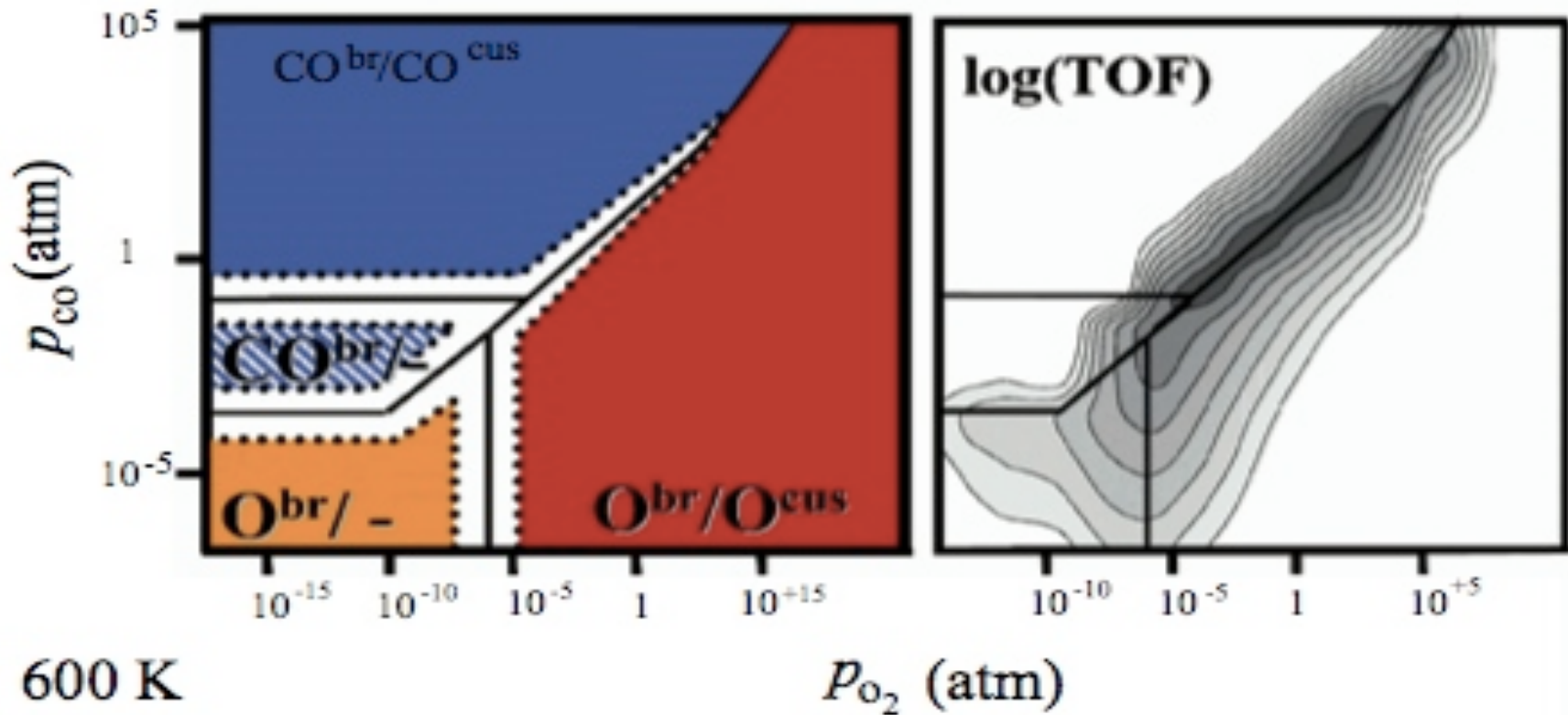
Chemical selectivity is a challenge.

Kinetic selection through chemical potentials of electrons and adsorbates.



A mature issue: Ru/O/CO

K. Reuter, M. Scheffler
K. Jakobi, G. Ertl



600 K

P_{O_2} (atm)