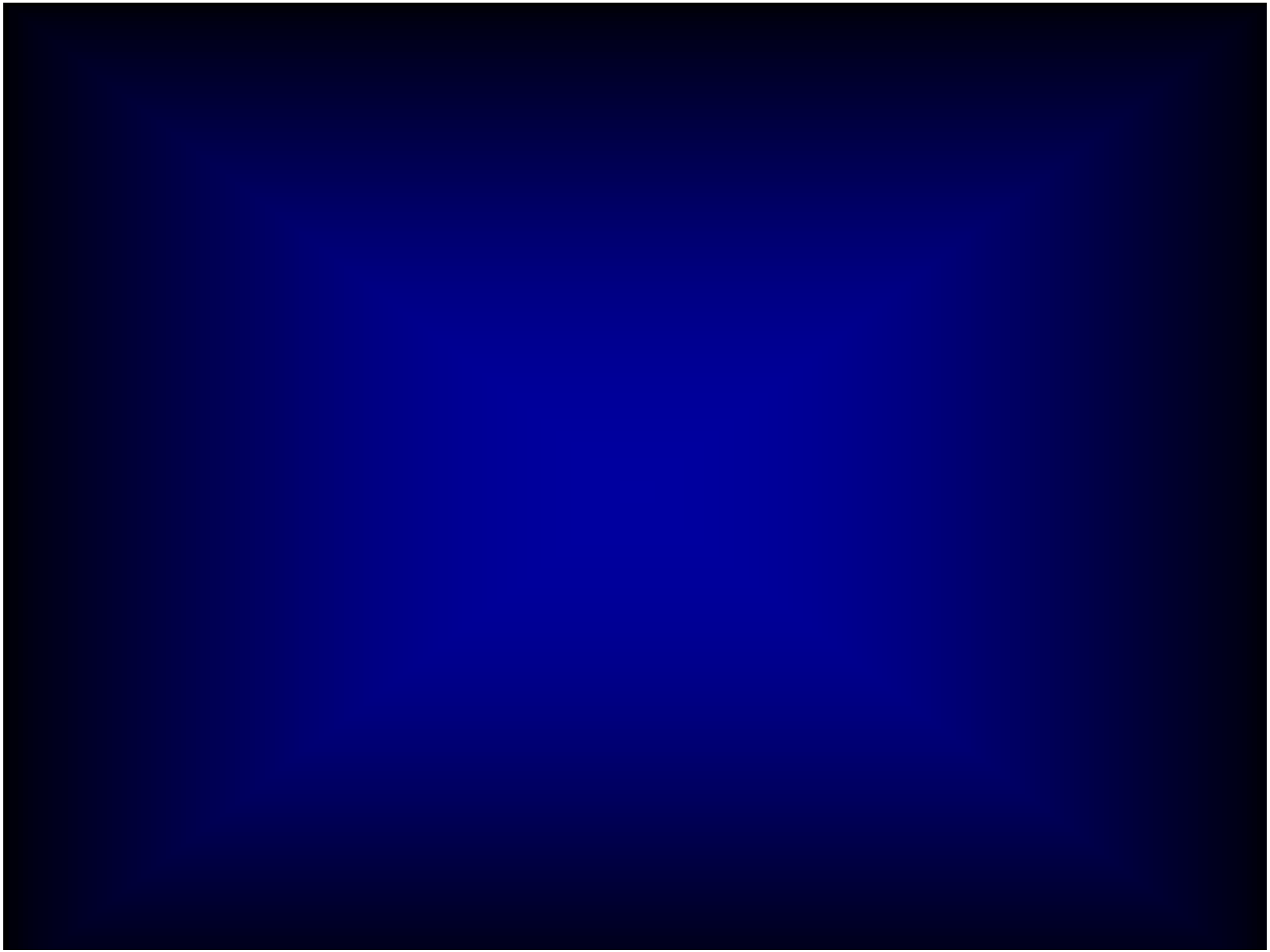
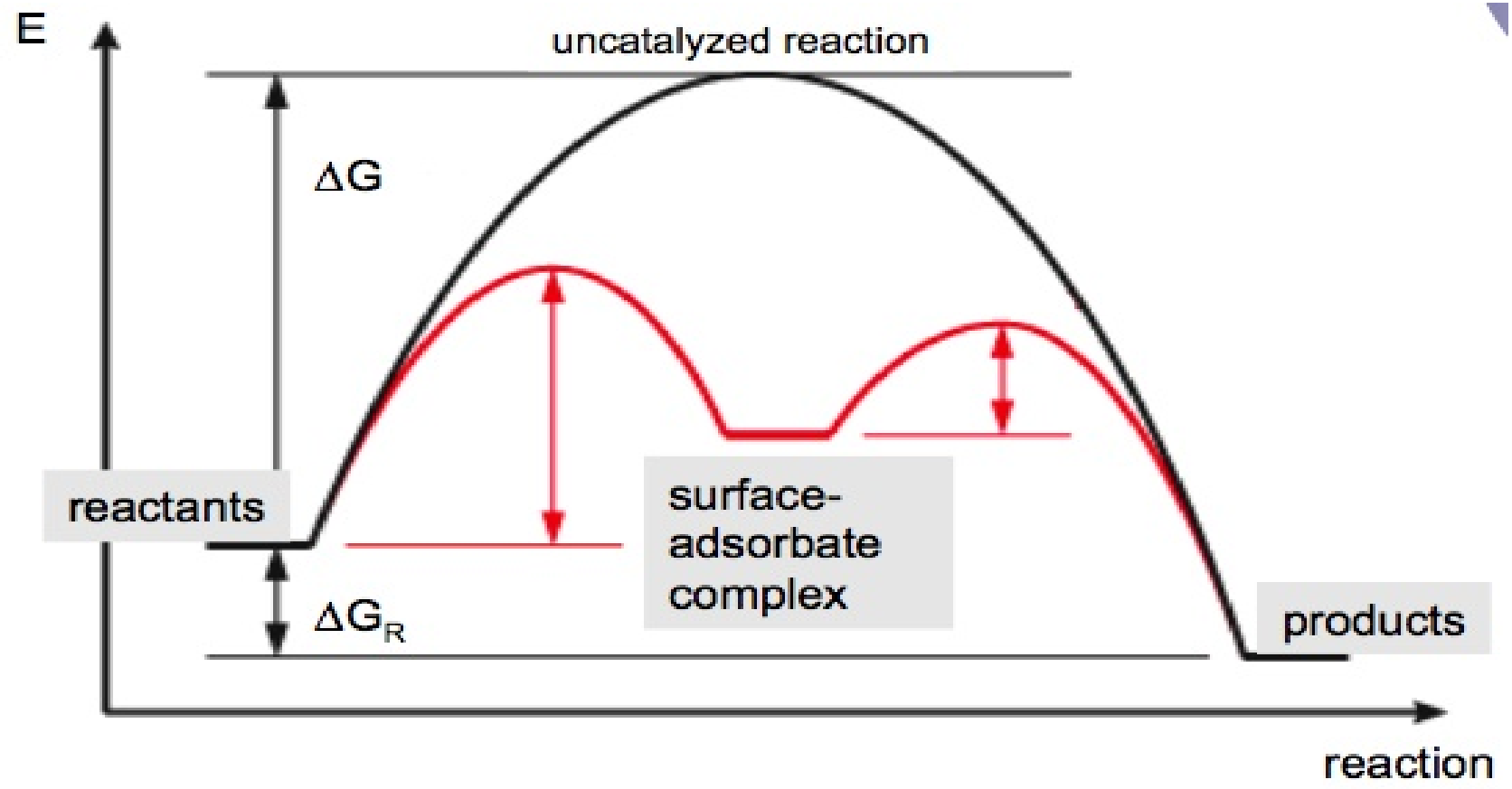


Robert Schlögl
Fritz-Haber-Institut der MPG

SELECTIVITY IN HETEROGENEOUS CATALYTIC HYDROGENATION AND OXIDATION:

FROM CONCEPTS TO MATERIALS?

Function of a catalyst: Static SM

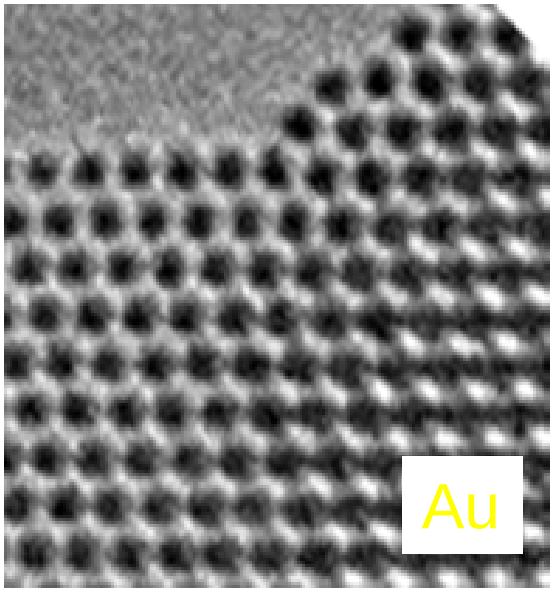


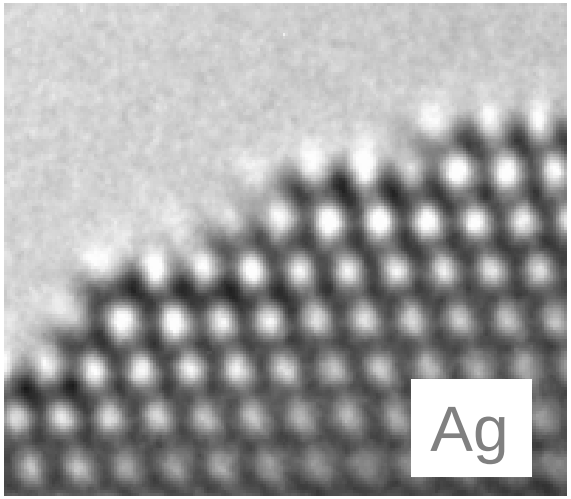
Adsorbate structures dynamical (chemical waves)

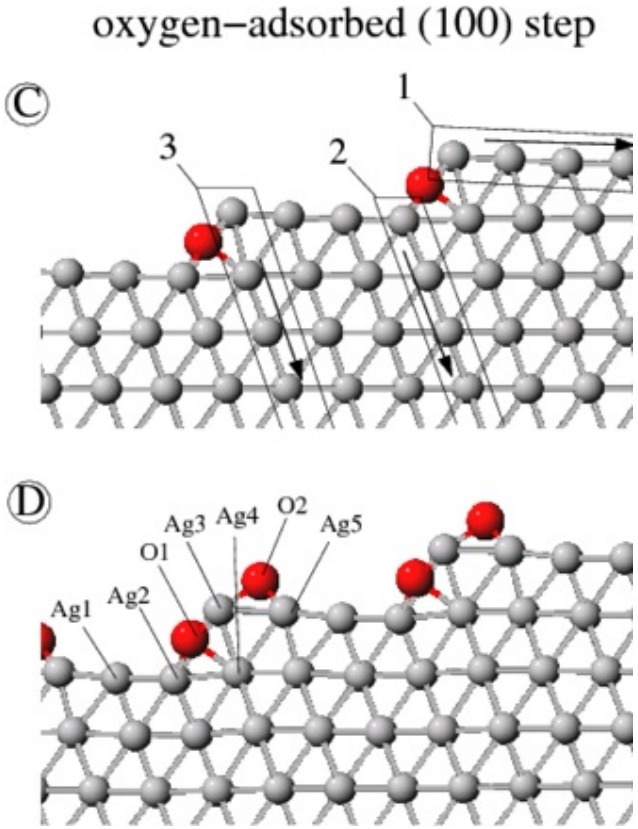
Bulk is “irrelevant”, no chemical transformations sub-surface

FUNDAMENTALS

High-energy sites







T. Jakob
M. Scheffler

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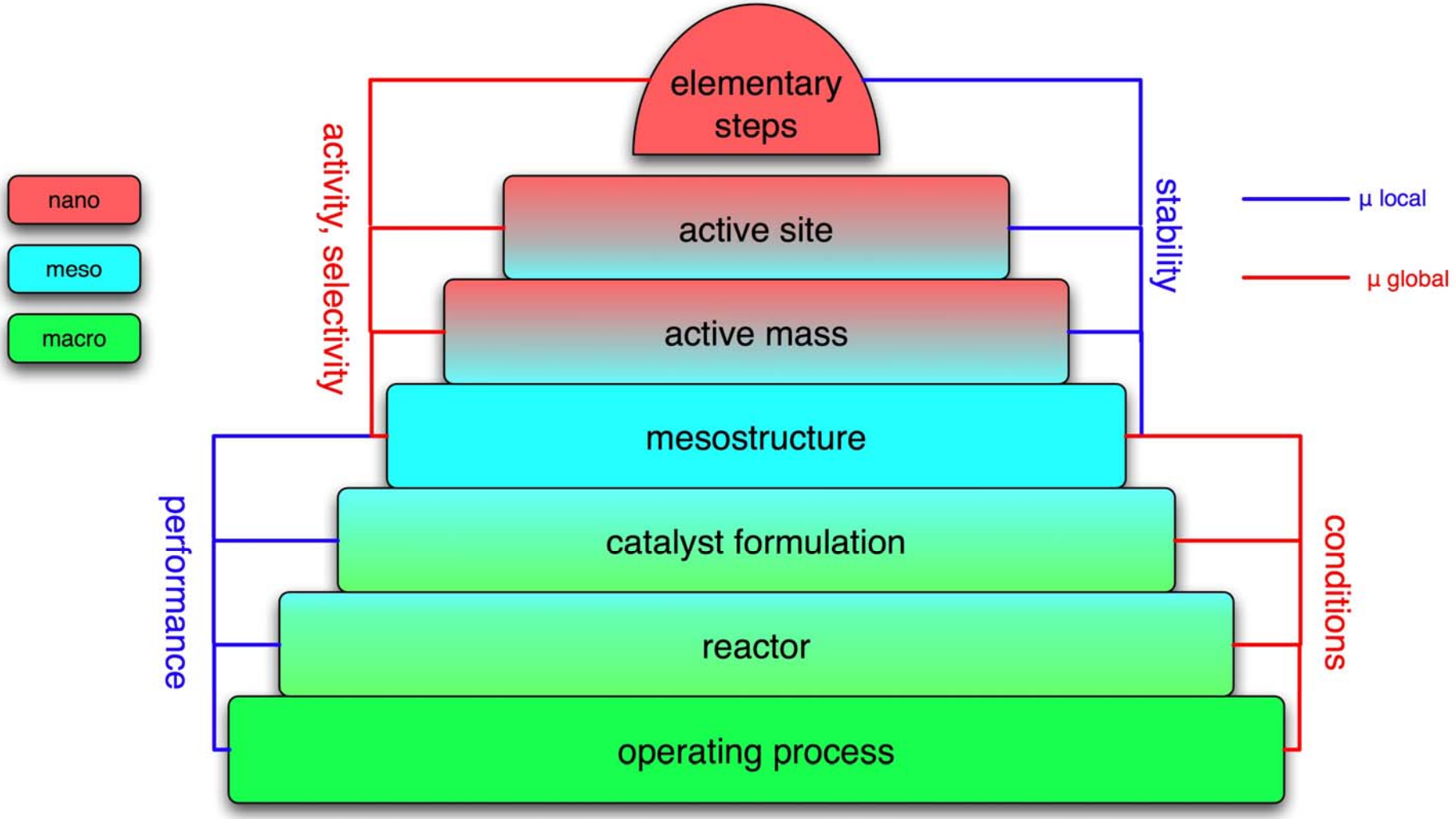
Translate function into process: material science and chemical engineering



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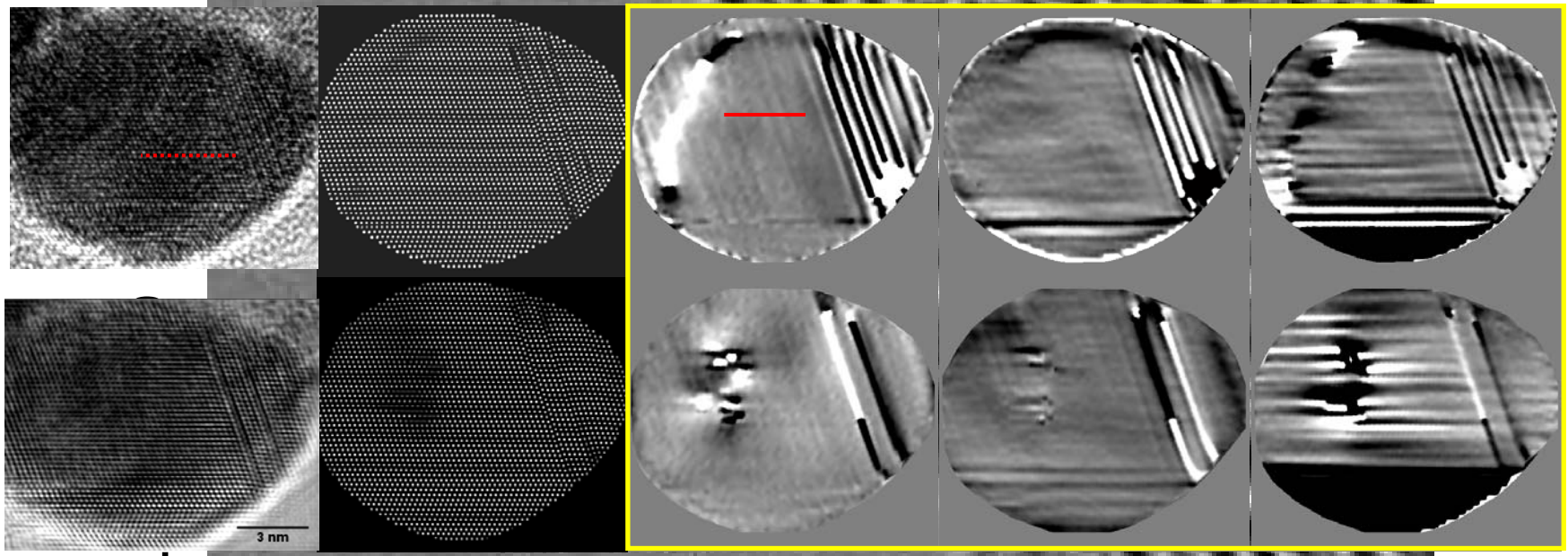
Beyond the SM: dynamics

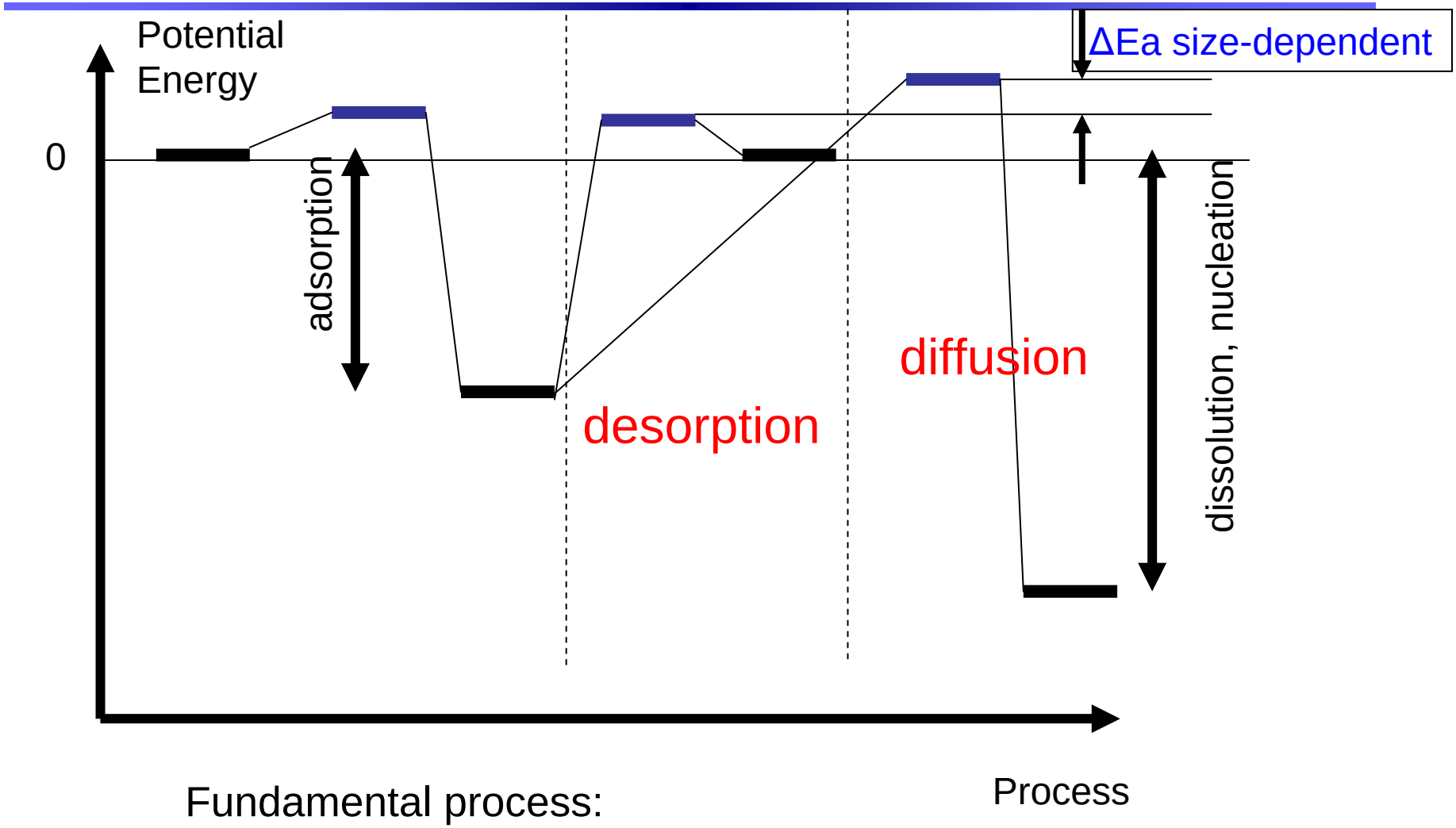
- Static model good for 1-step processes controlled by adsorption.
- Most reactions exhibit several pathways; multi-step process with selectivity.
- Catalysts are functional materials expressing isolated active sites through contact with their reagent.
- Kinetics of Catalyst-reactant interaction (gas-solid diffusion) is critical.

Nanostructuring in Catalysis

- His on of act



Dynamics: excluded for large objects



Fundamental process:
Desorption-dissolution (phase formation)

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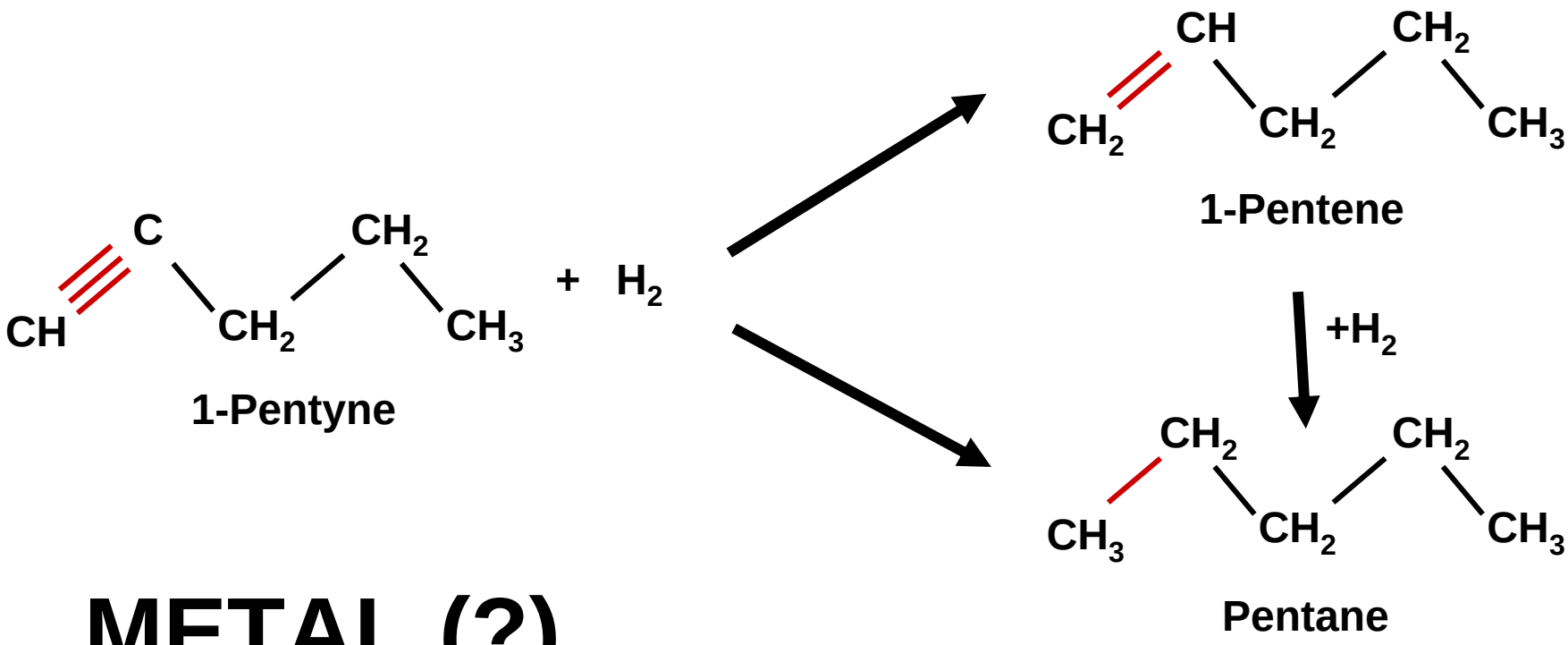
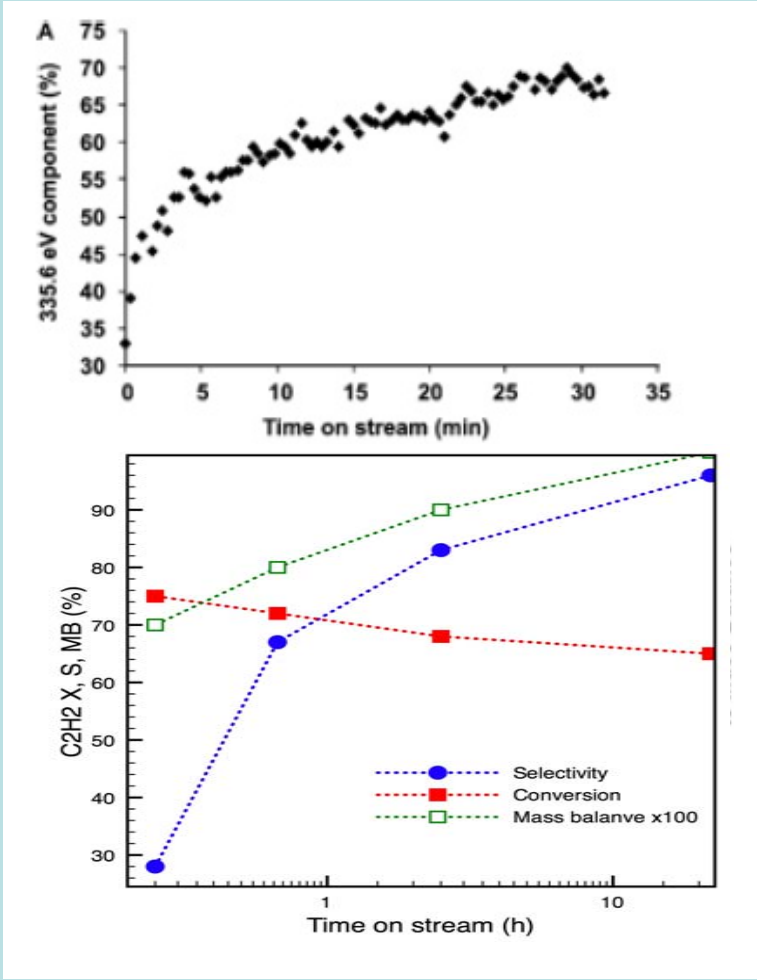
Selectivity

- Catalysts in “complex” processes act on several elementary steps.
- Selective, if only one step is accelerated or remains unaffected and all other steps are retarded.
- High specificity of the active site with strong reactant-catalyst interactions.
- Material tuning through effective reactant-precursor interaction.



METAL (?) HYDROGENATION CATALYSTS

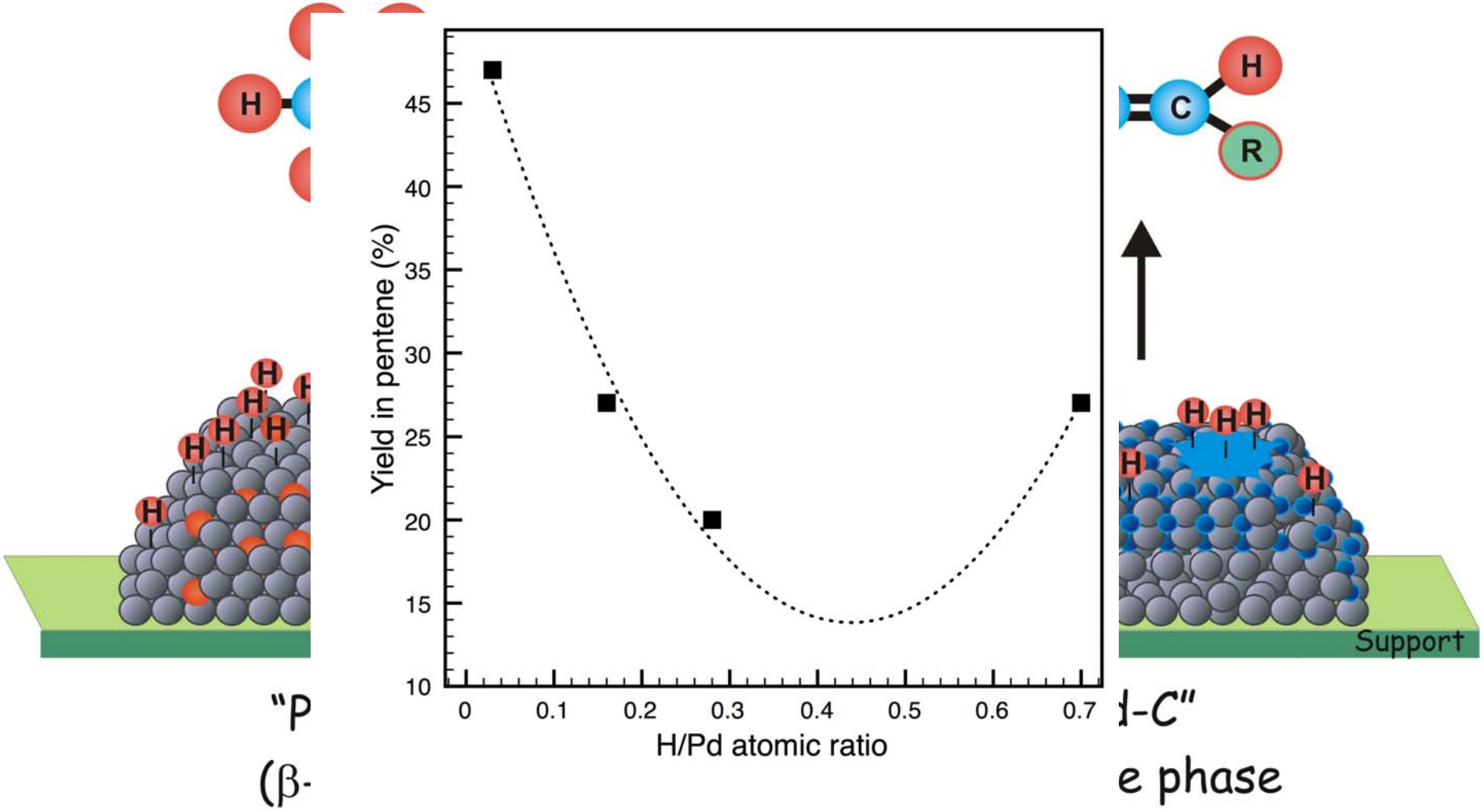
In-situ XPS: Pd 3d (720 eV): sub-surface C



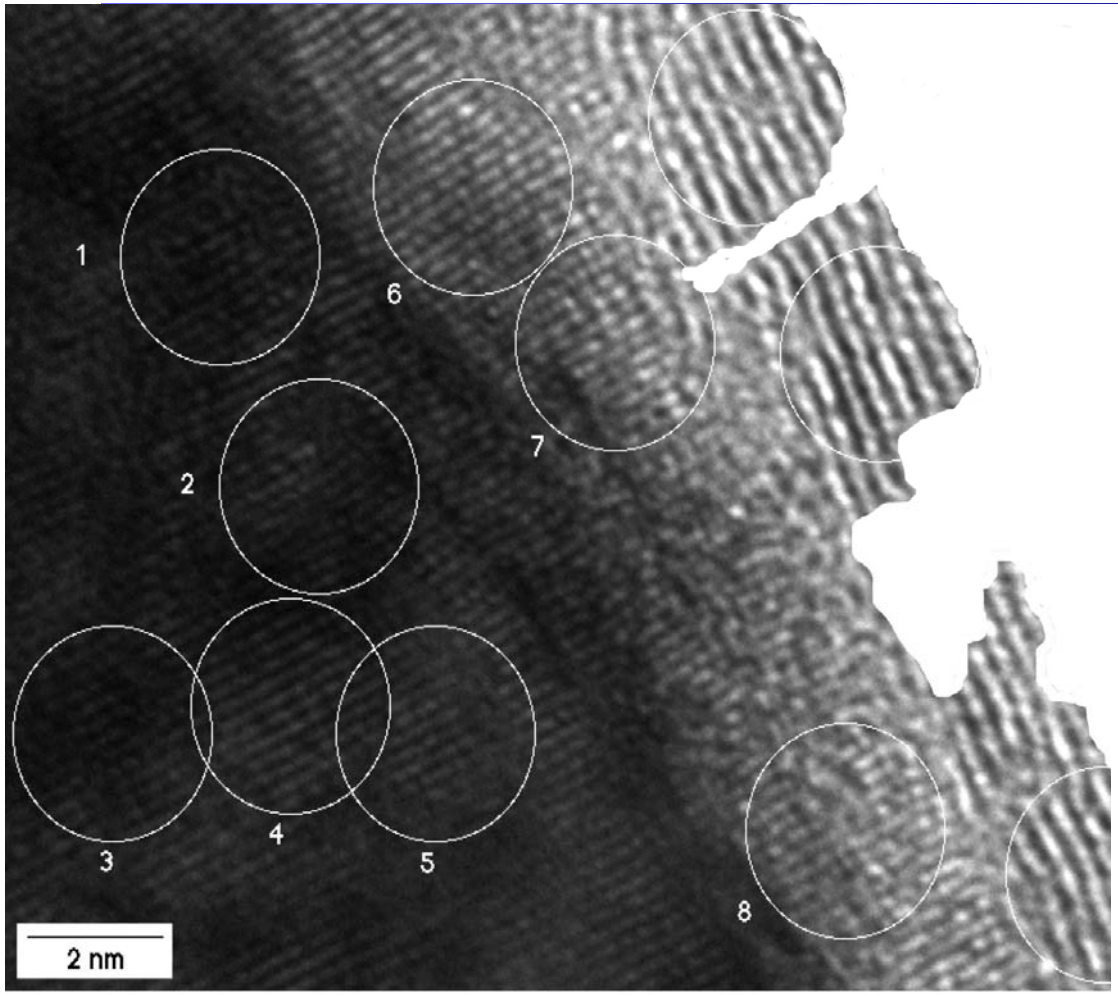
In-situ time-resolved XPS:

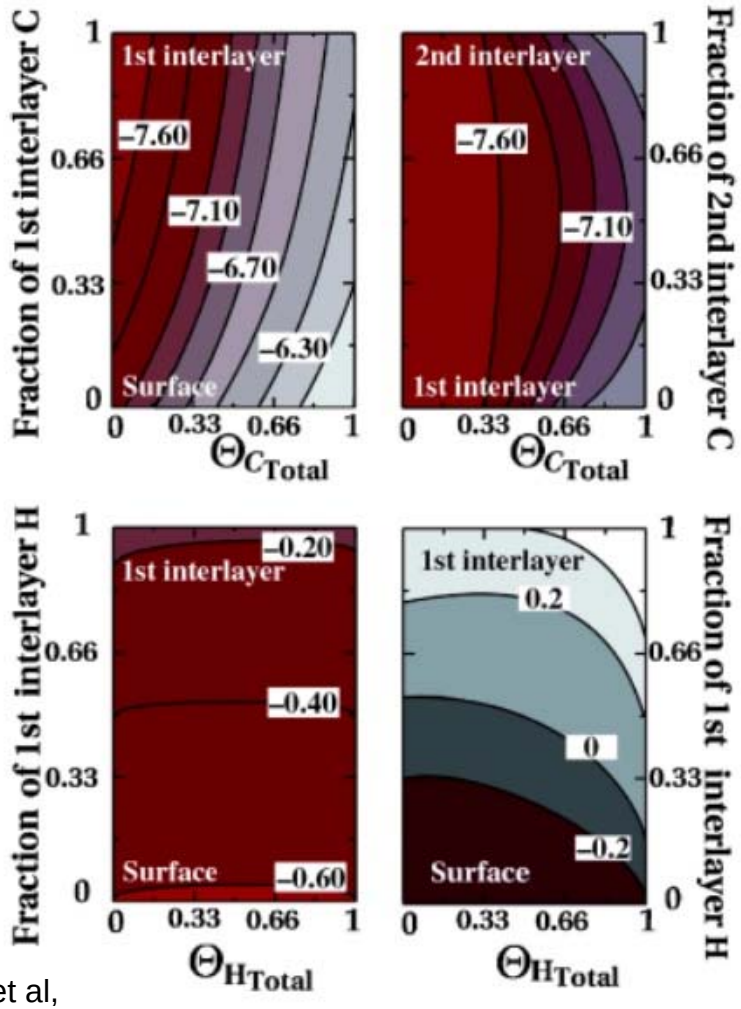
Correlation between equilibration and sub-surface C formation

Selectivity control



Origin of the effects

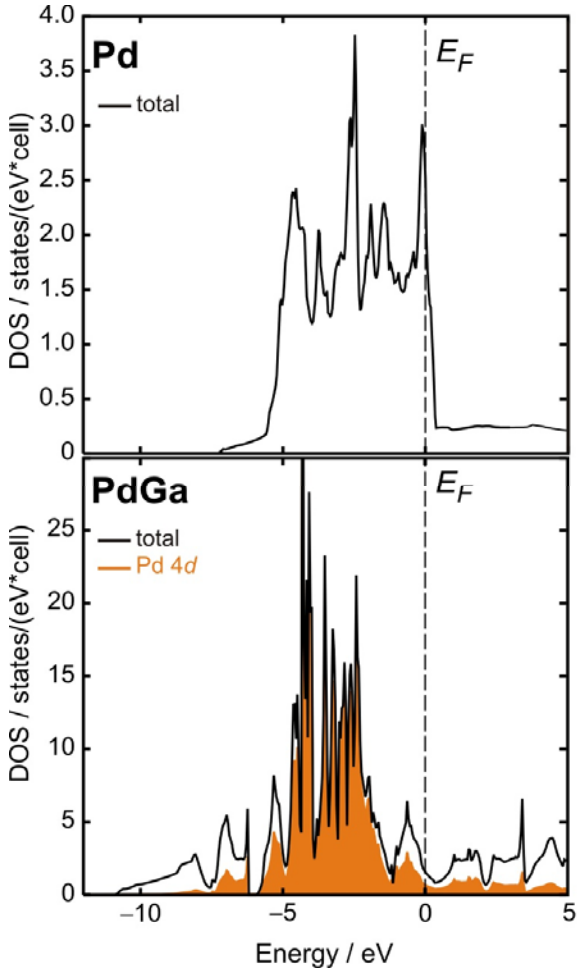


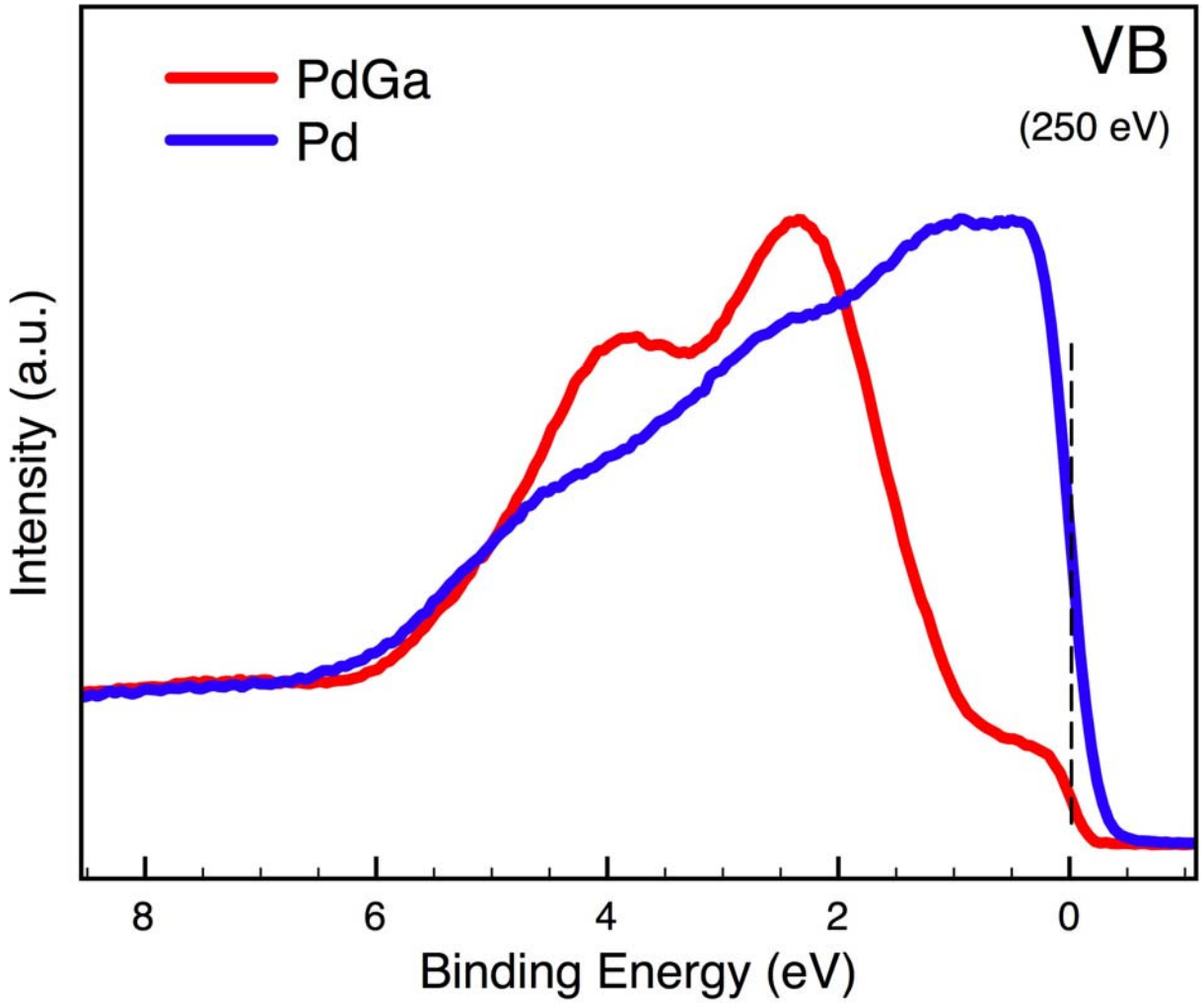


electronic structure of Pd

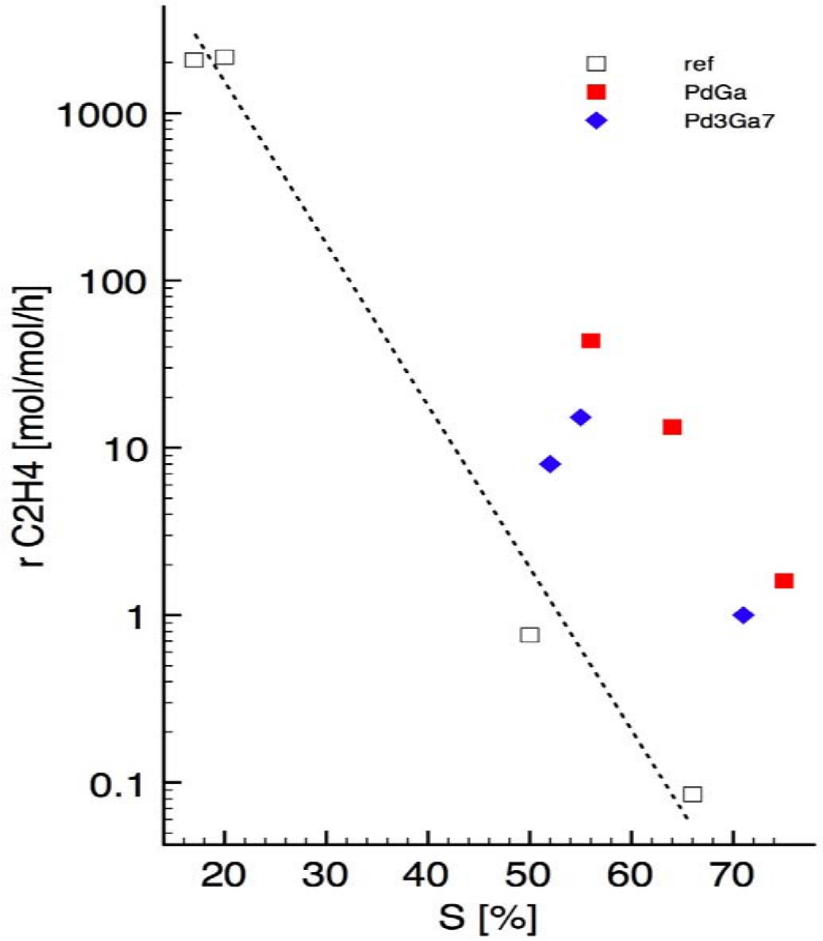
P. Sautet et al,
Angew. Chem.,2008

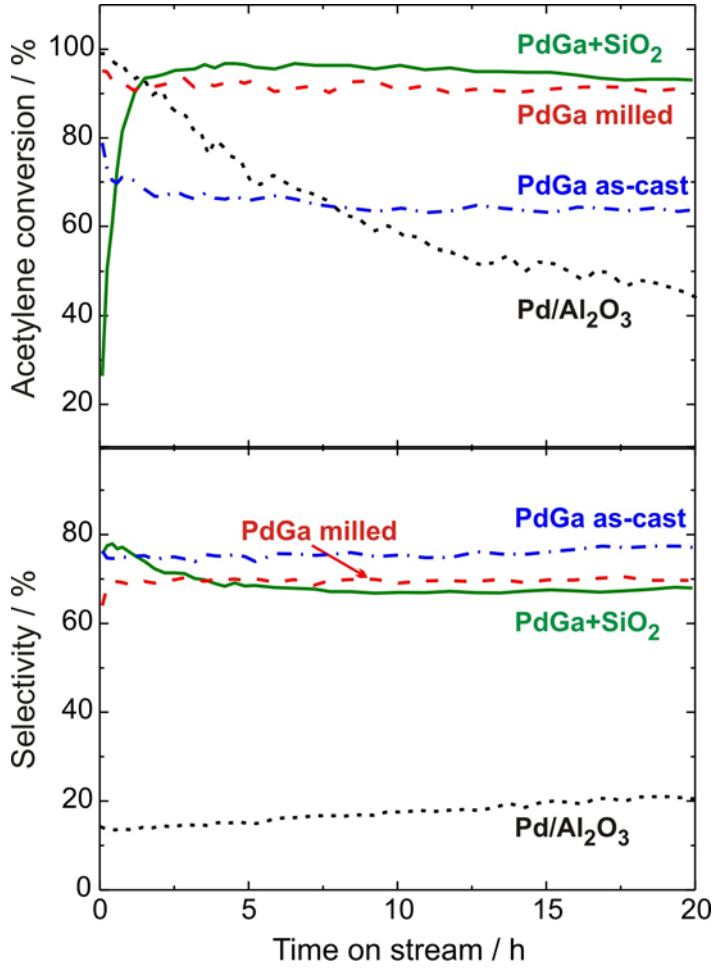
Intermetallics: kovalent interaction





PdGa: a designer system





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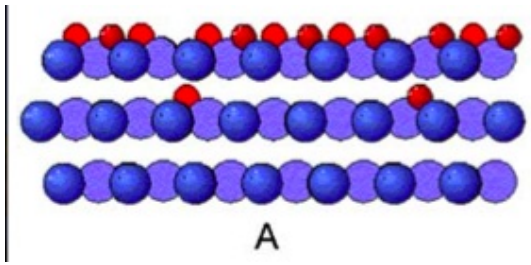
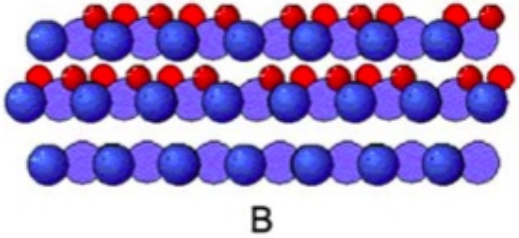
FIRST SUMMARY

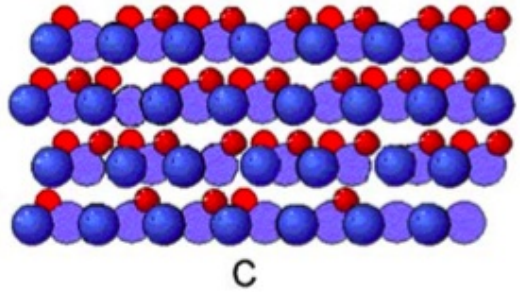
Surface and sub-surface species



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

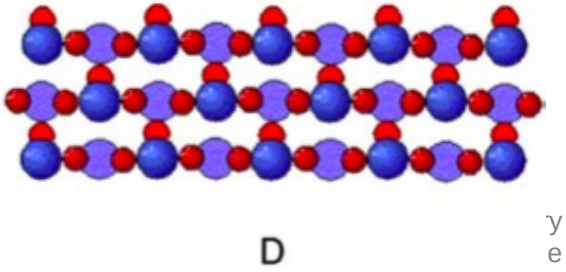
At slightly elevated potential: “trilayer” (theory)





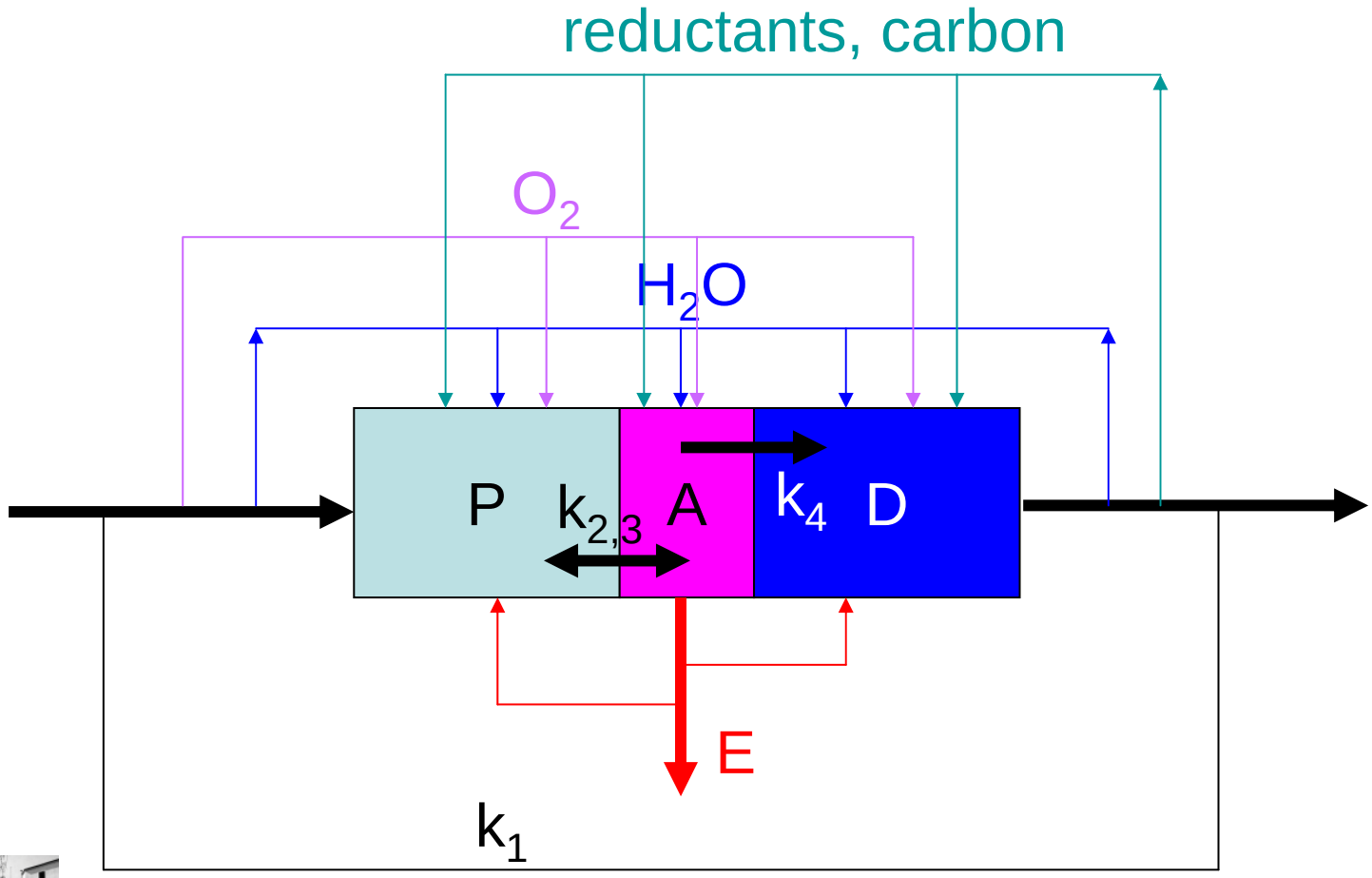
At potentials bejond the “pressure gap”: sub-surface compounds (transient)

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



Catalyst dynamics

Finite values of $k_{2,3}$ and k_4 under selective reaction conditions only when nanostructured

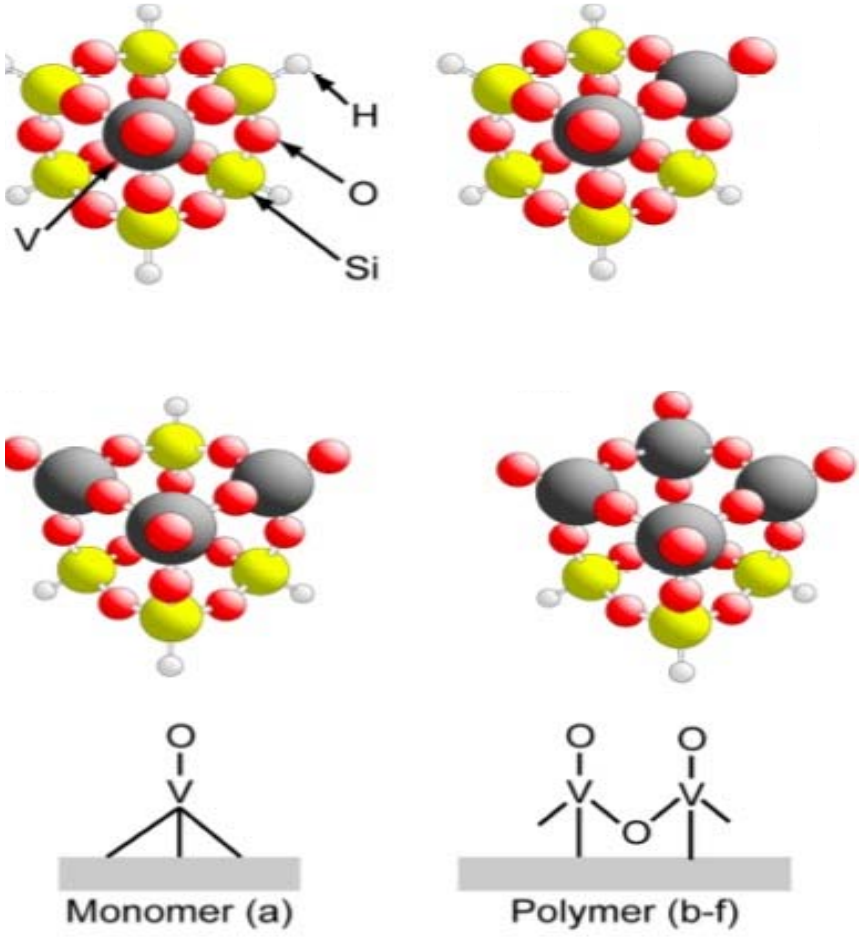


Consequences

- Active catalysts cannot be “prepared”: precursors activate in chemical potential of reactants.
- {Structure} of the precursor controls composition and structure of the active phase.
- Analysis of fresh precursors and ex situ allow limited conclusions about active state.
- The same precursor will catalyze different processes under different conditions: screen and optimize operation conditions as much as precursor compositions.

MMO vs. models

OXIDES AS CATALYSTS



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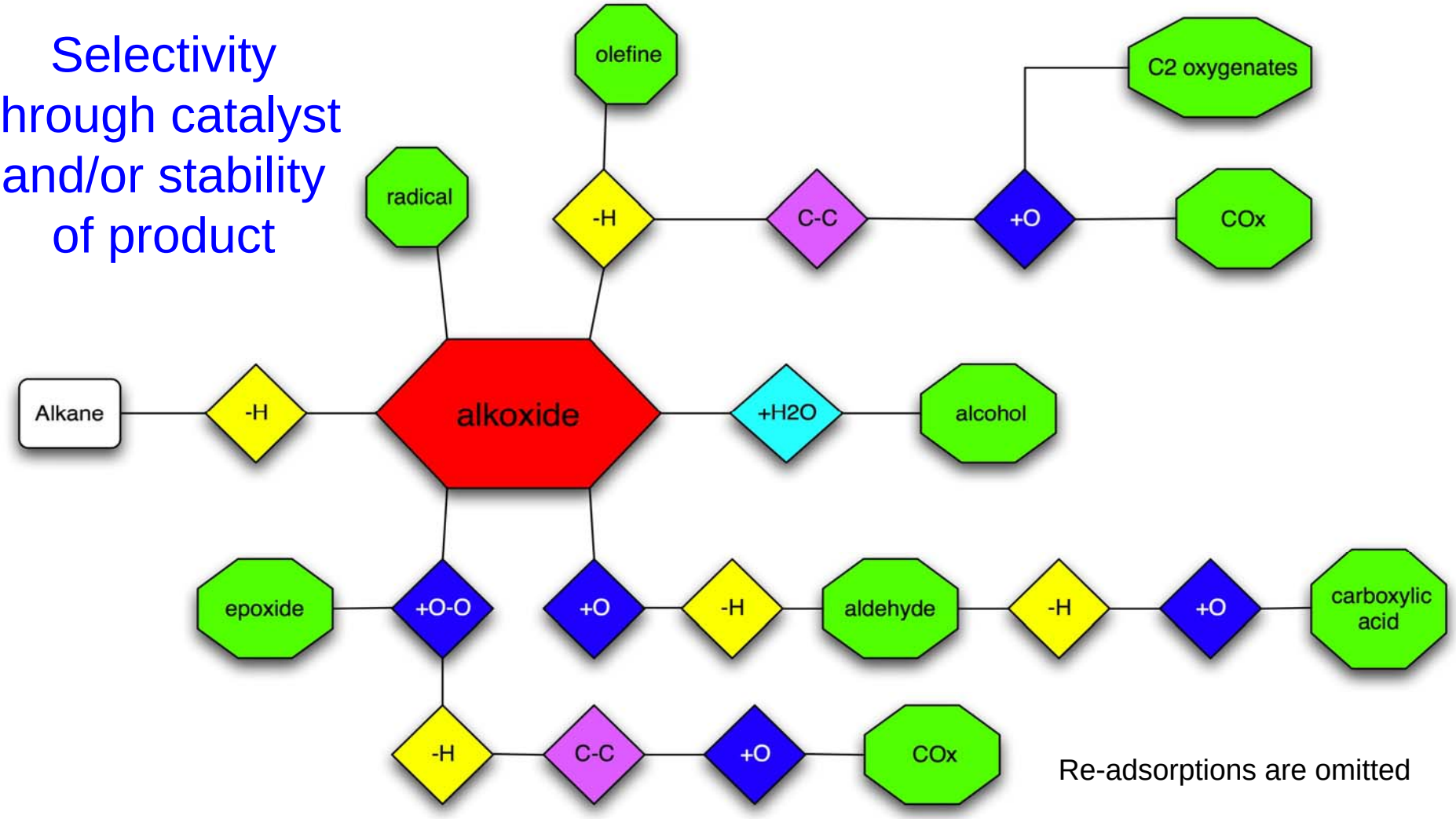
Alkane activation

Selectivity through catalyst and/or stability of product



Re-adsorptions are omitted

Some dehydrogenations are omitted

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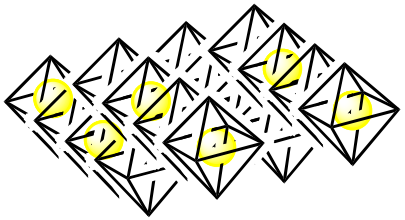
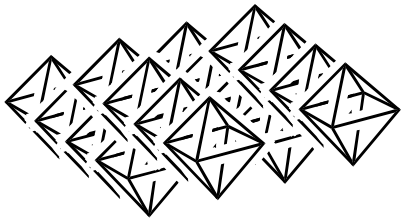
Self-organisation

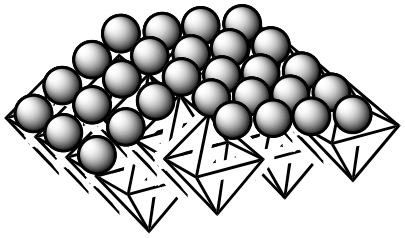


bulk insulator

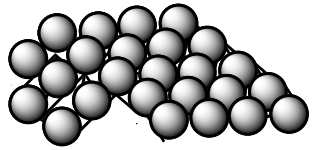
active phase



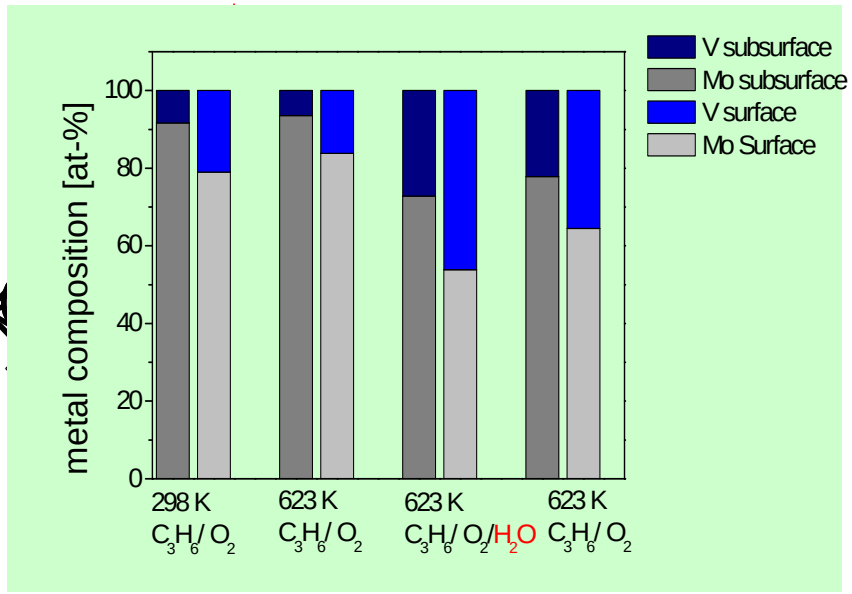
conductor



metal-insuator assembly



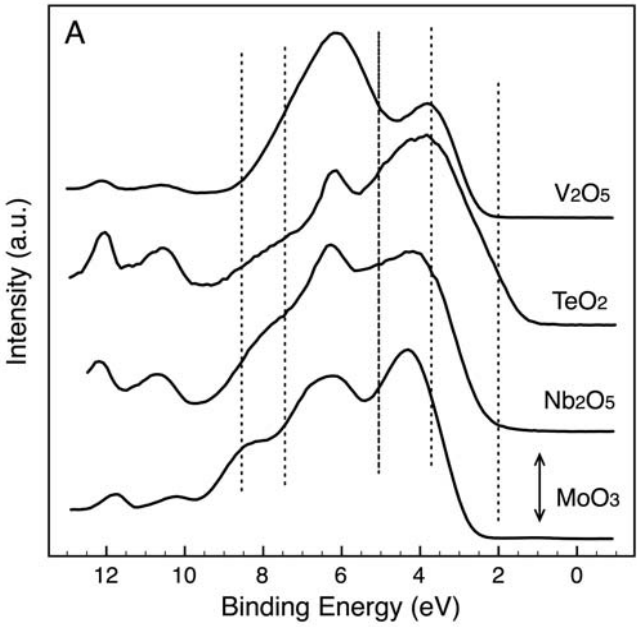
segregate



Redox catalysis is about electrons:
Conductivity and work function

Complex oxides: MMO

Reference oxides

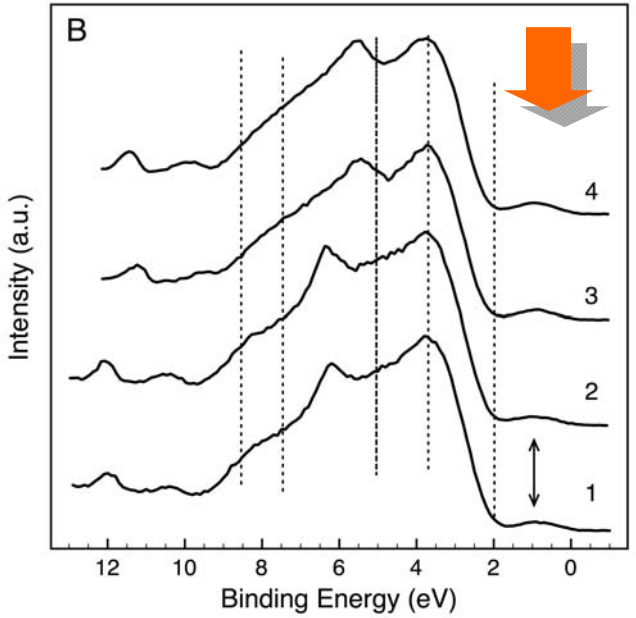


Exp. conditions: in O_2 at 623-673 K

MMO electronically derived from MoO_3: covalent rehybridisation

Catalysts

Oxygen vacancies



4 MoV: in $C_3H_6+O_2$ at 623 K
3 MoVW: in $C_3H_6+O_2+H_2O$ at 623 K
2 M1 (1886): in $C_3H_8+O_2+H_2O$ at 623 K
1 M1 (1761): in $C_3H_8+O_2+H_2O$ at 623 K

Theory: K Hermann et al.

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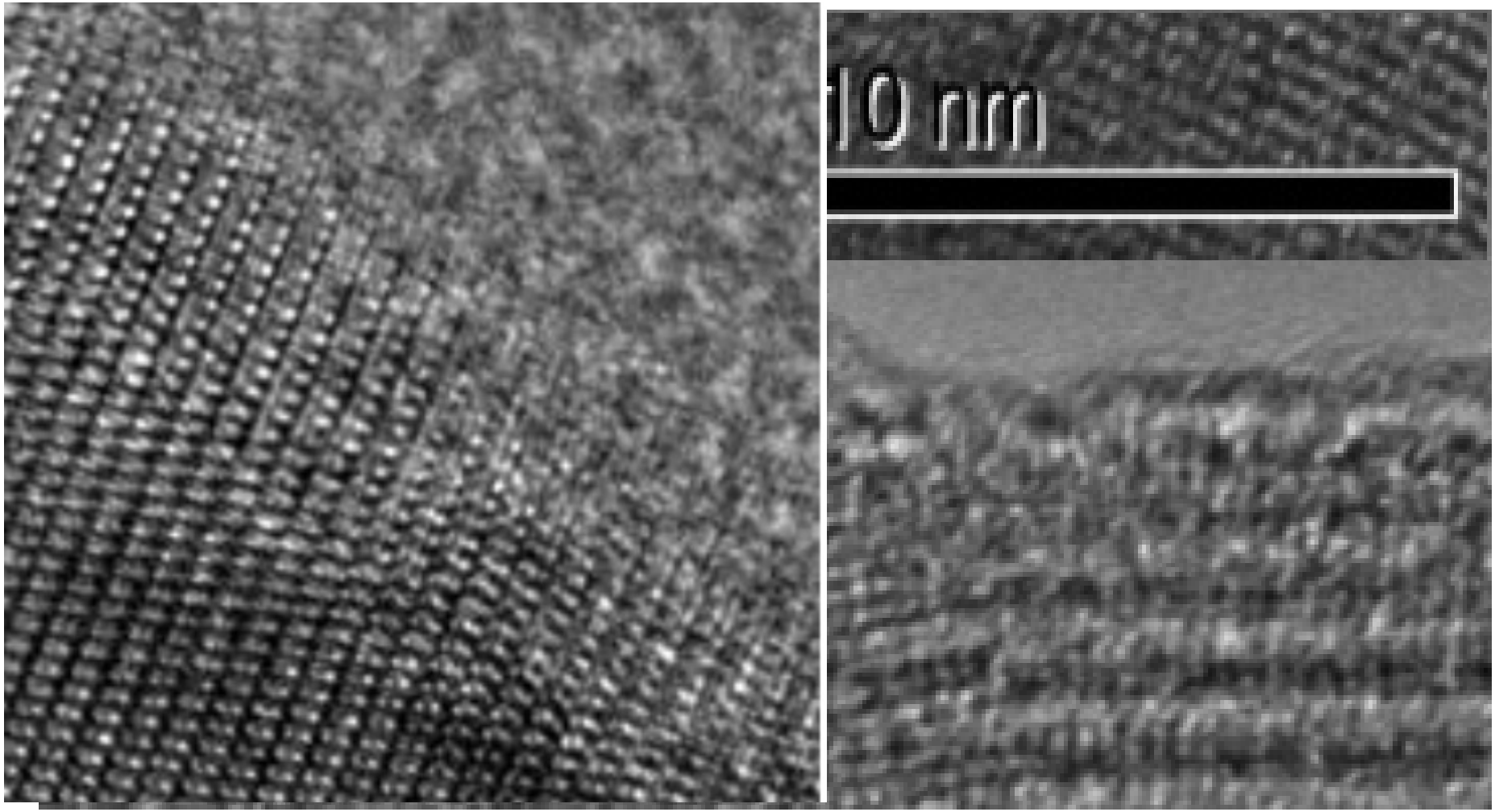
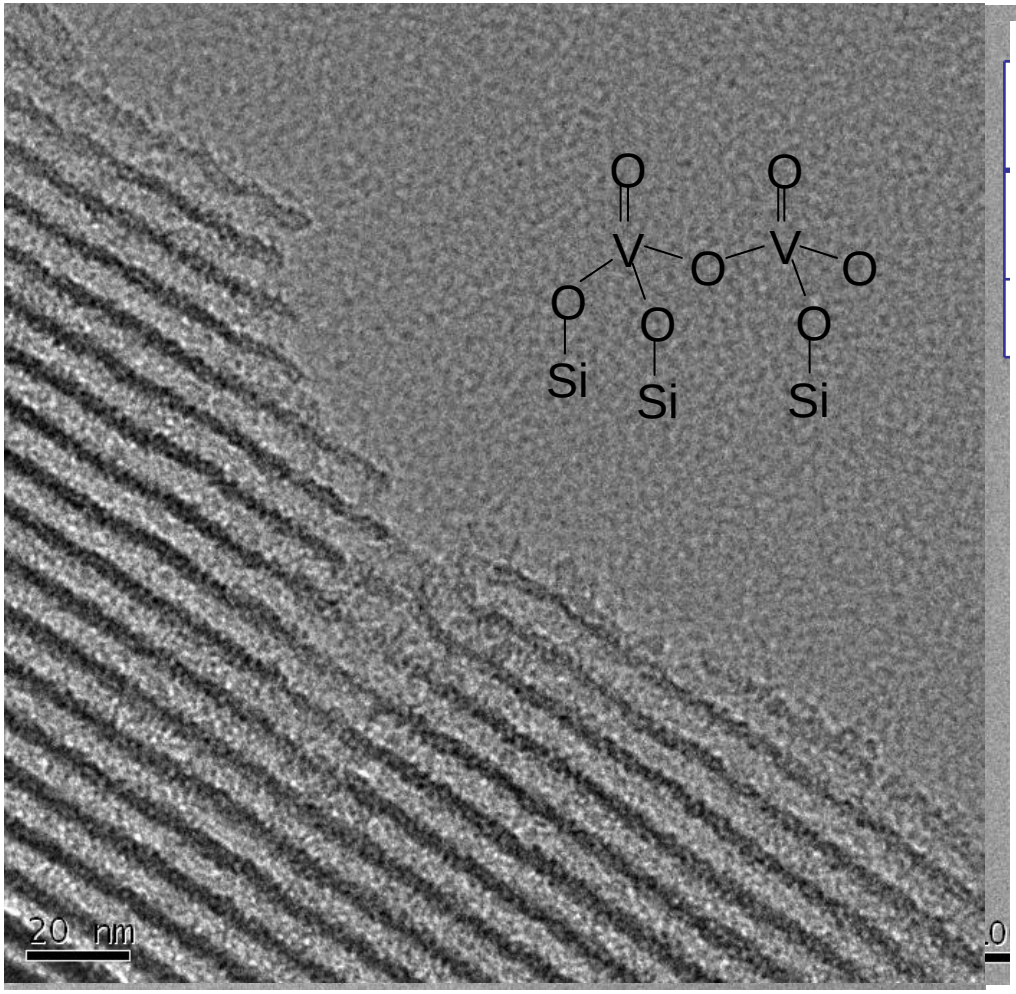
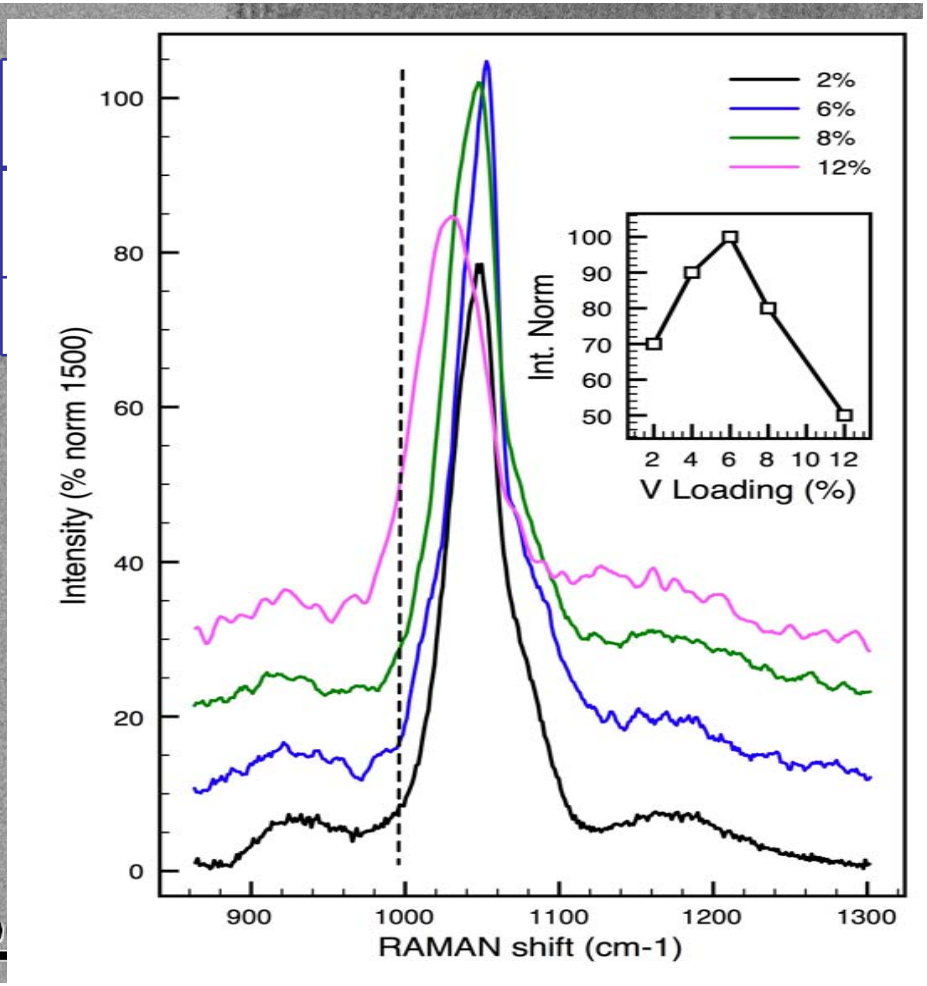
M1: $MoVTeNbO_x$: a typical system

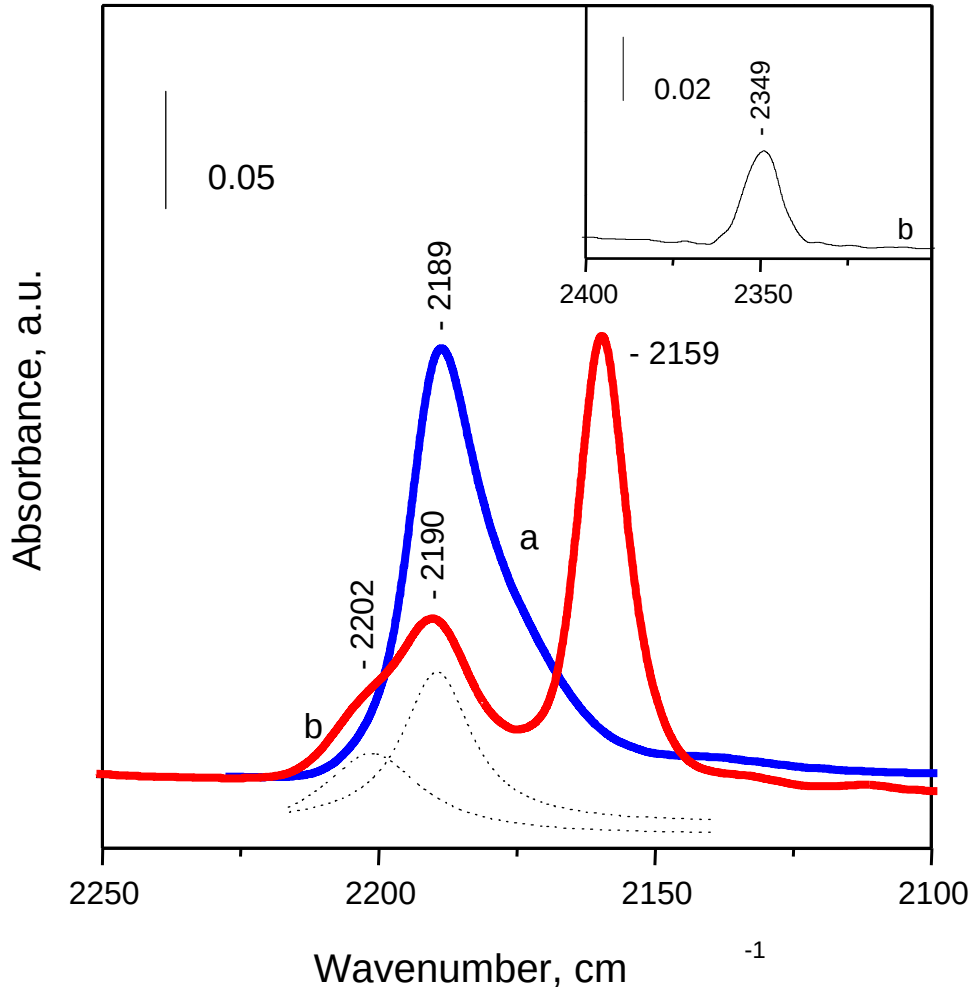


V-SBA 15: a “molecular model”





Surface dynamics



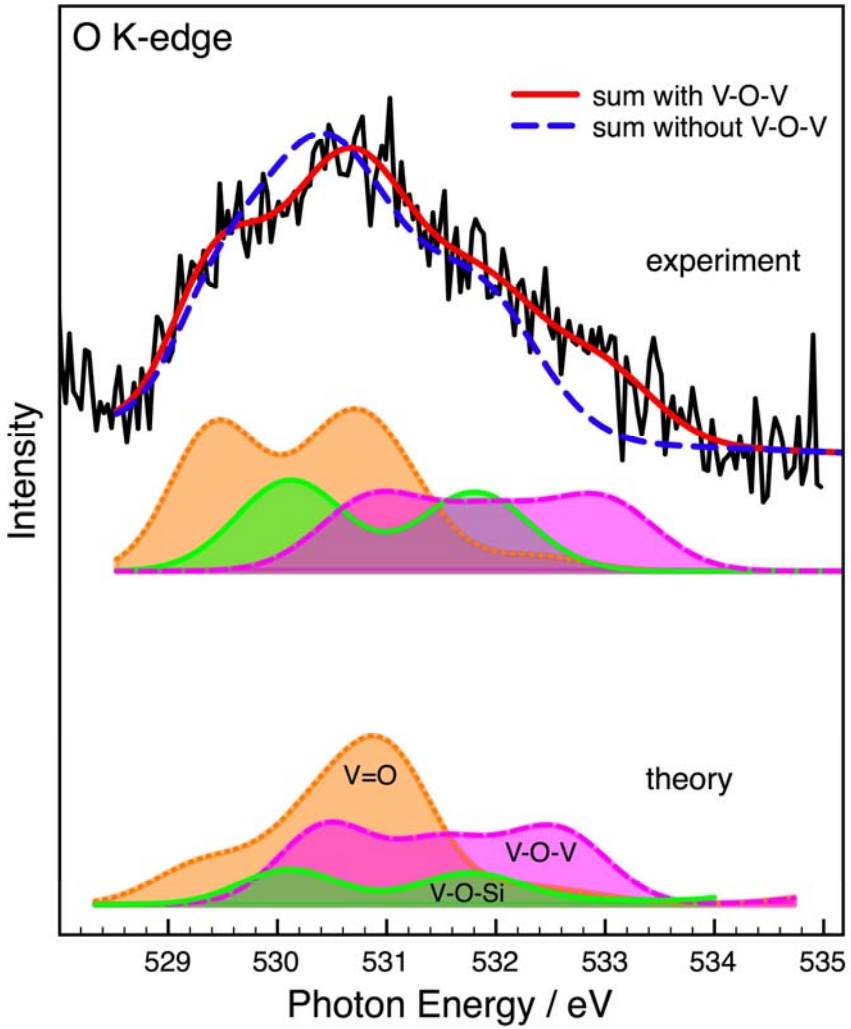
Low-temperature CO adsorption

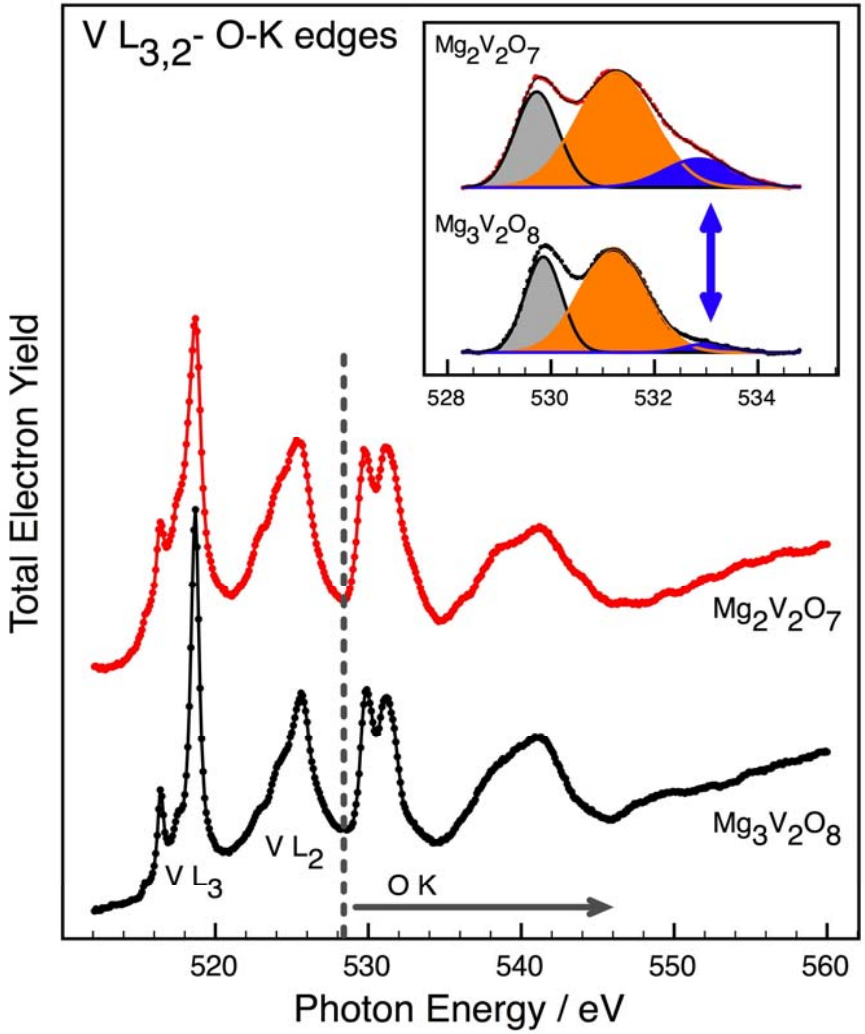
a) After dehydation and evacuation

b) After a following O_2 exposure at 85 K

Several active sites, incompatible with single species, reactivity towards co-ordinating oxygen

V-O-V





C. Hess, M. Cavallieri, K. Hermann

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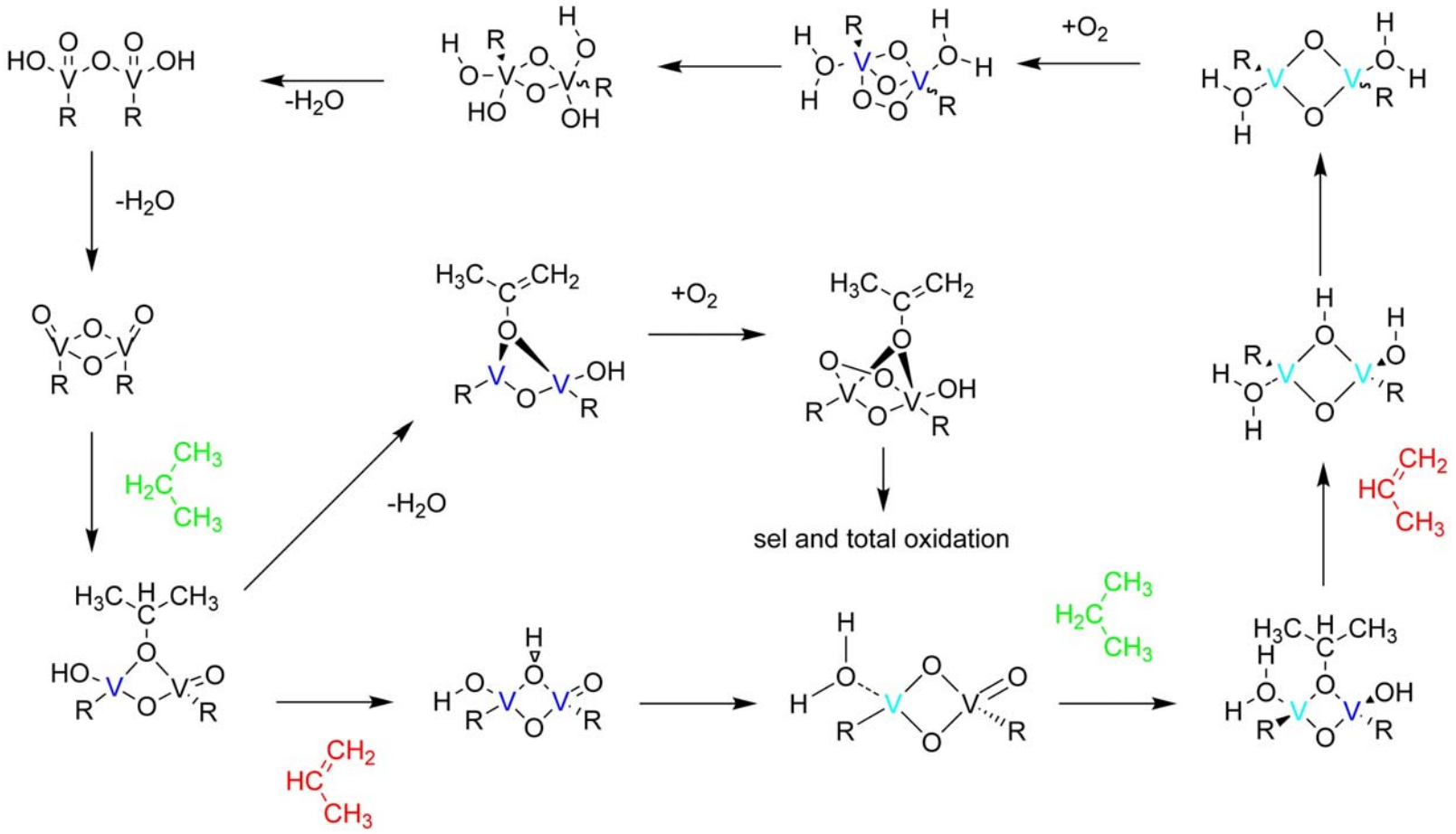
Reaction pathway



Dynamics and adaptation

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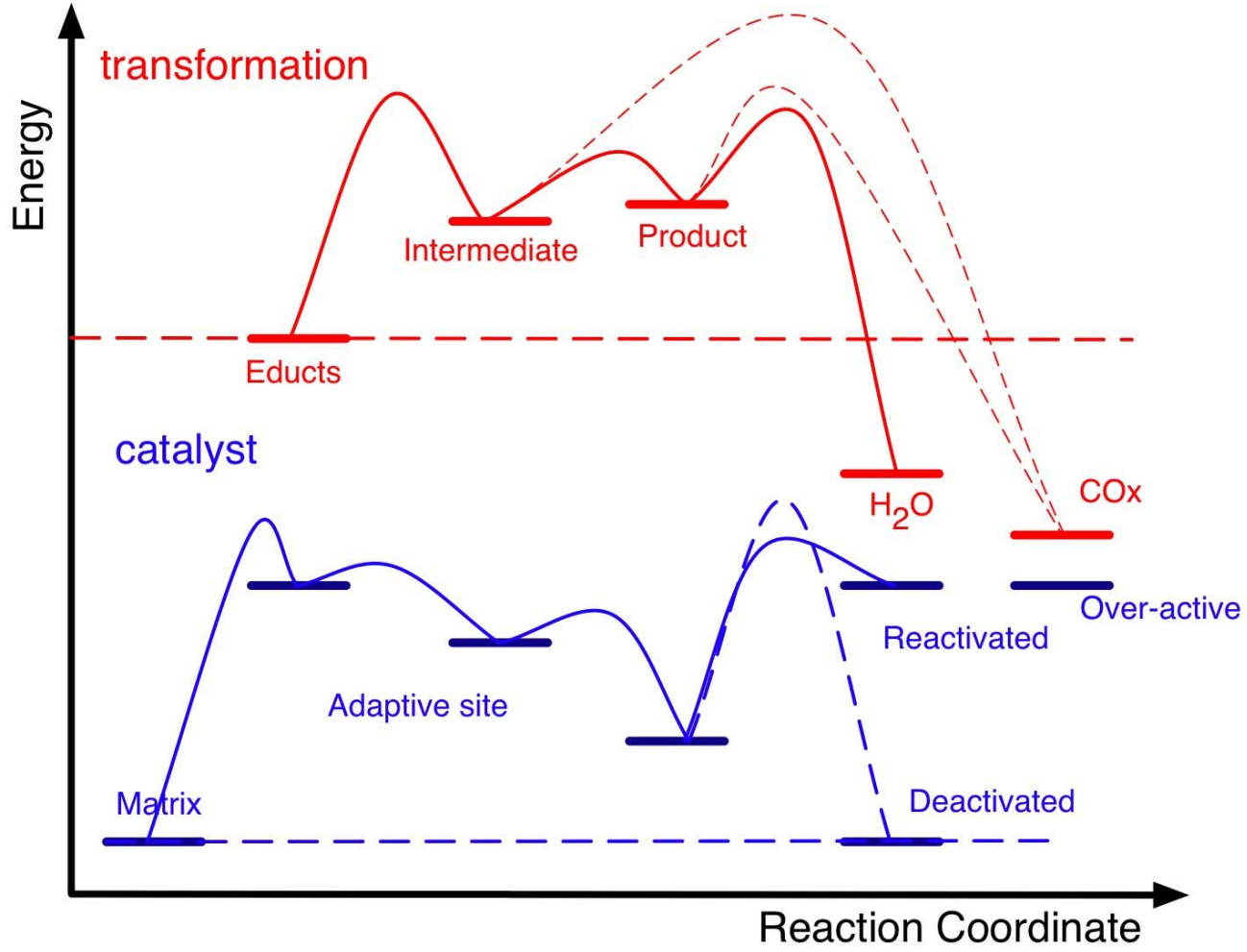
SECOND SUMMARY

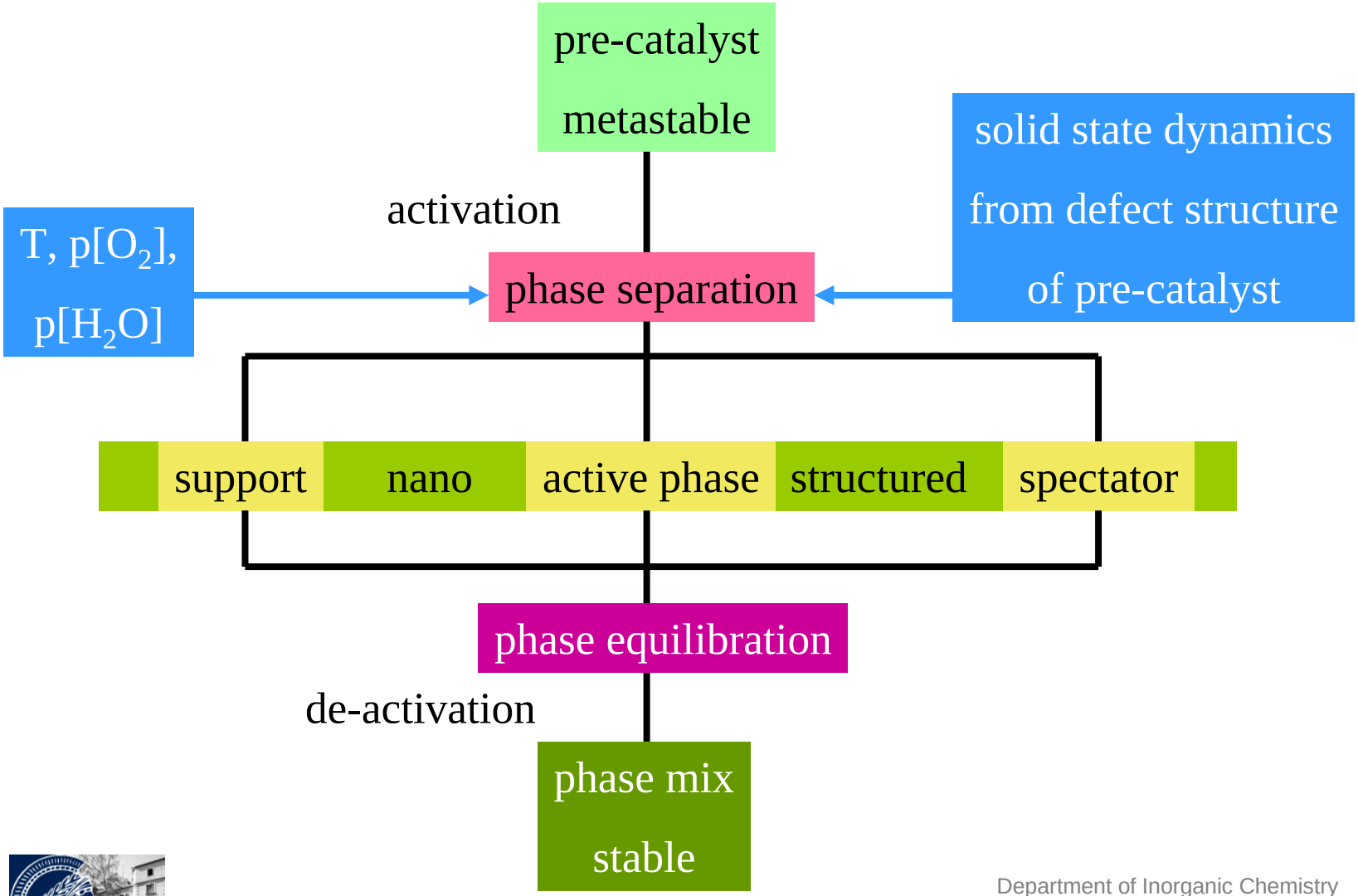
Active sites in a high performance catalyst

- An active heterogeneous catalyst contains few adaptive sites for reaction.
- They adapt their structure according to the local chemical potential and guarantee selective operation on progressively more reactive adsorbates.
- The complex structure of the precursors is required to fix the chemical potential of the active phase in the reaction environment.

Selective oxidation:
Coupling of transformation and material



Catalyst dynamics



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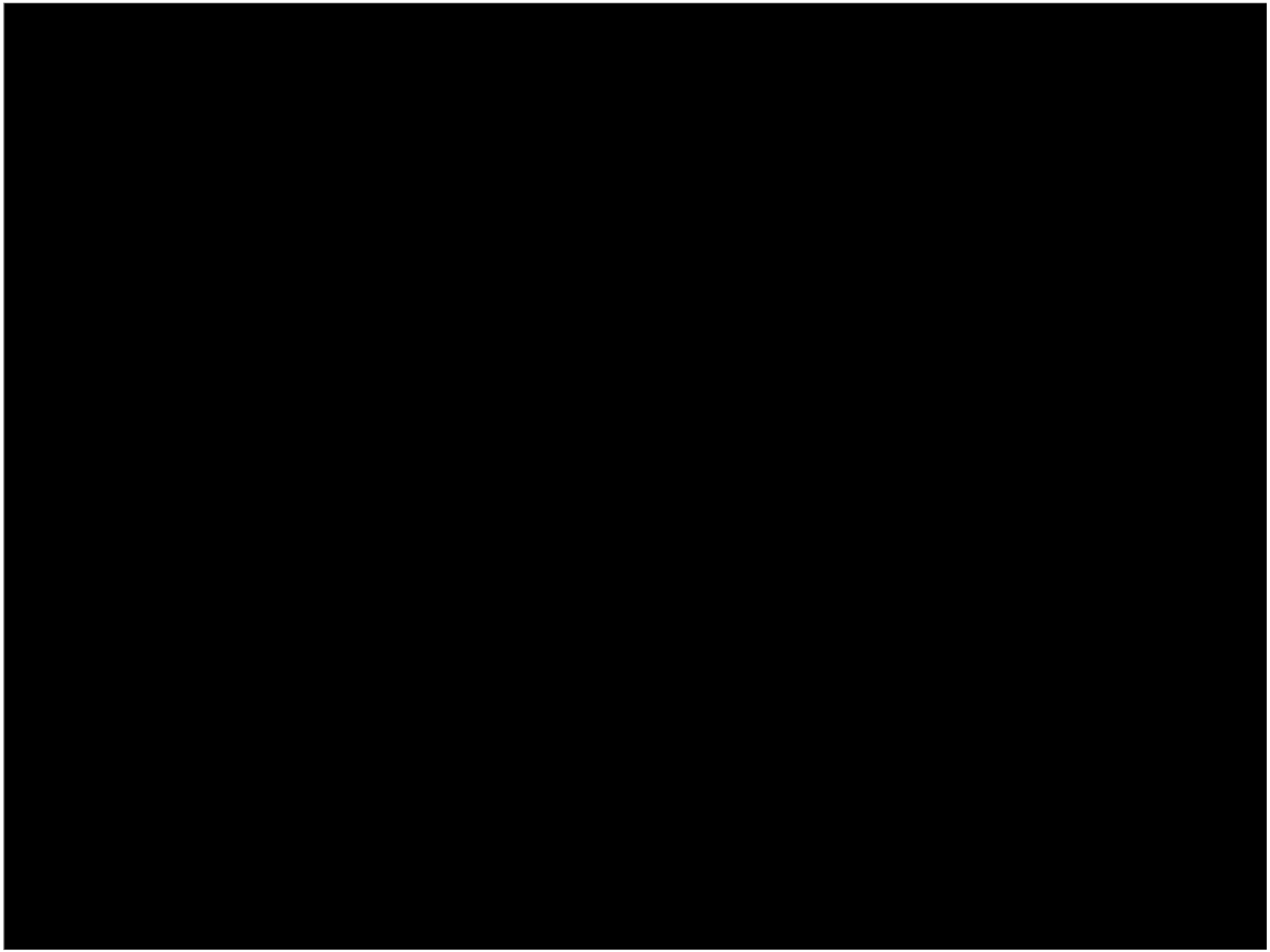
Make things as simple as possible -
But not simpler
(A. Einstein)
Catalysis is a facinating challenge
and not yet a “mature technology”
Thank You



Catalyst dynamics