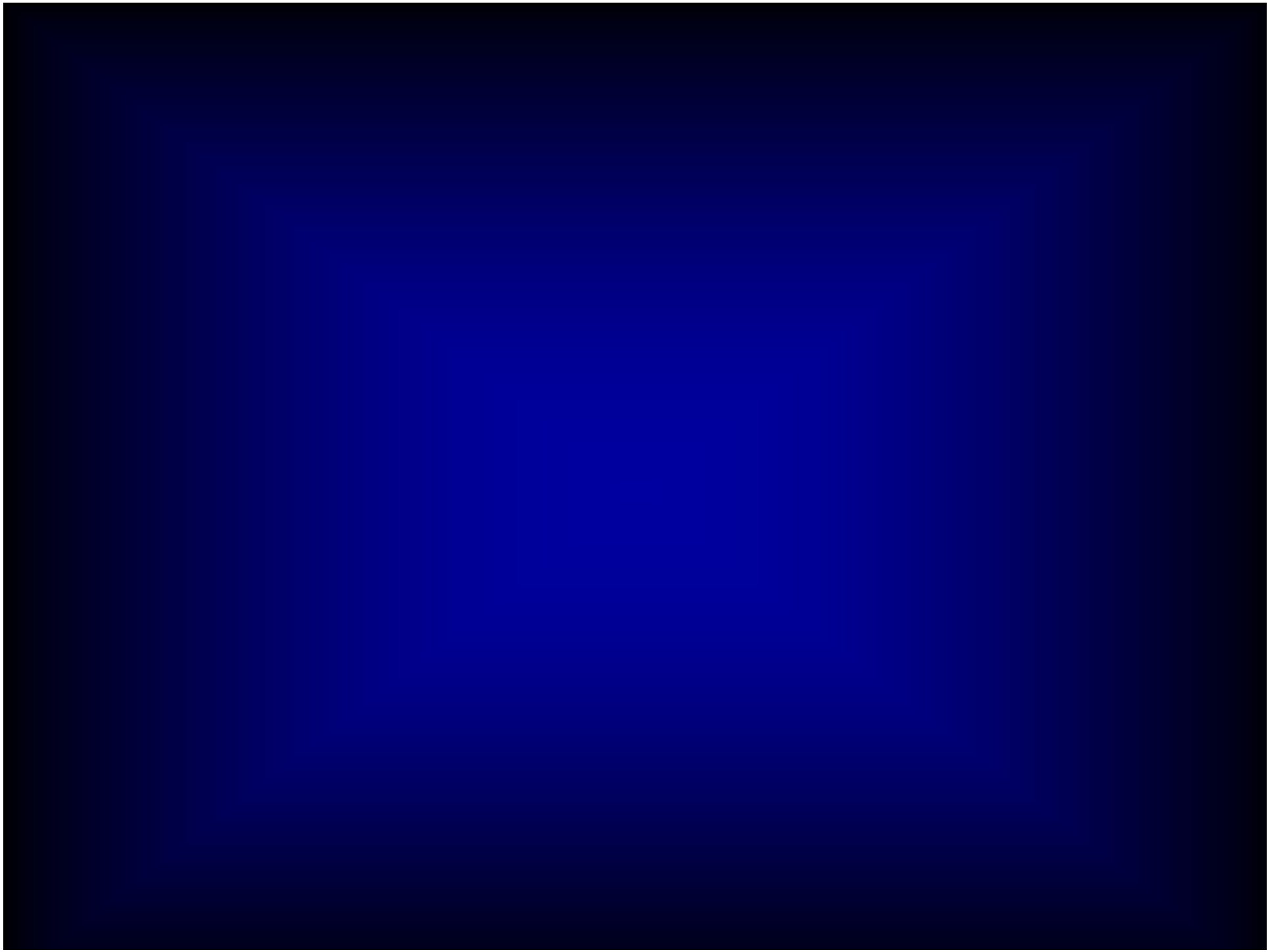


Robert Schlögl
Fritz-Haber-Institut der MPG

VANADIUM OXIDES IN SELECTIVE OXIDATION CATALYSIS: DYNAMICS


IDECAT
Integrated Design of
Catalytic Nanomaterials
for a Sustainable Production
unicat
Unifying Concepts in Catalysis

FUNDAMENTALS

The function of a catalyst: The single crystal approach

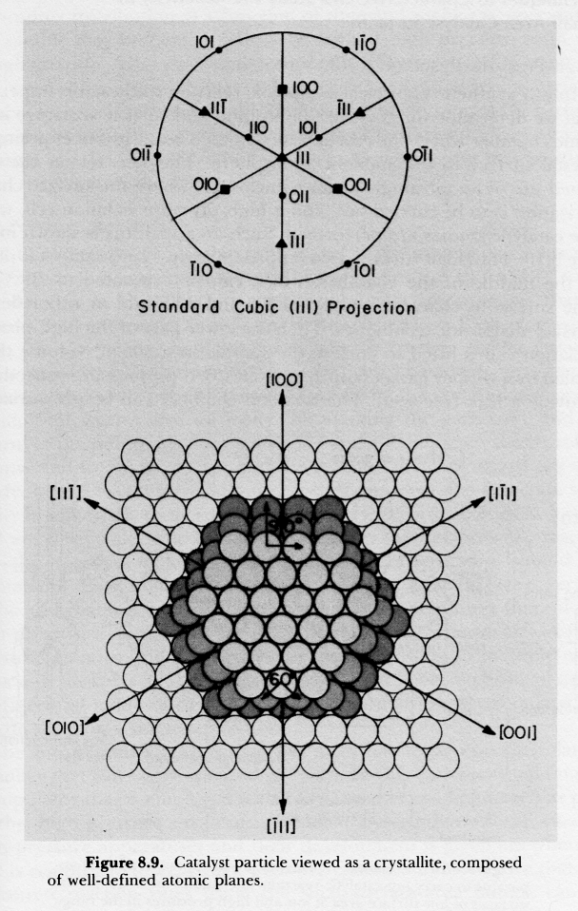
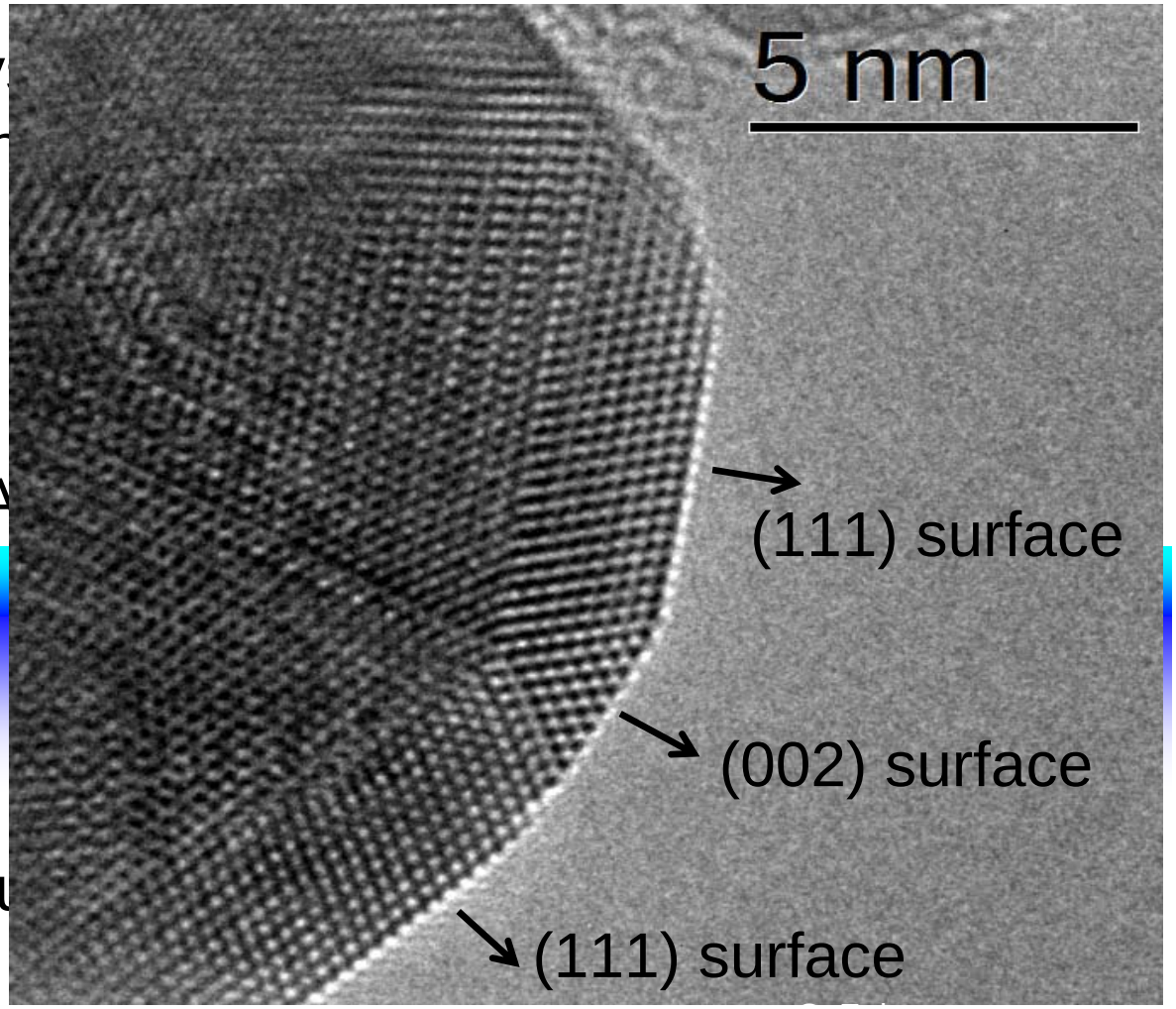


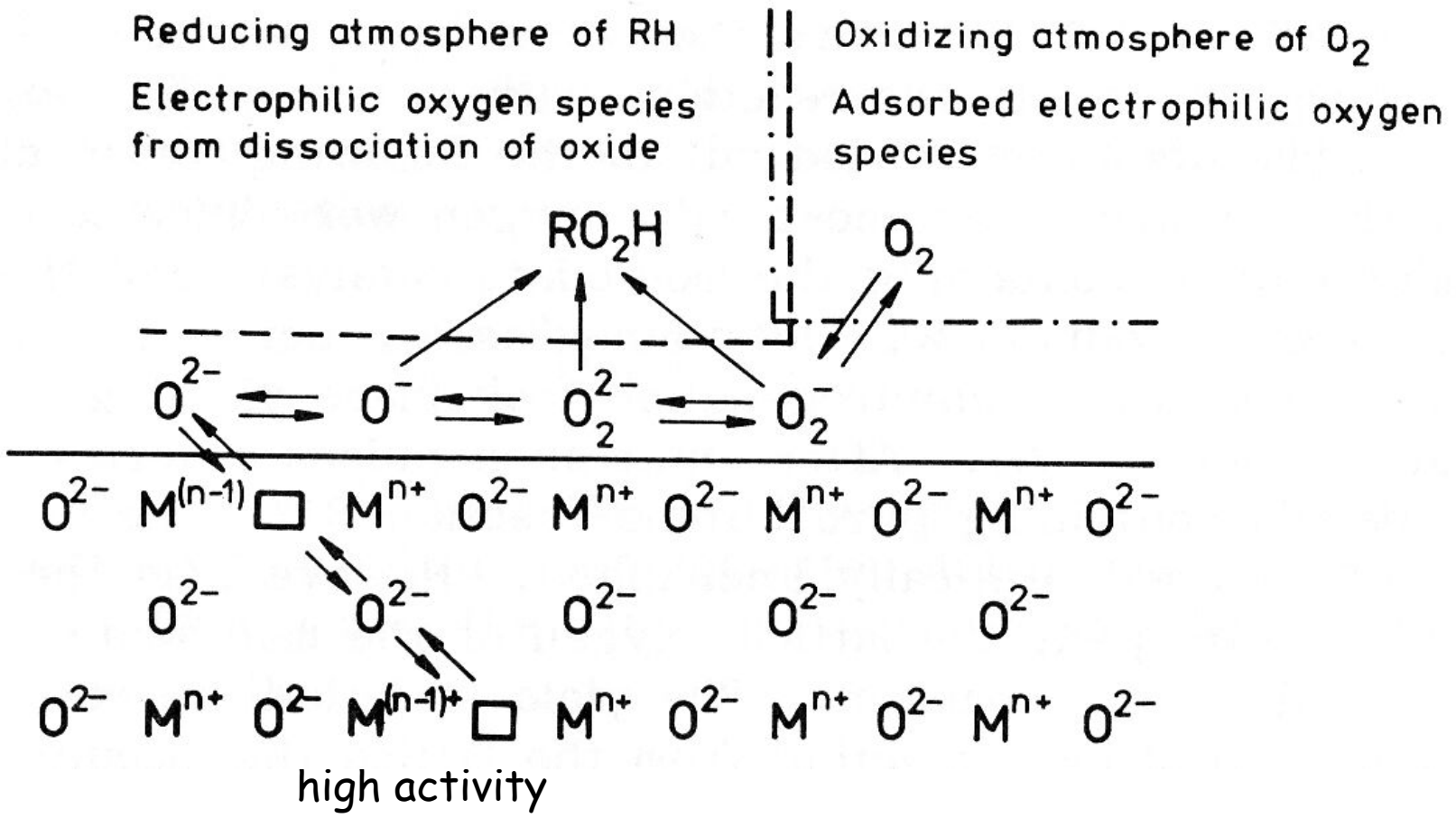
Figure 8.9. Catalyst particle viewed as a crystallite, composed of well-defined atomic planes.



Bombrial 1981

Bulk is "irrelevant",

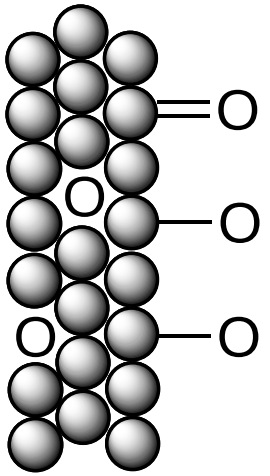
Bulk lattice oxygen vs surface lattice oxygen



J. Haber, 1991

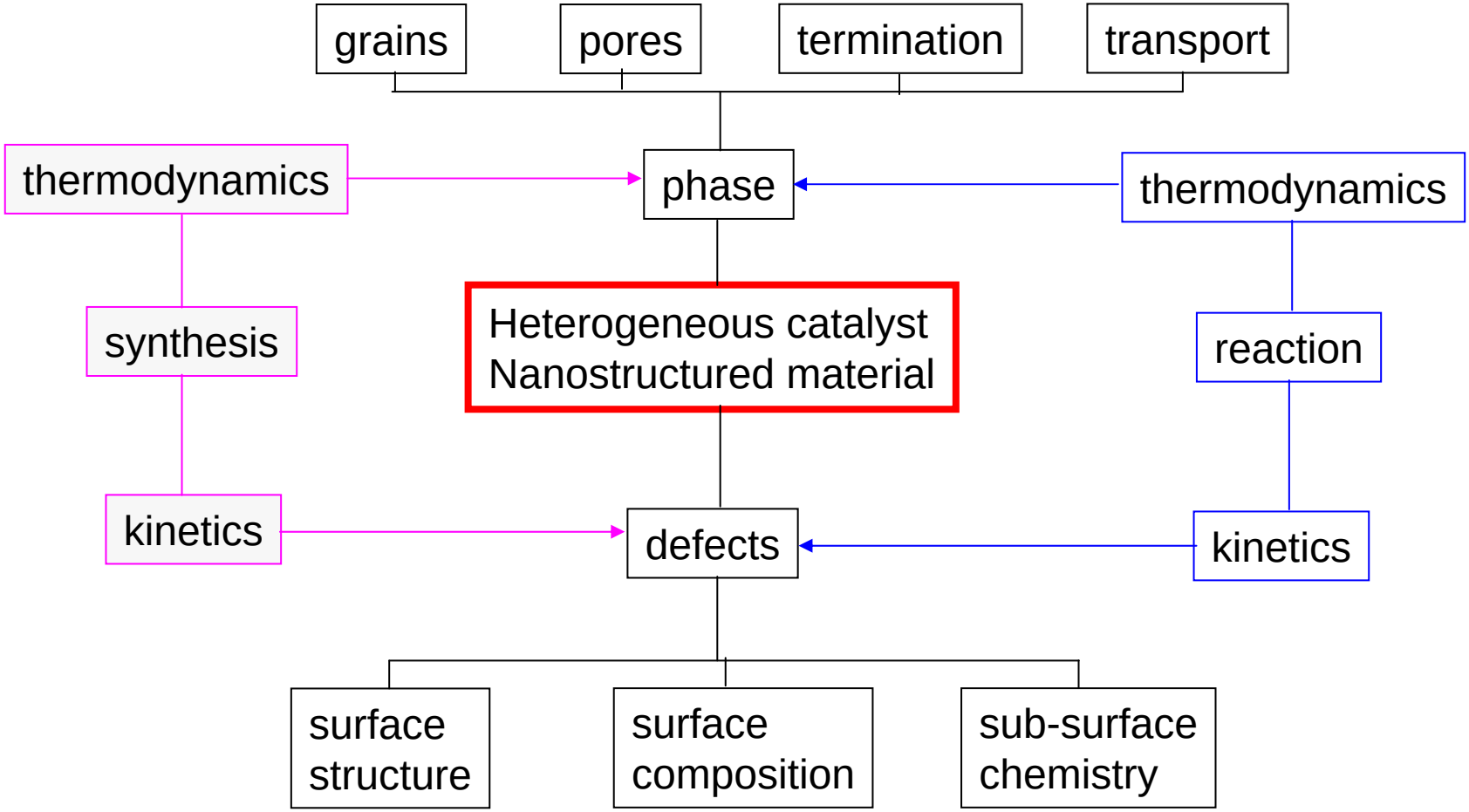
Di-oxygen as oxidant

- Atomic chemisorbed oxygen (created typically in UHV) is amphoteric in redox properties: at “virtual pressure” → sub-surface
- Sub-surface oxygen is not reactive but
  - Polarizes the surface for adsorption
  - Restructures the surface by incorporation (autocatalytic)
  - Segregates to the surface as O nucleo
  - Polarizes atomic oxygen into O electro
- Electrophilic oxygen
  - Oxidizes functional substrates (CO, olefines)
  - Creates all oxygenate organic molecules
- Nucleophilic oxygen
  - Activates C-H bonds into functional substrates
  - Creates basicity and binds water (OH)



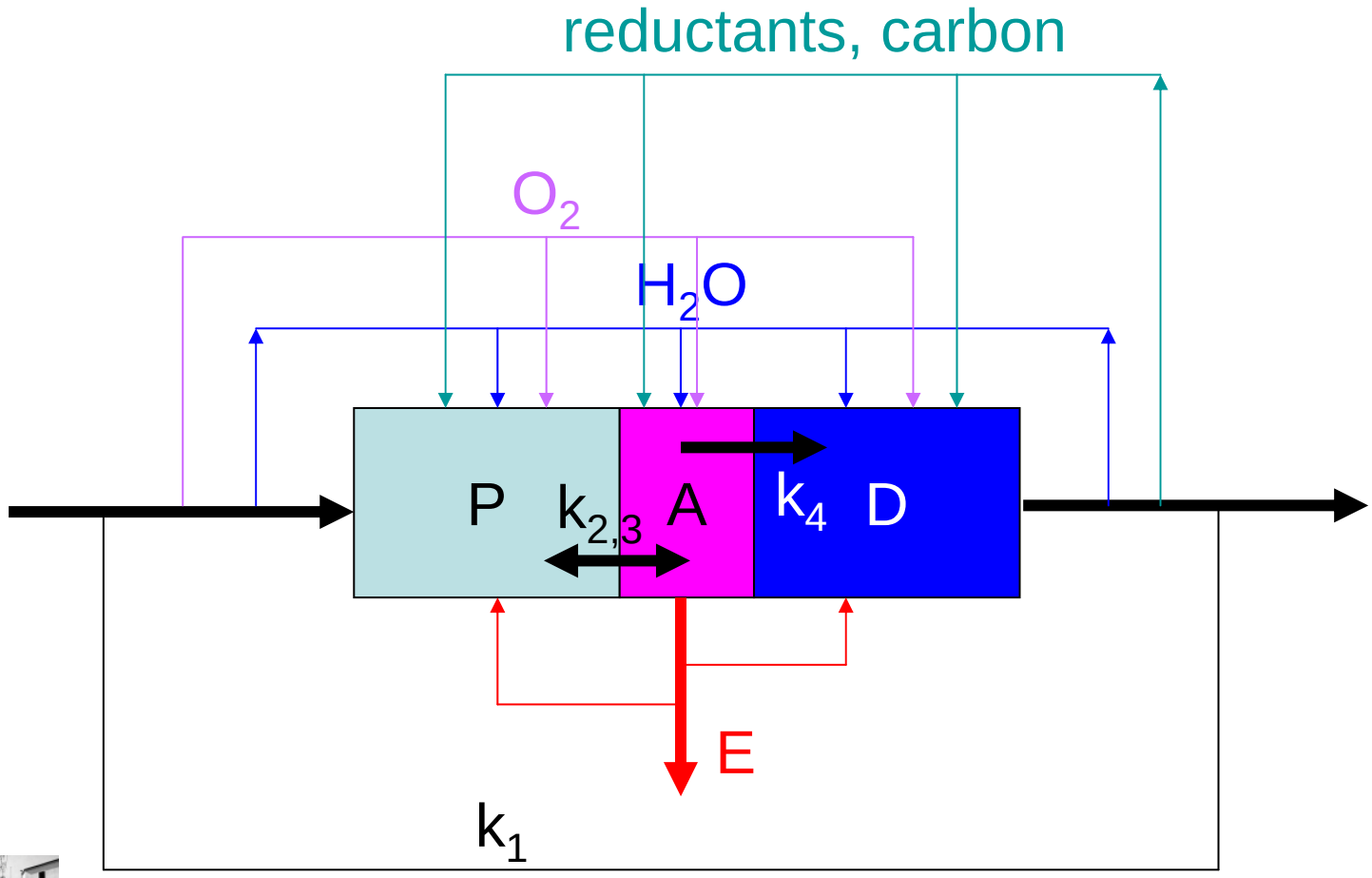
With metals

Catalyst material science



Catalyst dynamics

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



Consequences

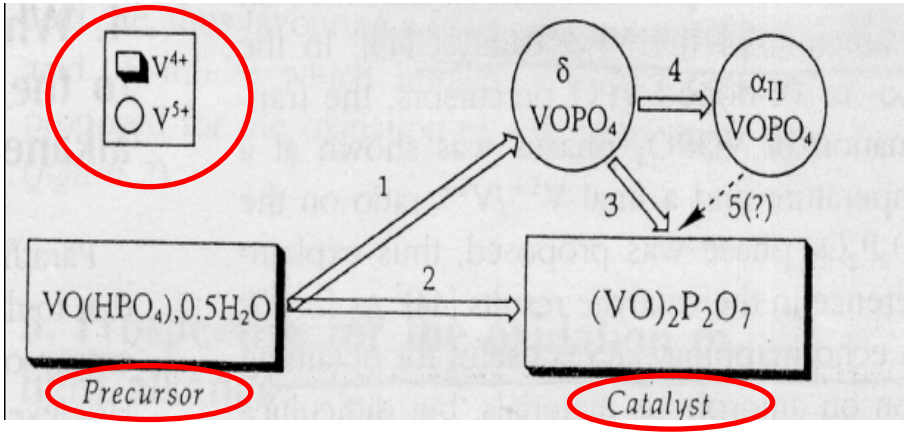
- Active catalysts cannot be prepared: precursors activate in chemical potential of reactants.
- {Structure} of the precursor controls composition and structure of the active phase.
- Analysis of fresh precursors and ex situ allow limited conclusions about active state.
- The same precursor will catalyze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

CASE STUDY: V_XO_Y IN VPO FOR BUTANE OXIDATION

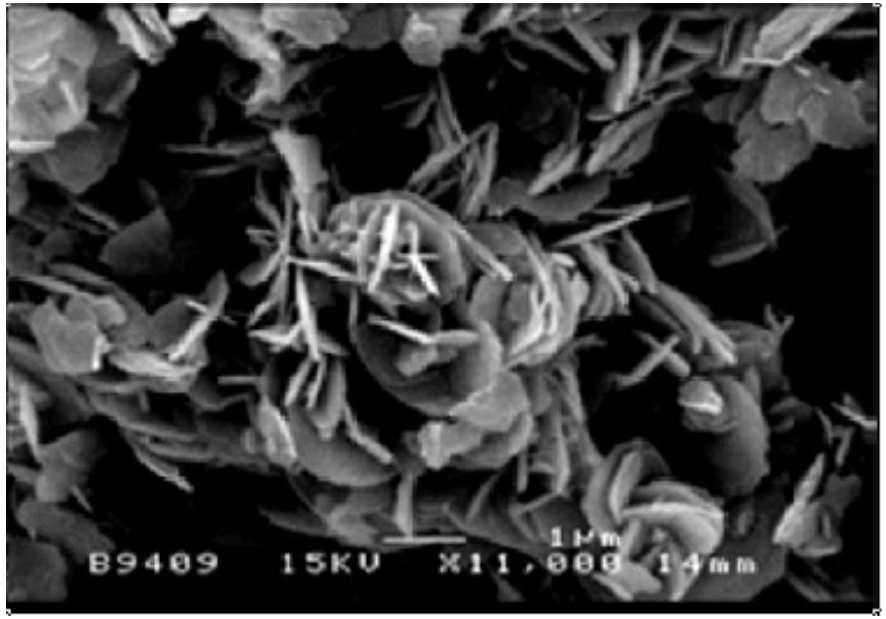
Butane oxidation: the challenge

n-butane **maleic anhydride**

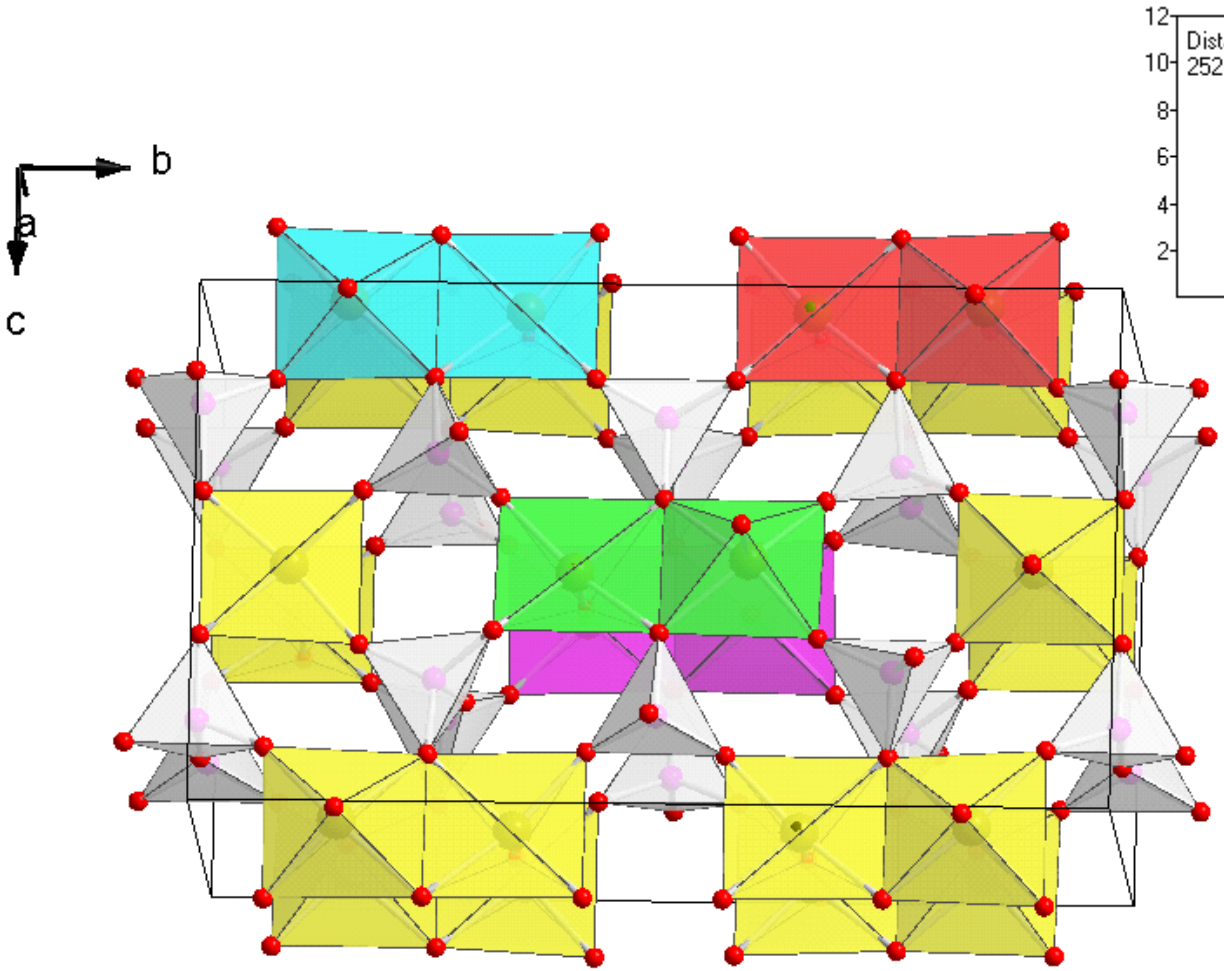
$C_4H_{10} + 7/2\ O_2 \rightarrow C_4H_2O_3 + 4H_2O$

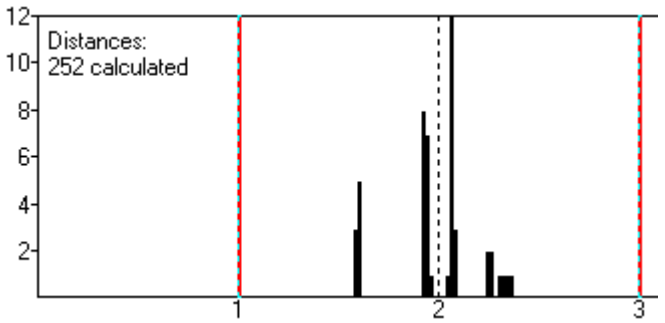


J.-C. Volta, (2000)



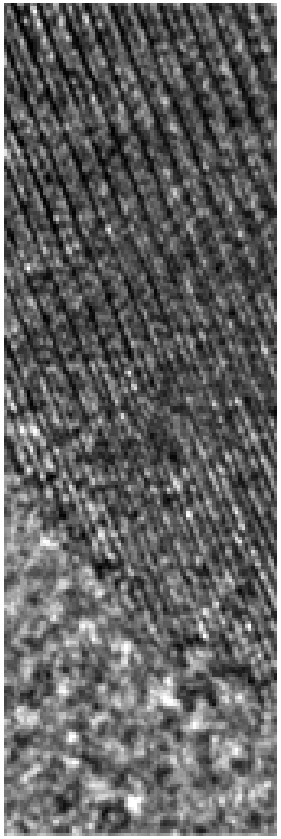
VPP structure: crystal?

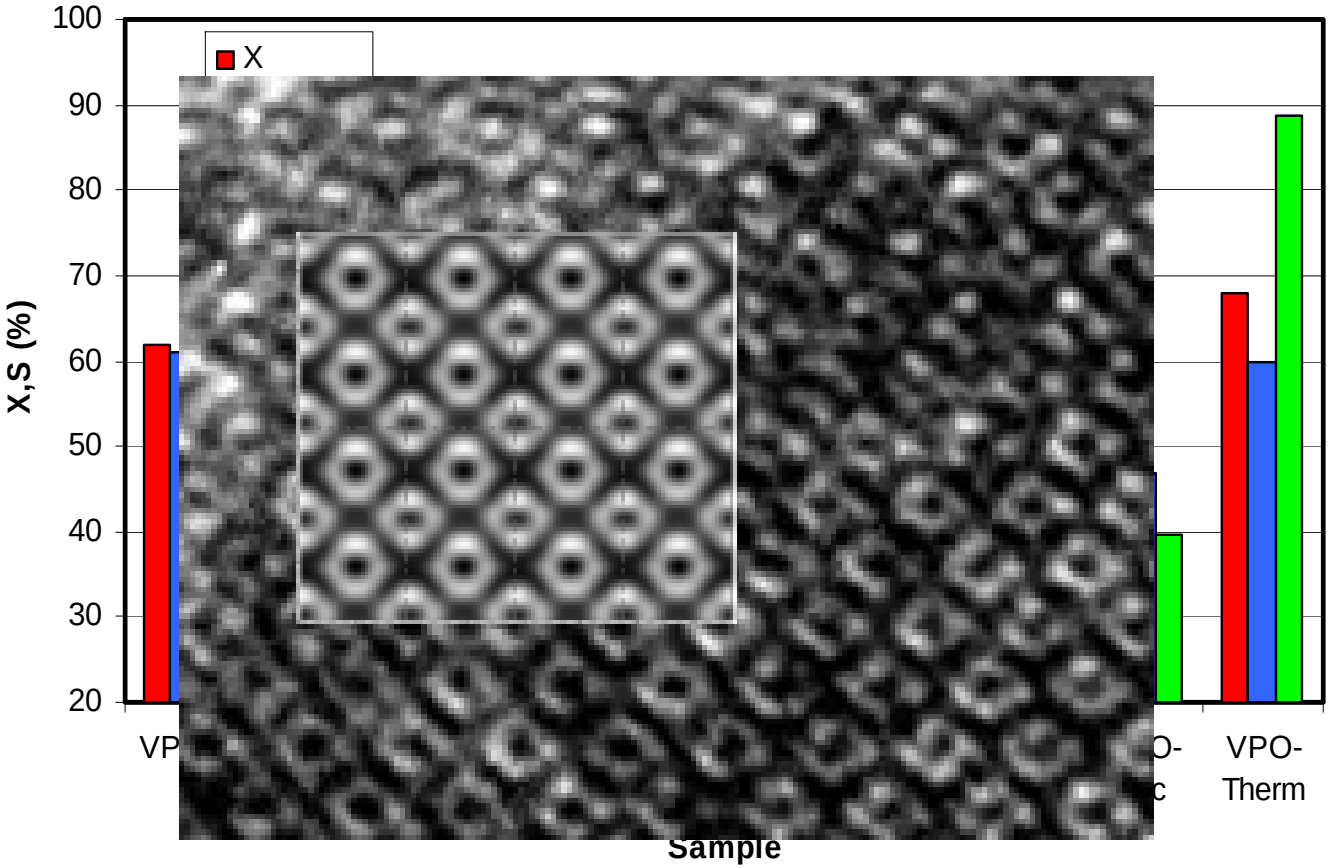


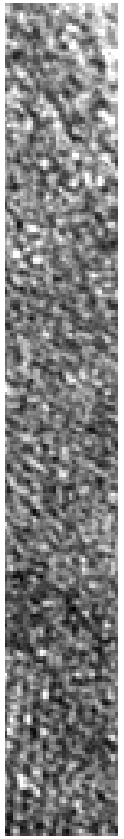


Nguyen et al.
Mat. Res. Bull.,1995

Order and activity





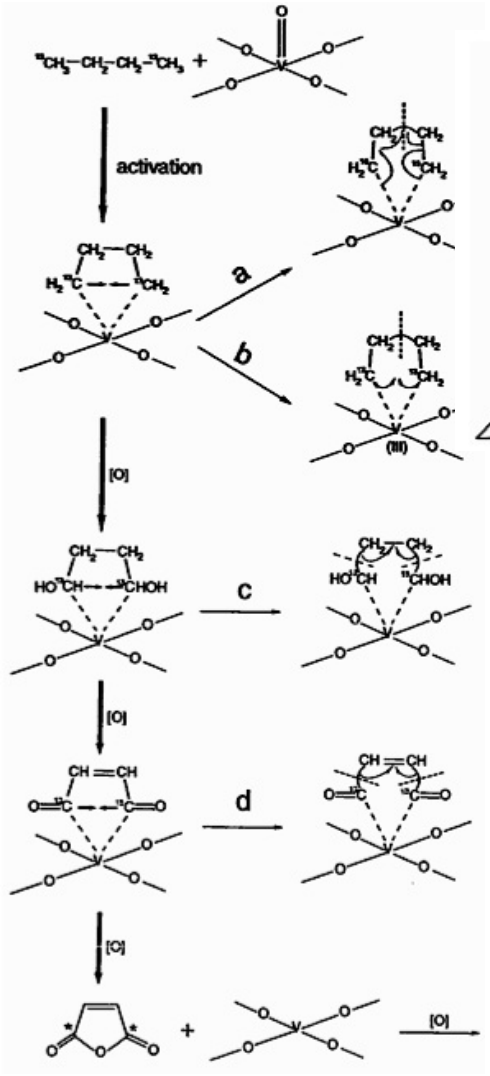


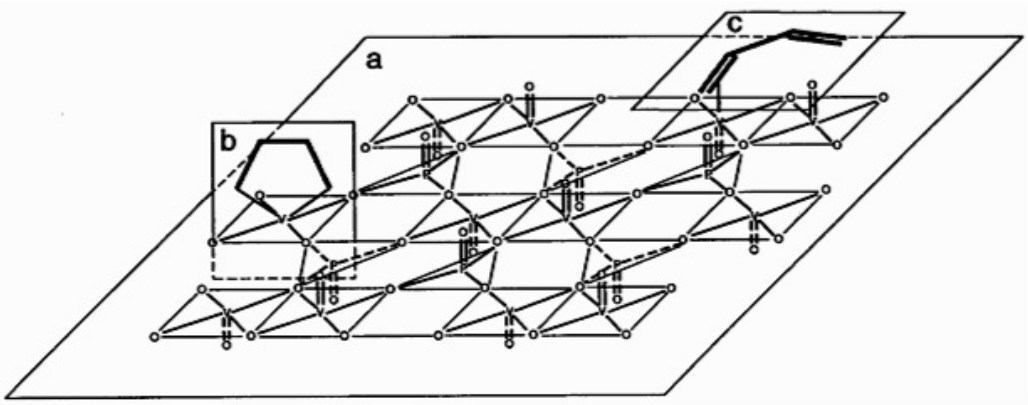
2.5 nm

flop

top

VPO The mystery of a reaction





J|A|C|S
ARTICLES
Published on Web 01/24/2002

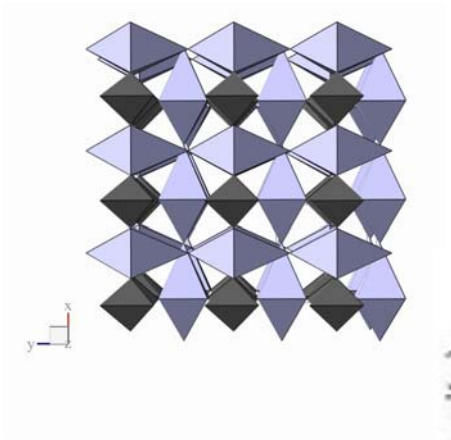
Investigation of the Mechanism of *n*-Butane Oxidation on Vanadium Phosphorus Oxide Catalysts: Evidence from Isotopic Labeling Studies

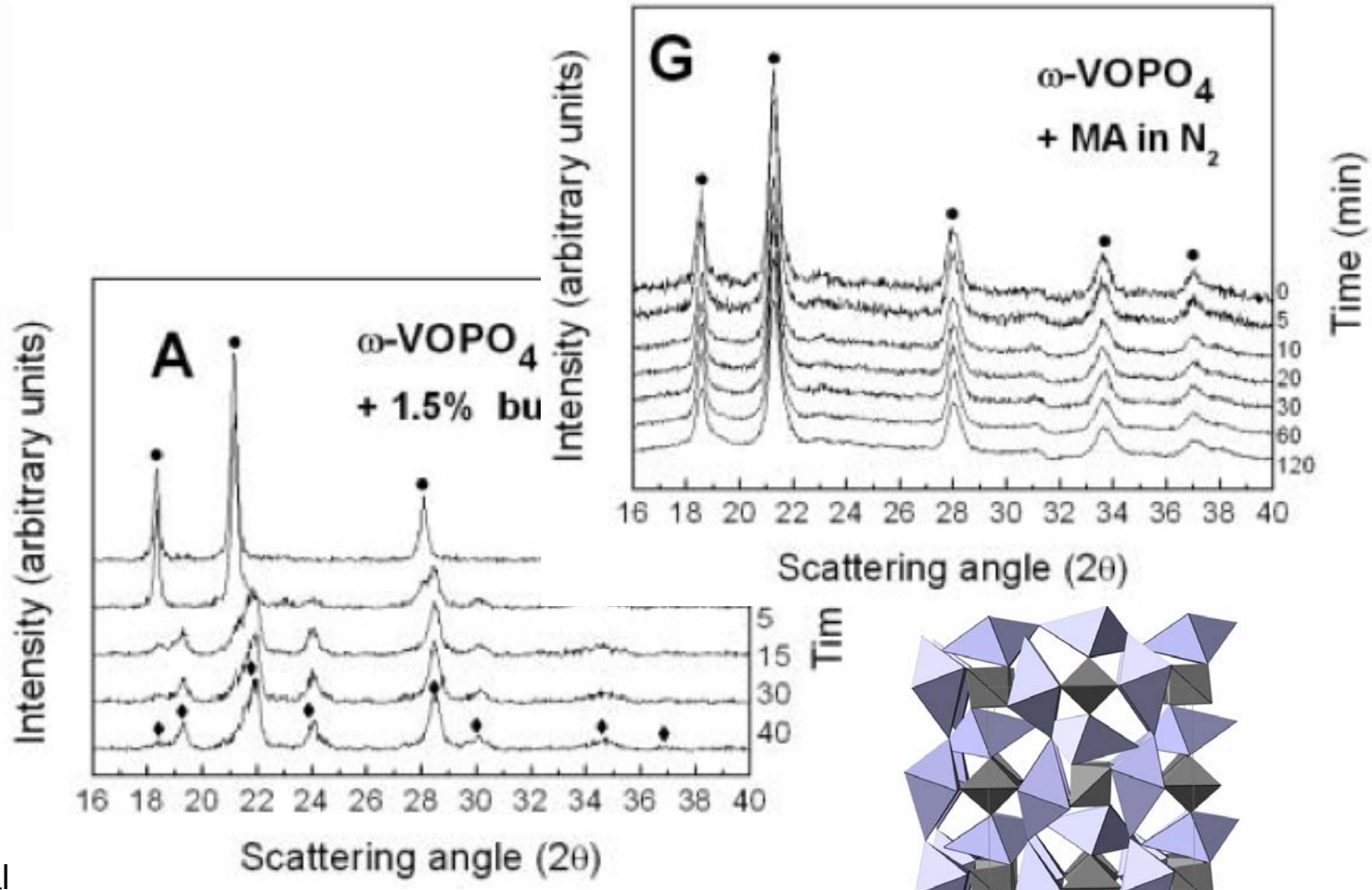
Bin Chen and Eric J. Munson*

Contribution from the Department of Chemistry, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455

Received February 2, 2001

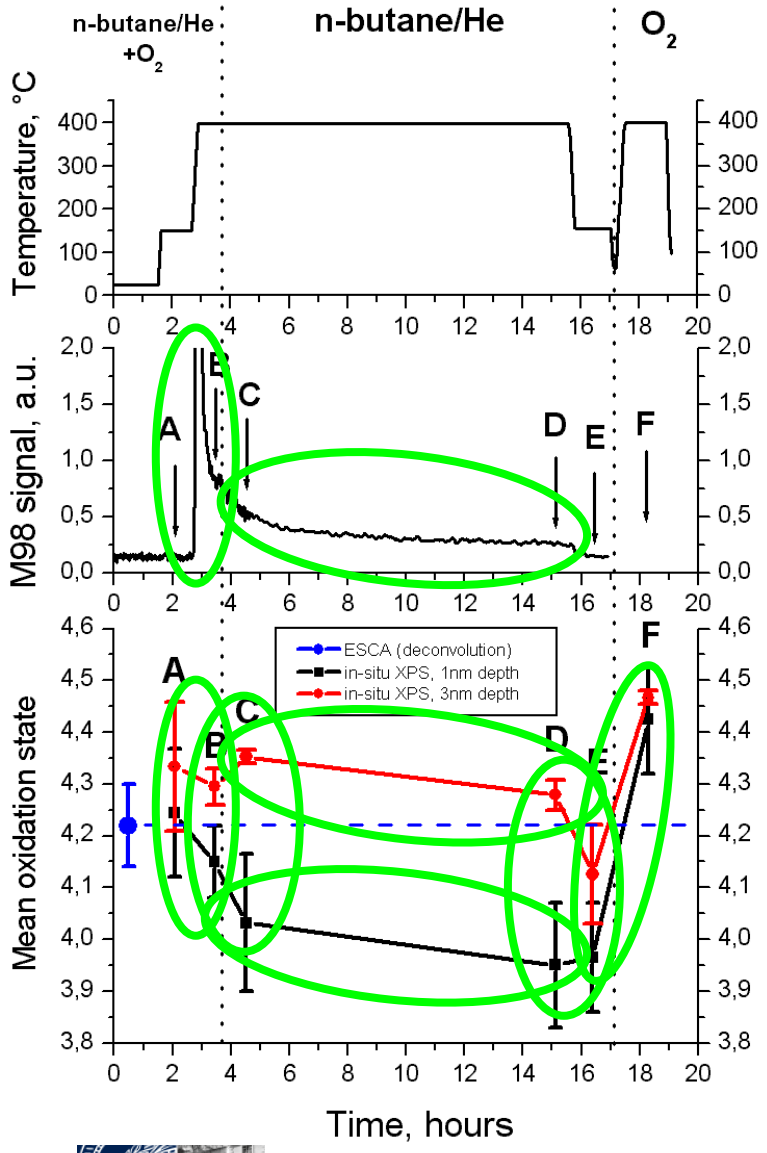
Bulk structural dynamics: The V^{5+} component

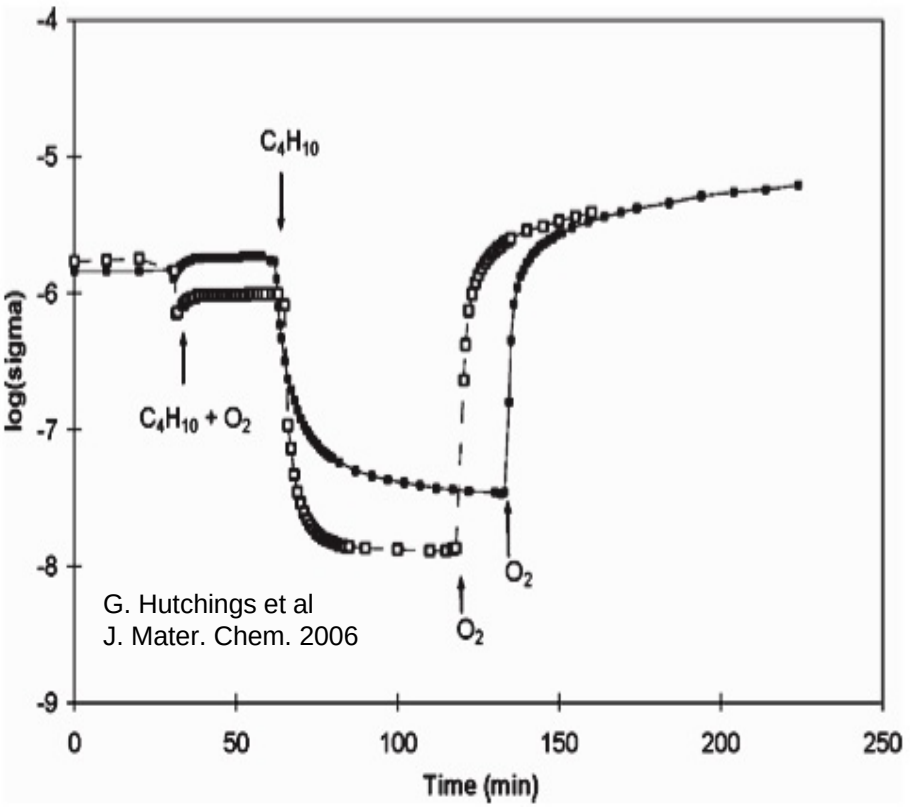




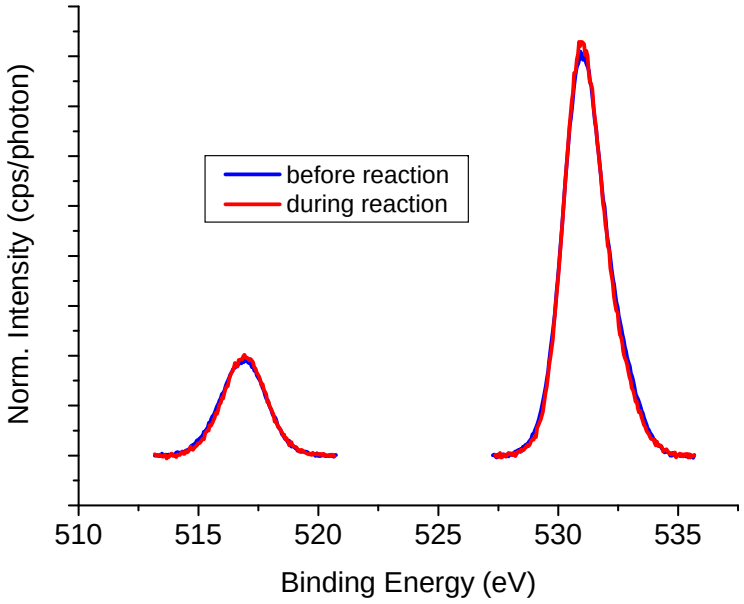
G. Hutchings et al
Science, 2006

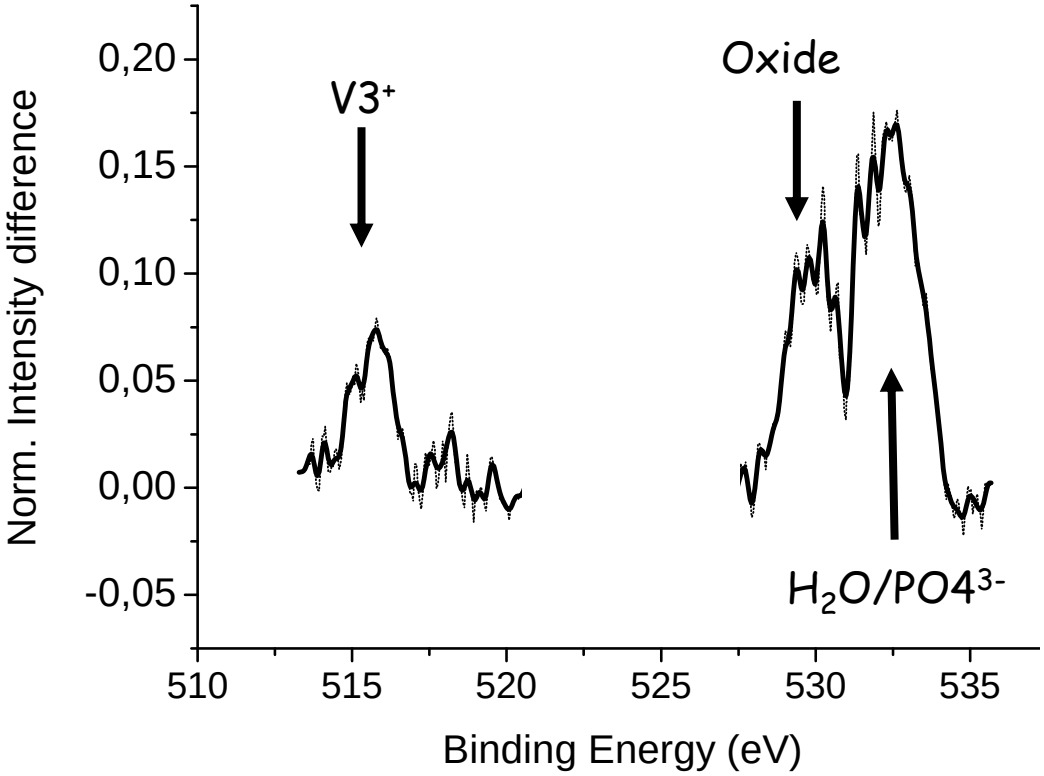
In-situ XPS of VPO in Riser Mode





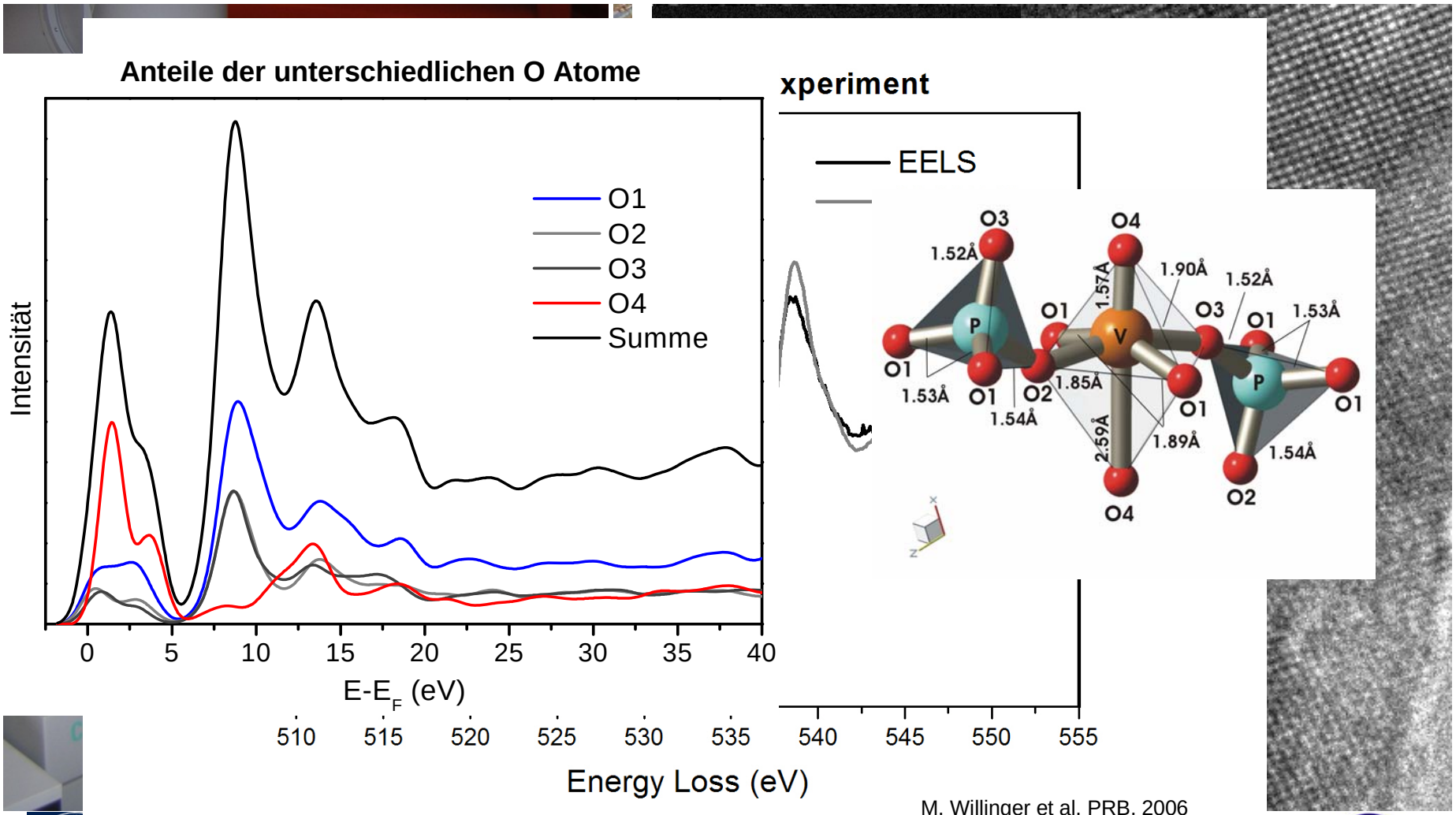
How much of a catalyst is “active” in steady state ?





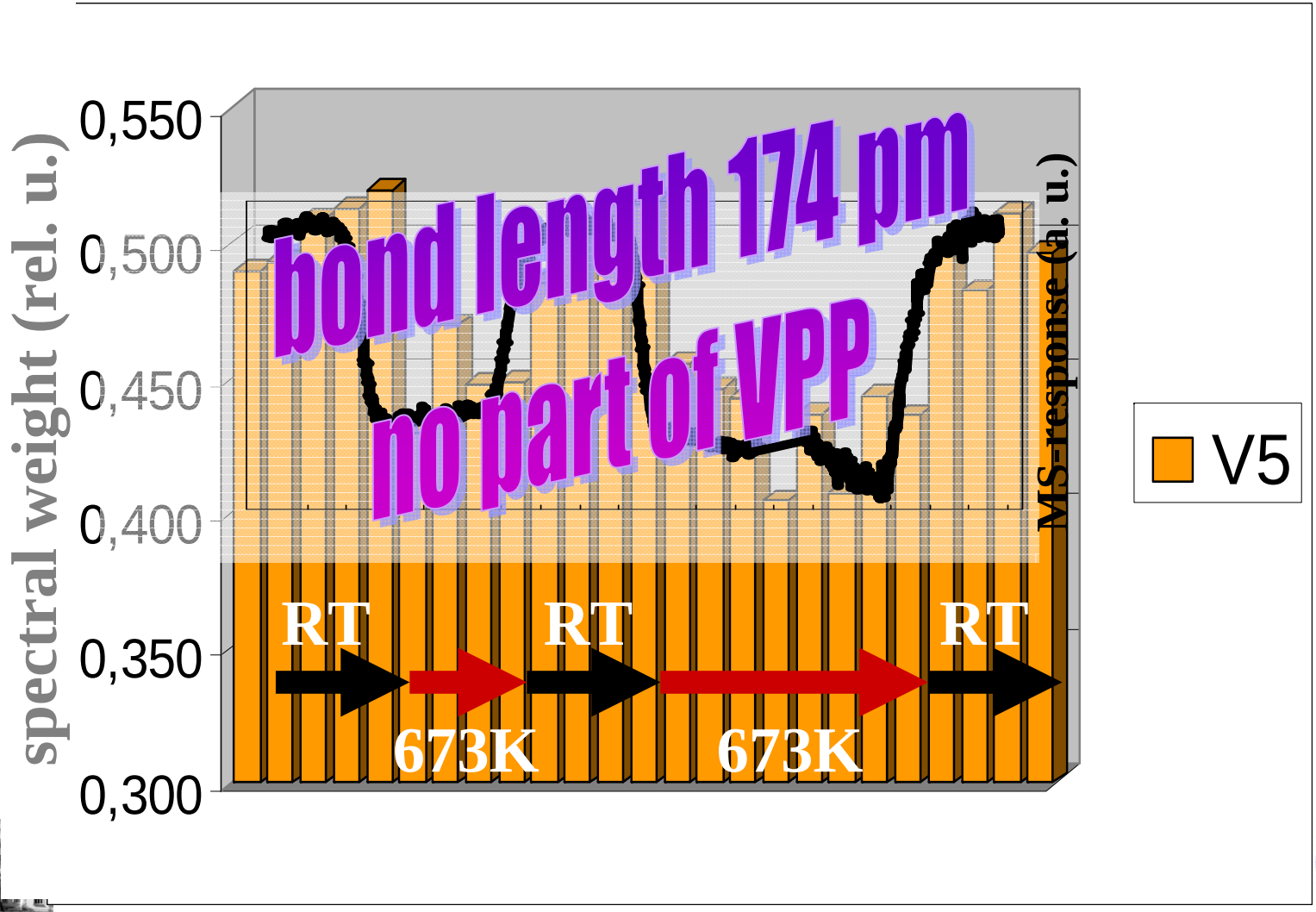
Reversible modifications of a fraction of the surface

Electronic Structure: EELS vs NEXAFS
Spatial vs surface sensitivity



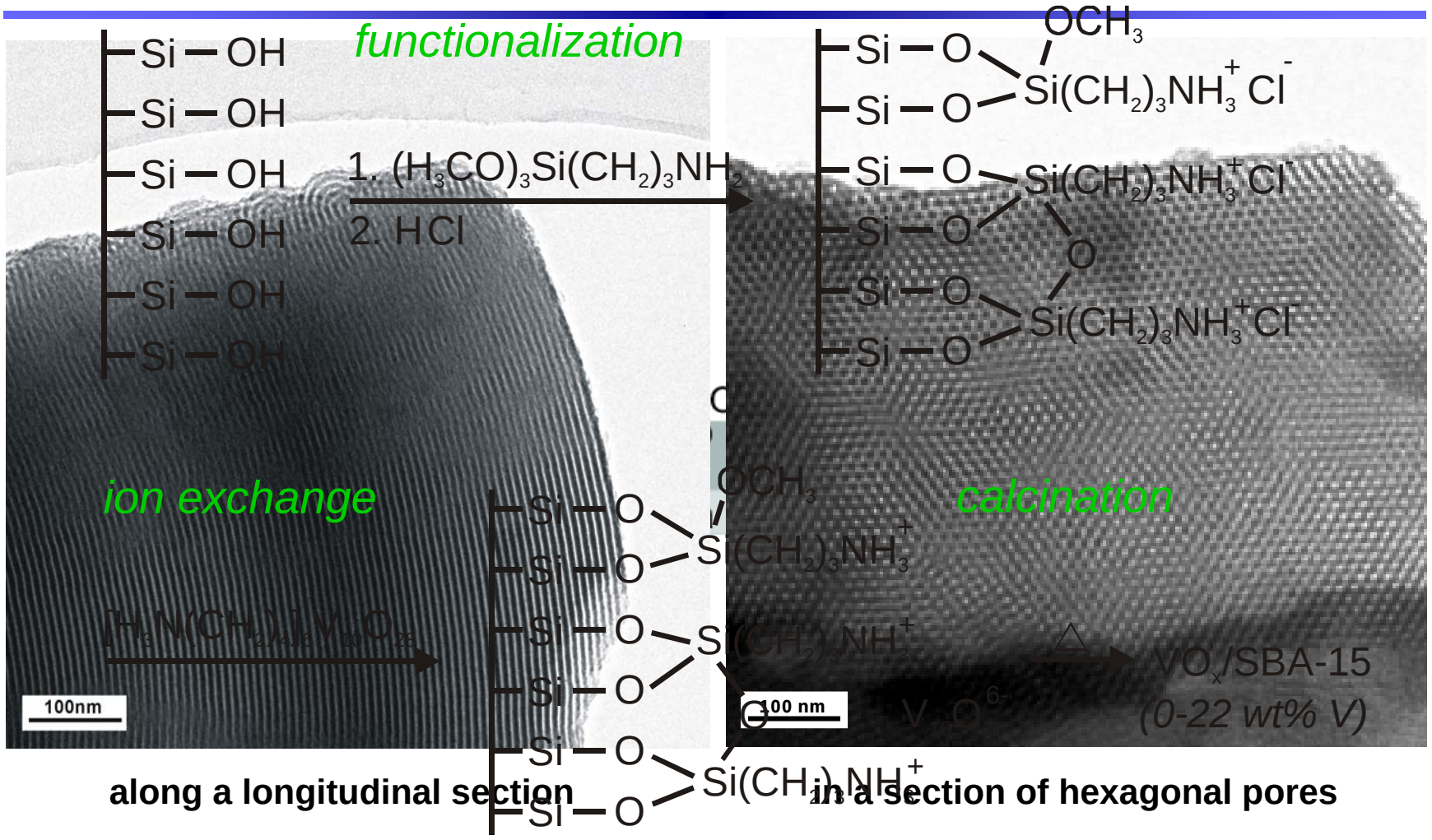
M. Willinger et al. PRB, 2006

Dynamics of the active phase



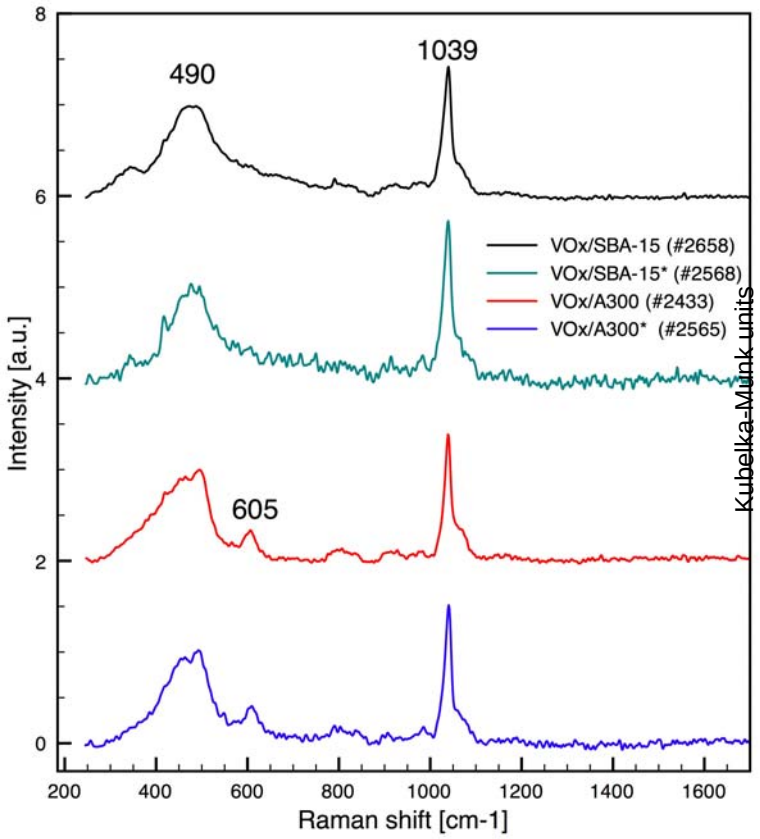
MODEL CATALYSTS

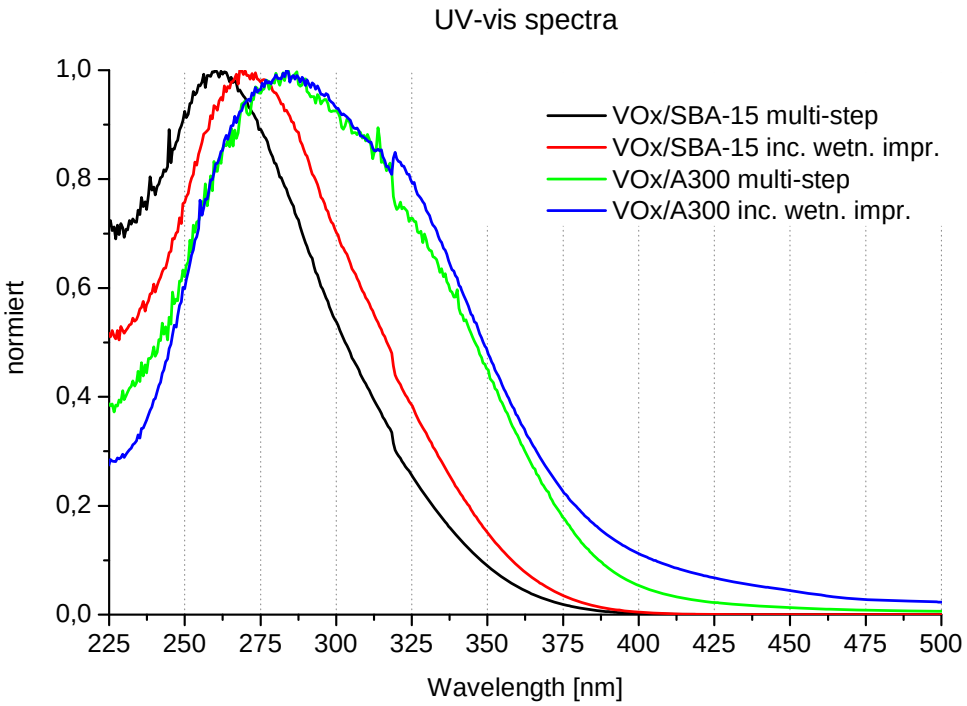
Surface organometallic synthesis: V-SBA 15 as active model



⇨ Silica SBA-15 is a very ordered large-pore (7 nm) material

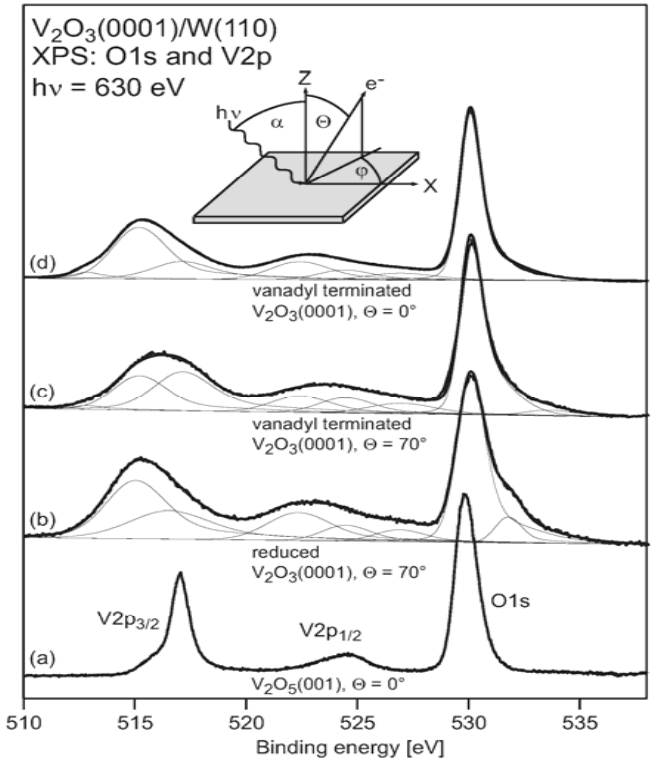
Support effects: “silica”
How sensitive are detection methods?

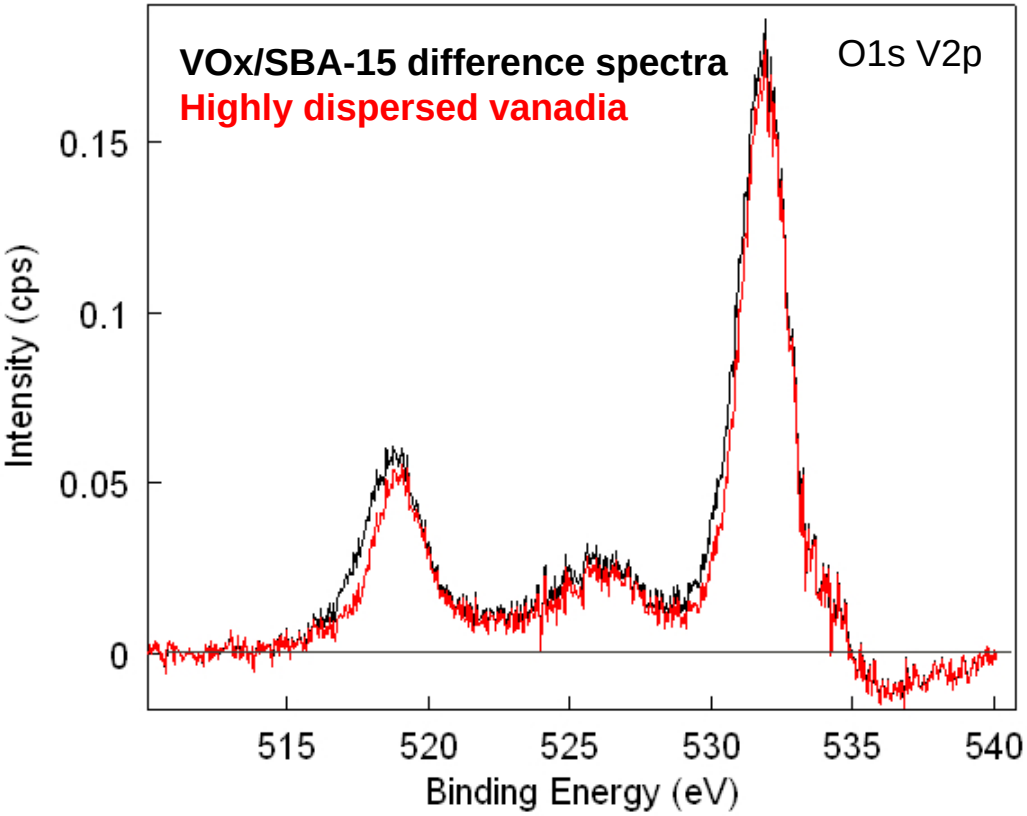




Two impregantion methods on powder and mesoporous silica

The activated state

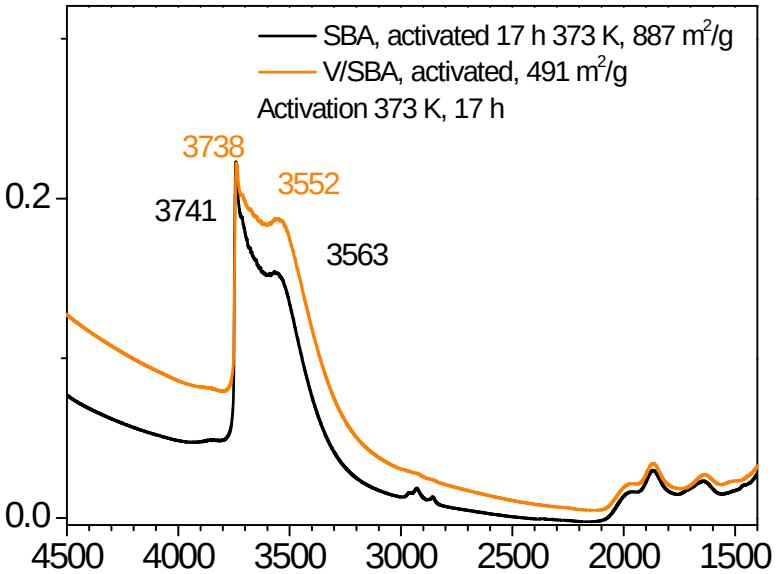


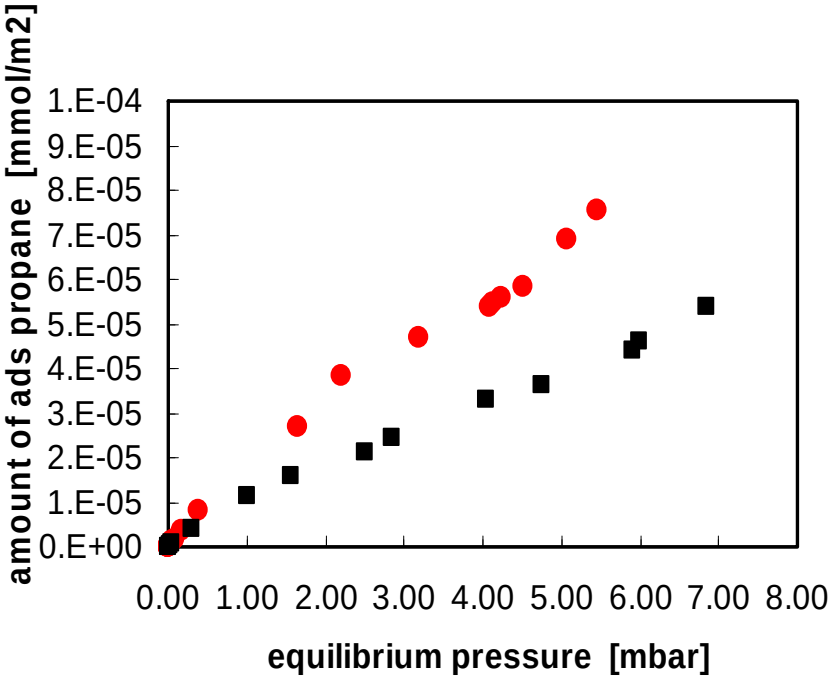


Freund et al., Surf. Sci. 539, 2003

XPS sees a local coordination similar to pyramidal but with a reduced electron density than in V_2O_5 giving rise to a relaxation shift ("naked V atom")

0.8V/SBA 15: propane adsorption





Per surface area, the V-containing catalyst adsorbed more propane.

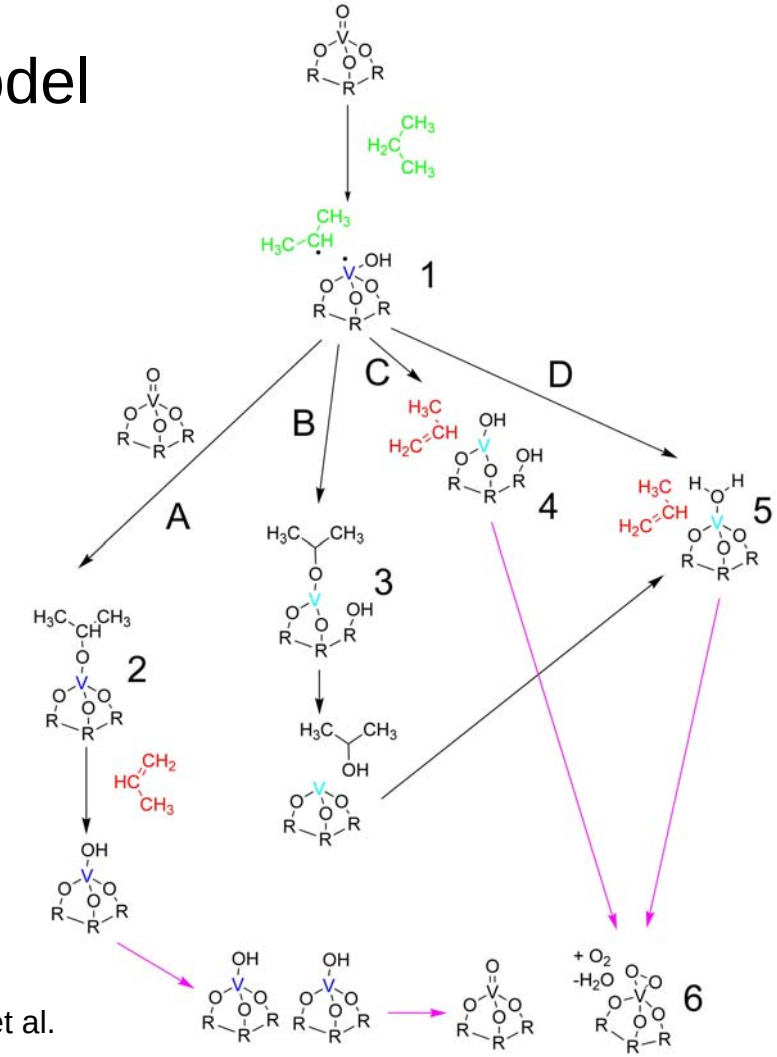
→Δn_{ads} ~ 0.5 µmol/m² Si-OH + Si-O-V-OH / V-O-V-OH

→ not detectable in the IR spectrum

10^{10} sites per mm²

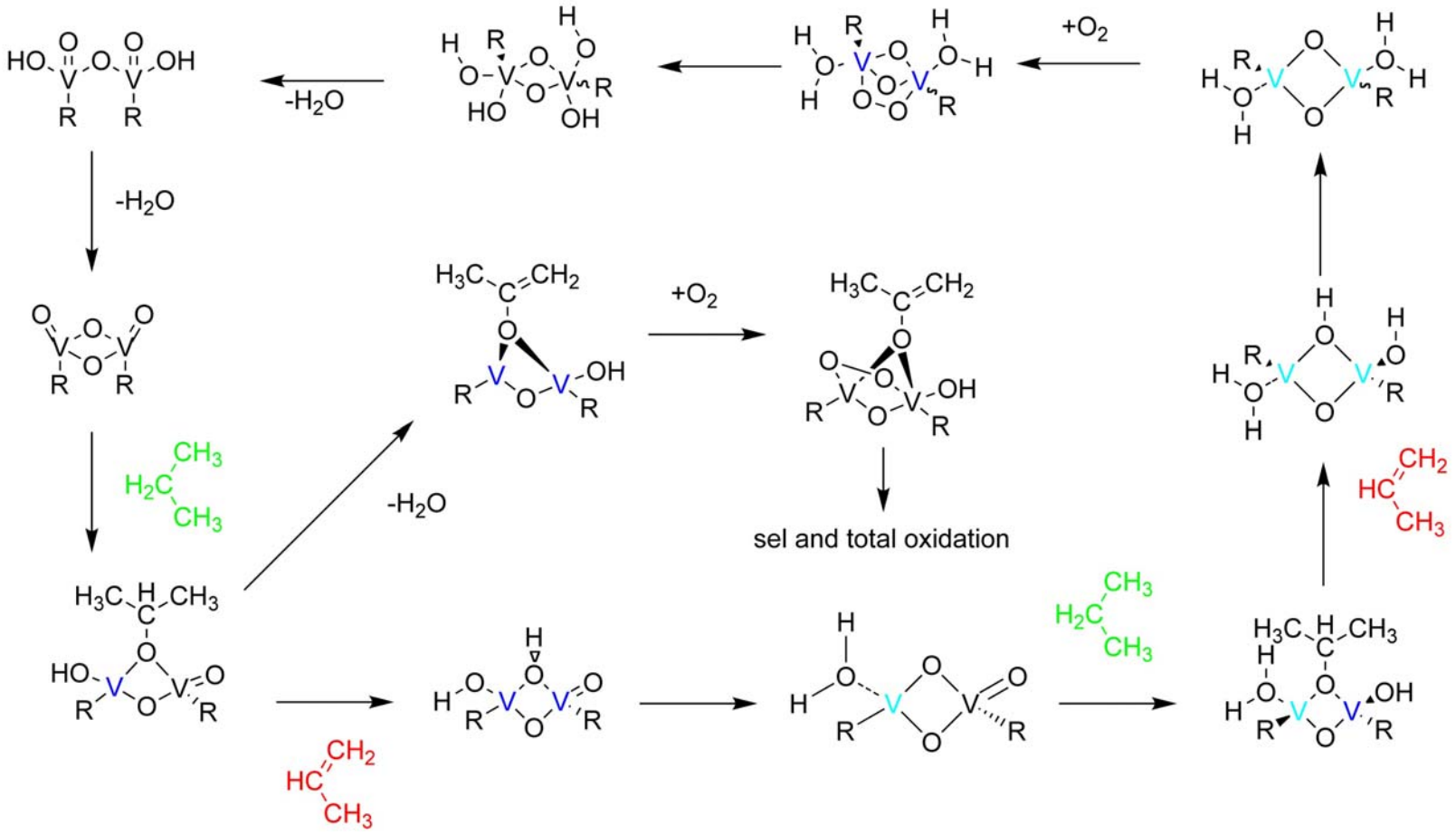
Reaction pathway

Single site model



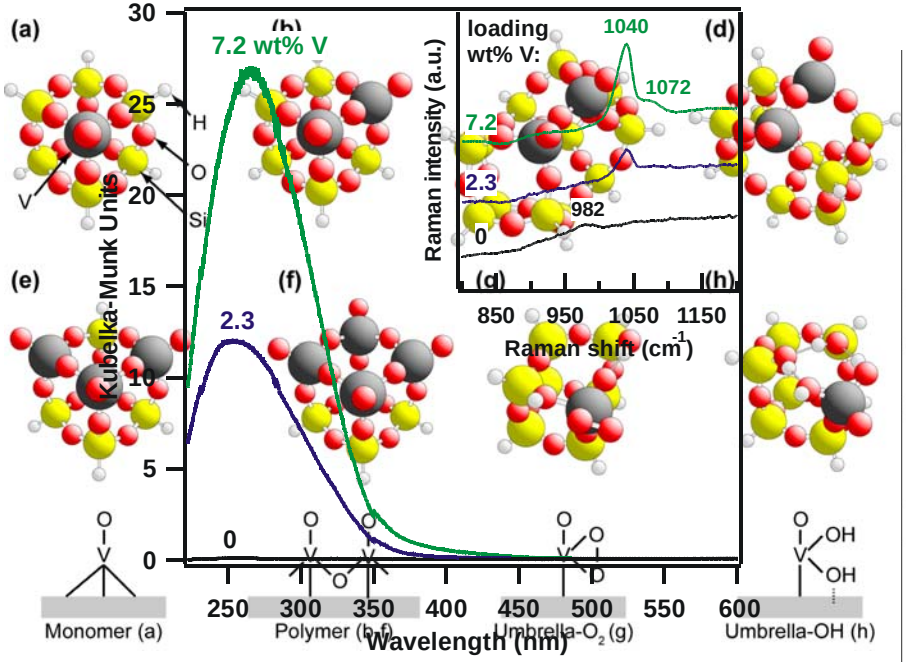
J. Sauer et al.

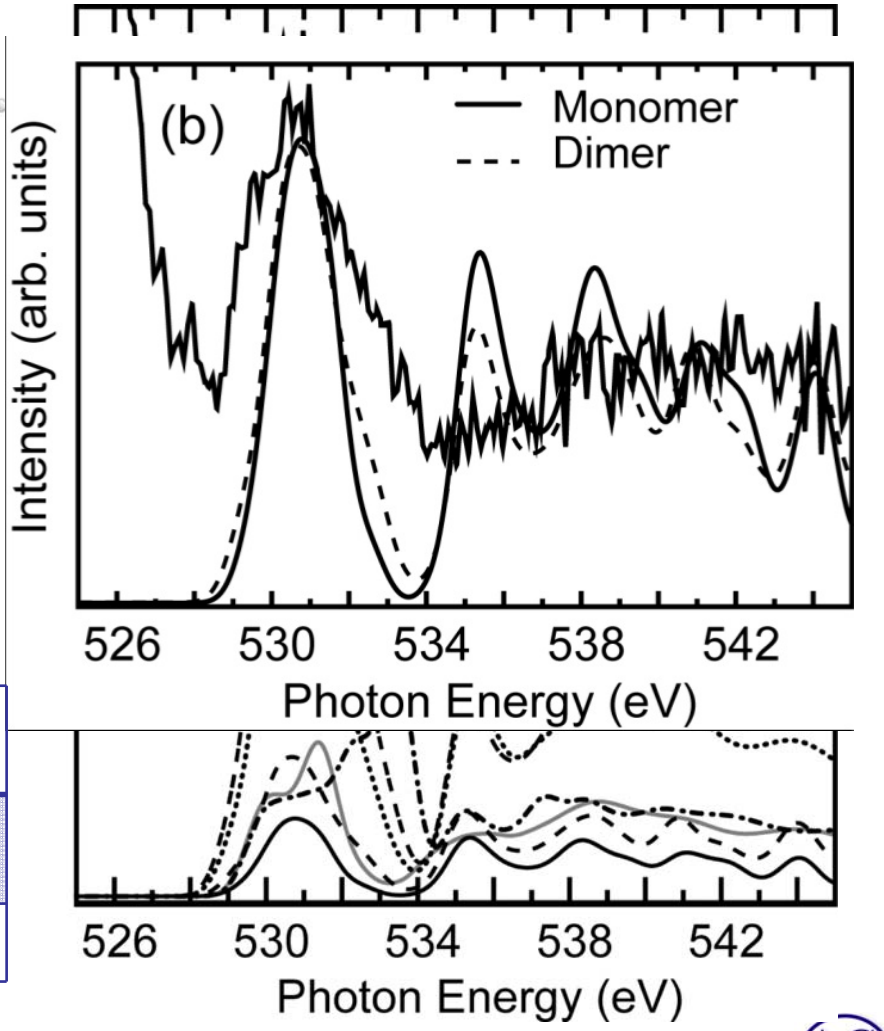
Reaction pathway



Only sites with V-O-V allow for facile catalytic cycles

V-SBA15: a functional model





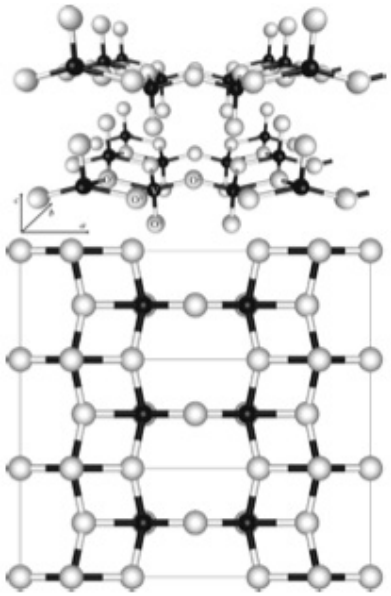
Sample	X C3H8 (%)	S AA (%)	S C3H6 (%)	S COX (%)
3.3 wt V-SBA15	8	84	10	4
SBA 15	0	0	0	0

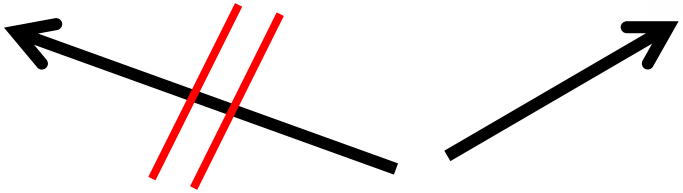
C. Hess, M. Cavallieri, K. Hermann

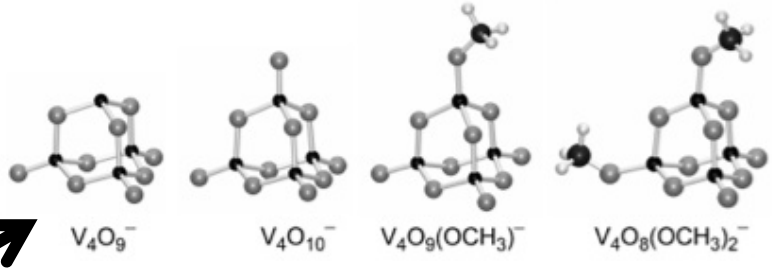
Department of Inorganic Chemistry
www: fhi-berlin.mpg.de

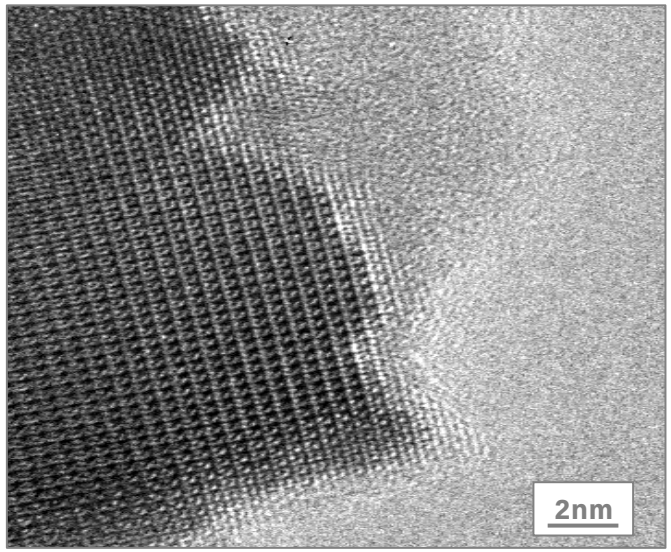
CONSEQUENCES OF A CASE STUDY: V_XO_Y AS CATALYST

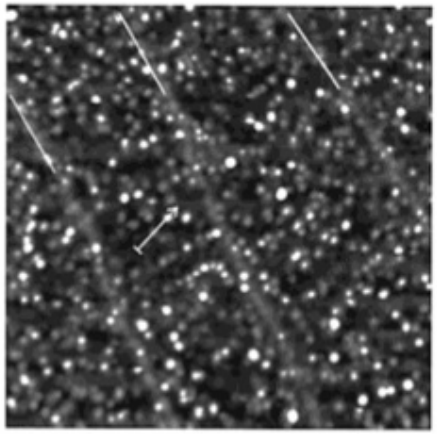
What have we learnt





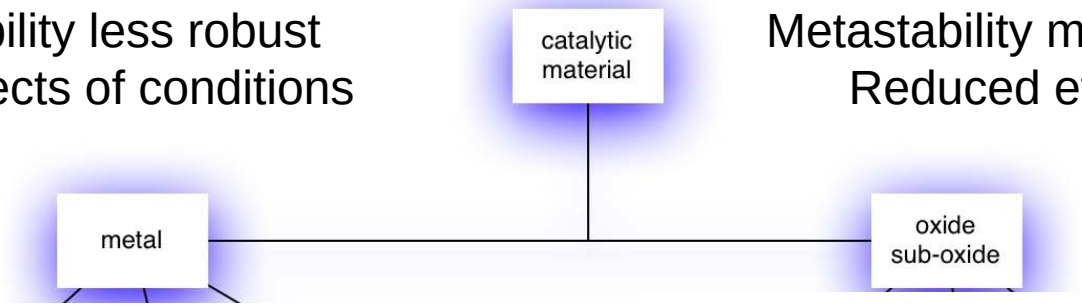






Termination

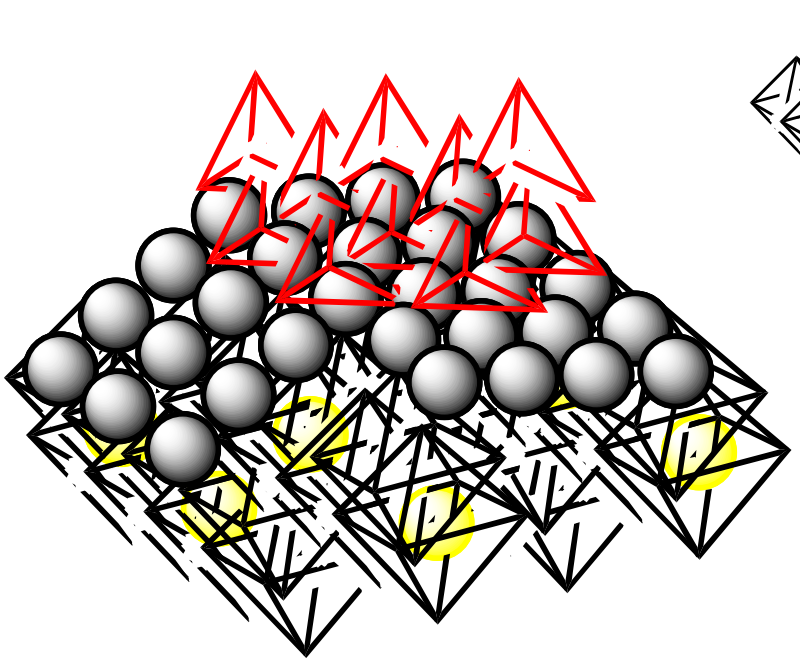
Metastability less robust
Strong effects of conditions



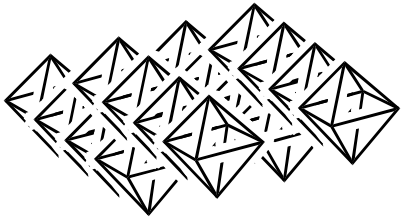
Metastability more robust (covalency)
Reduced effects of conditions

Analytical challenge of identification: only in situ, sub-monolayer

Compositional dynamics

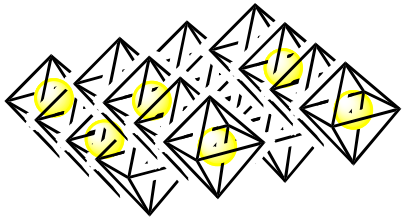


working catalyst

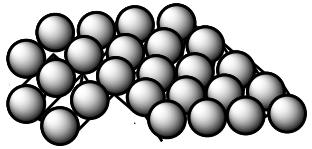


conductor

active phase

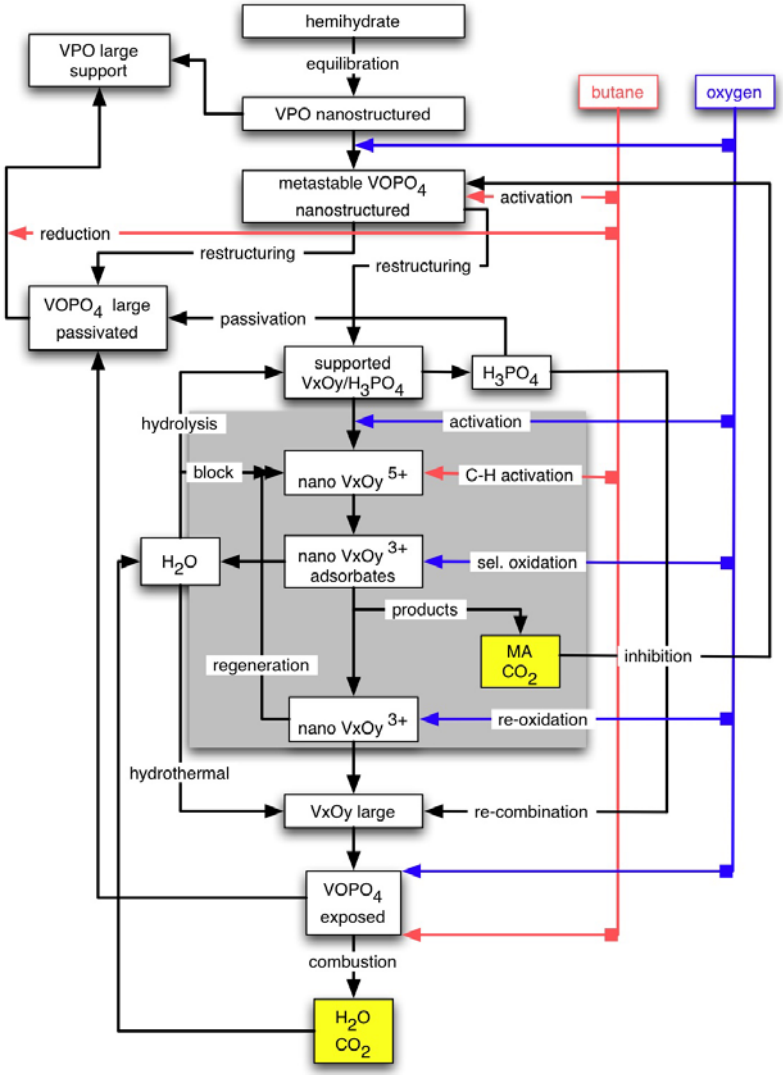


bulk insulator



insulating segregate

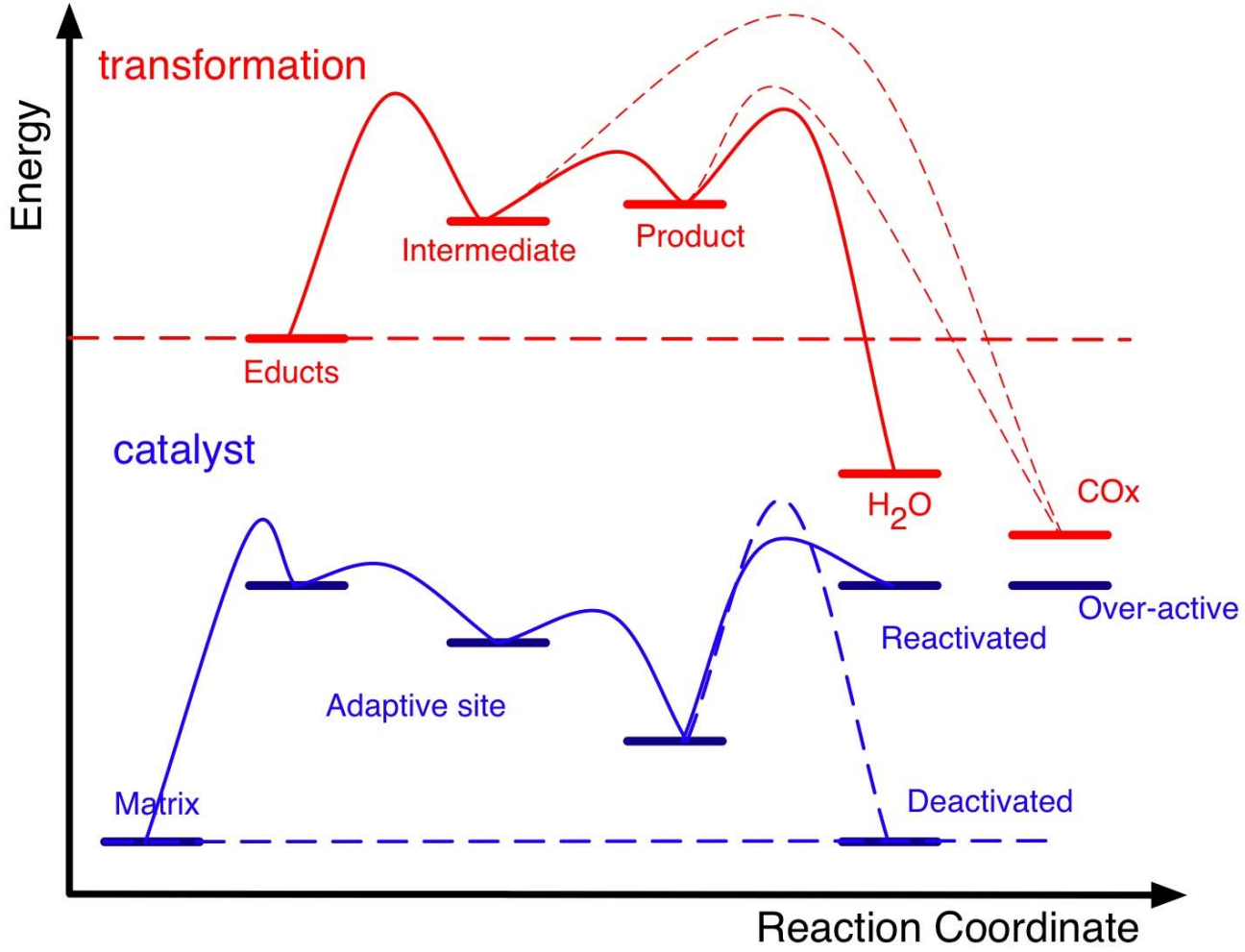
Catalyst dynamics



Active sites in a high performance catalyst

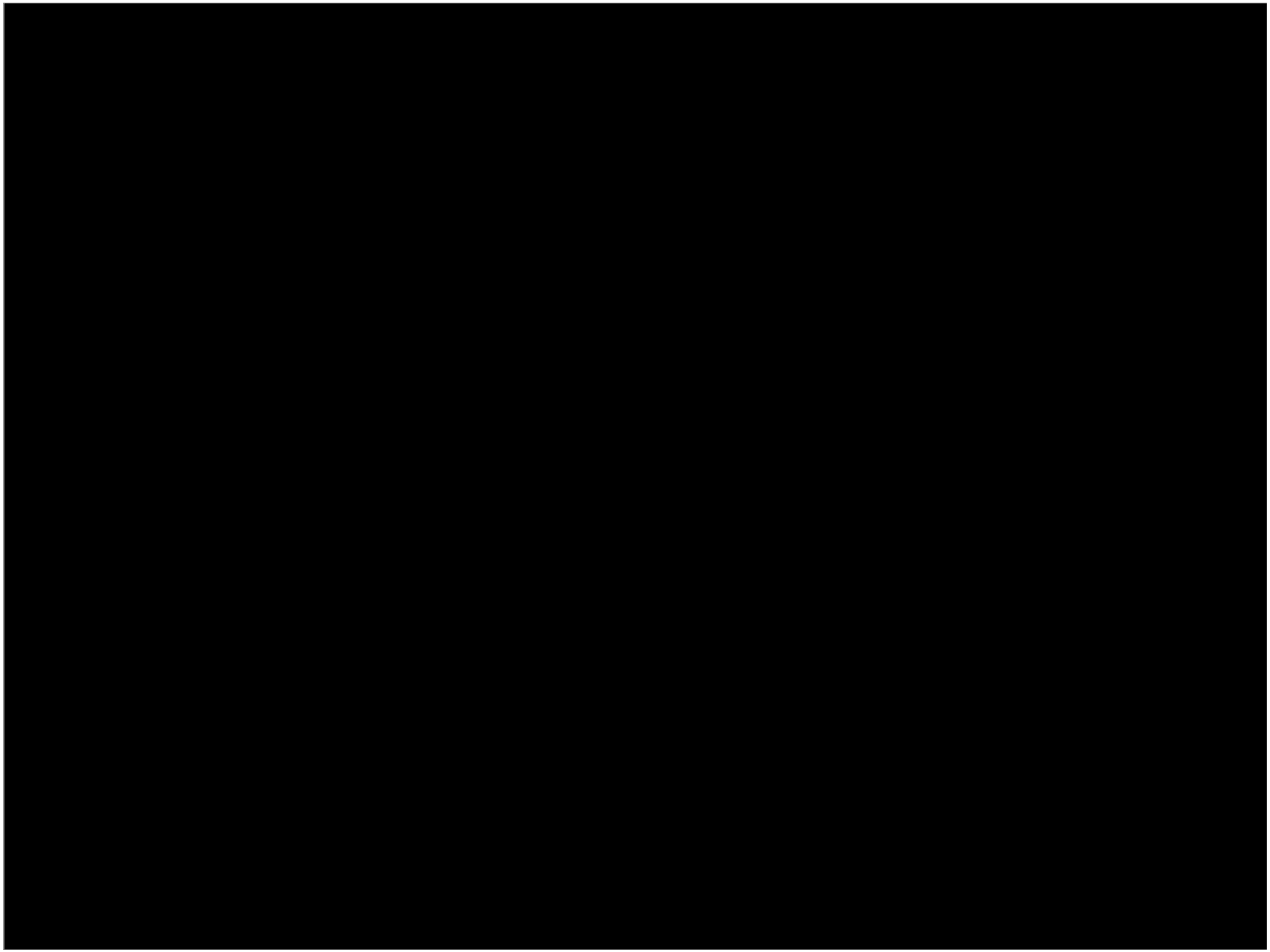
- An active heterogeneous catalyst contains adaptive sites for reaction.
- They adapt their structure according to the local chemical potential and guarantee selective operation on progressively more reactive adsorbates.
- The complex structure of the precursors is required to fix the chemical potential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

Coupling of transformation and material

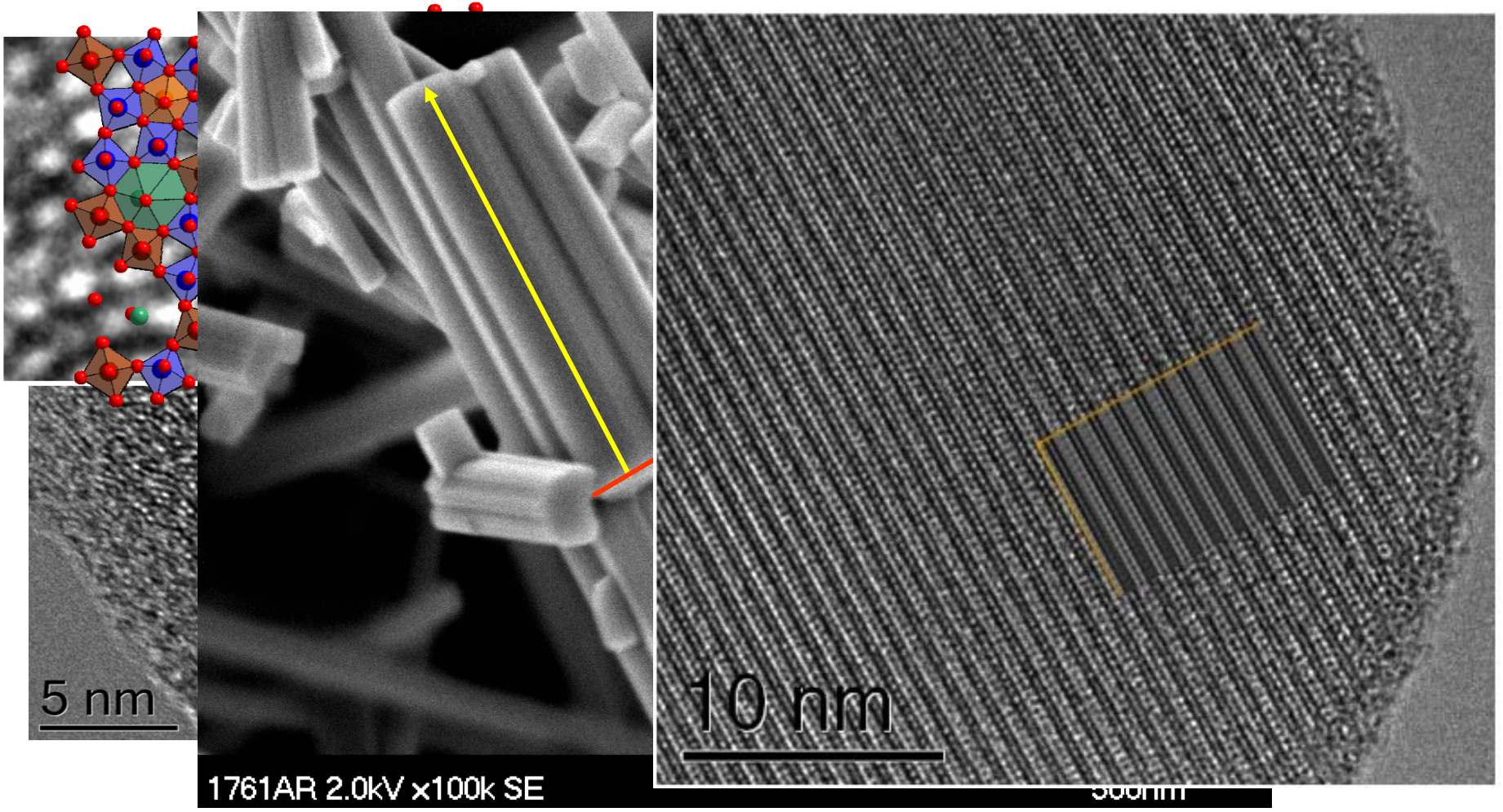


Dynamics: Formation and regeneration of adaptive sites

Thank You



M1 phase in C_3H_8 selective oxidation

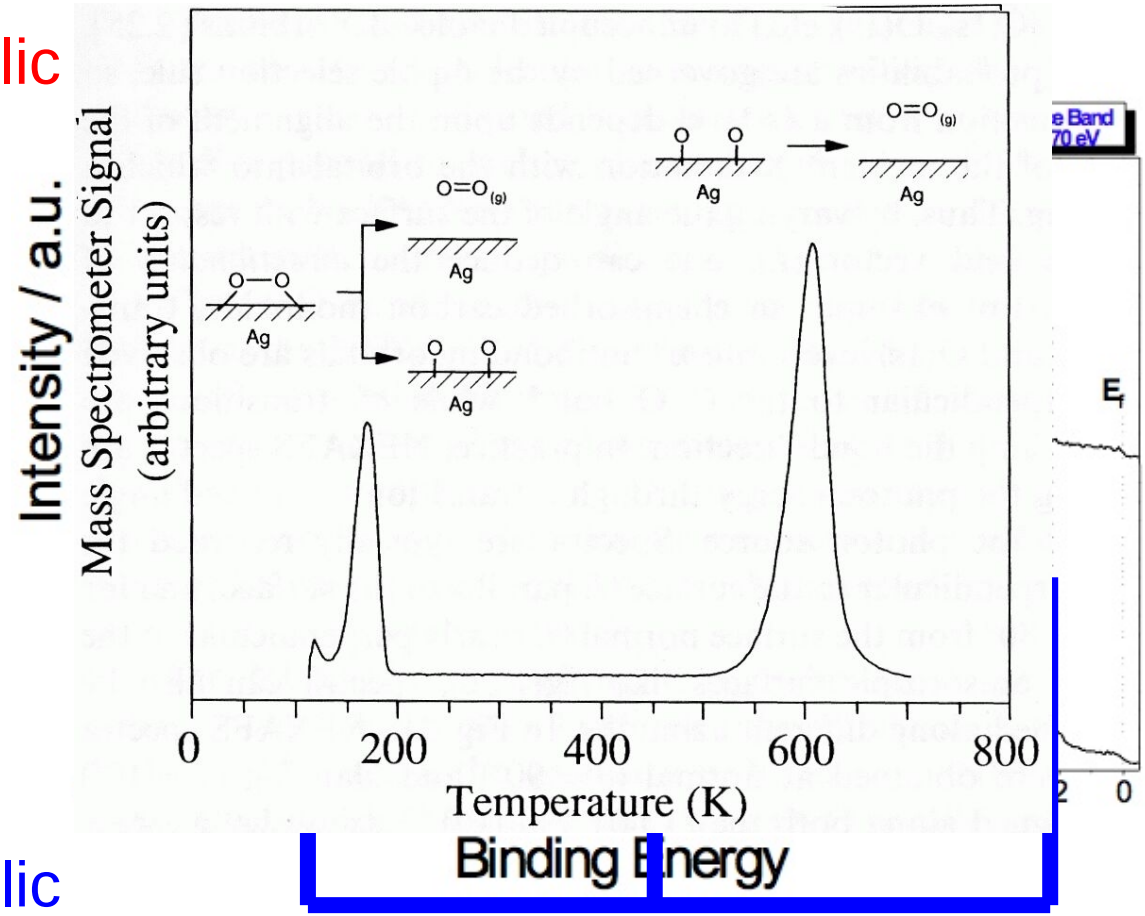


Activity scales not with SA (001); nature of active sites?

Department of Inorganic Chemistry
www: fhi-berlin.mpg.de

“Atomic oxygen” on silver

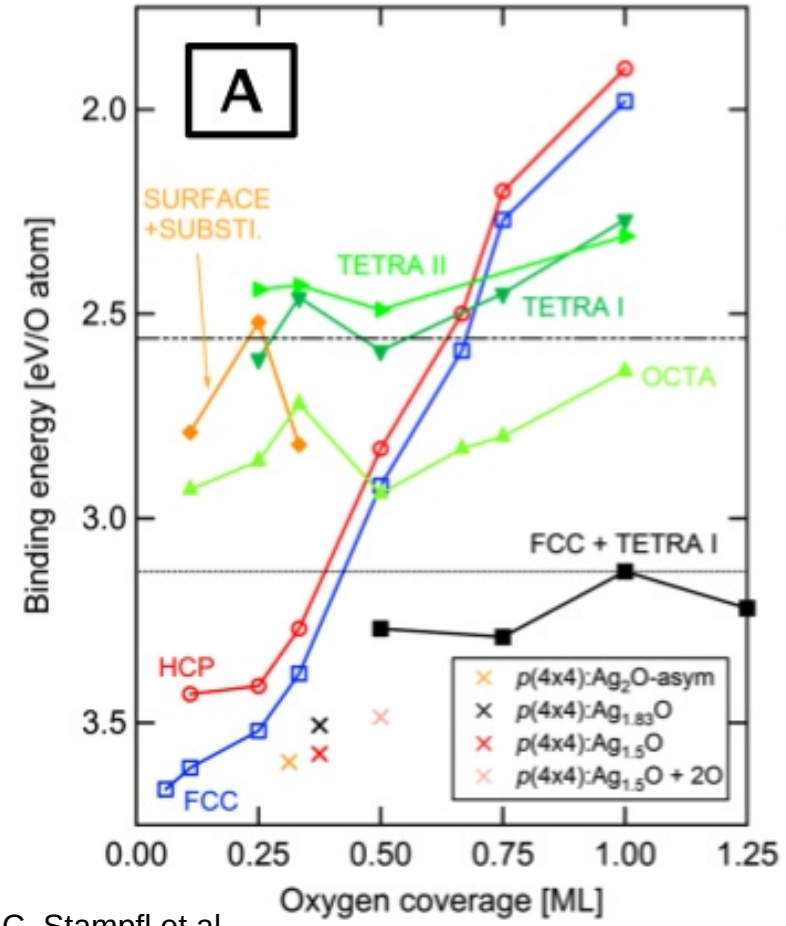
electrophilic



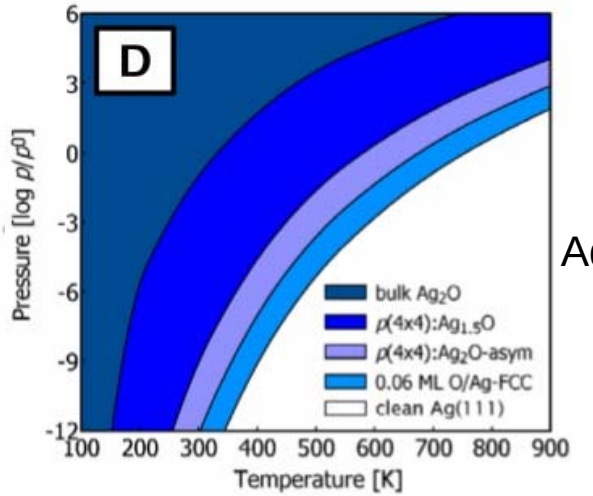
nucleophilic

R.J. Madix , J.T. Roberts, Springer Series in Surface Reactions, Vol. 34, 1994, p.9

Theory of Ag-O interaction

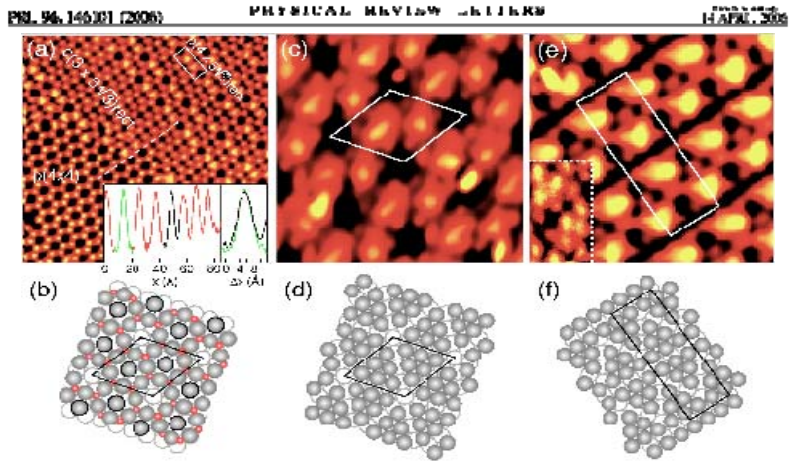


C. Stampfl et al.
J.Phys.C, 2008



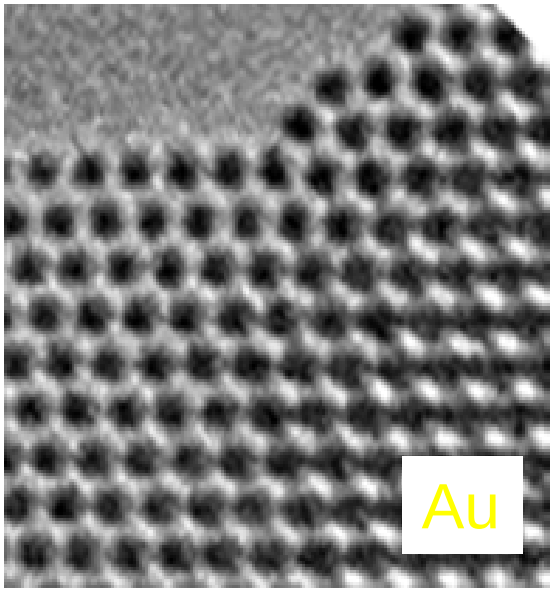
In decreasing stability:

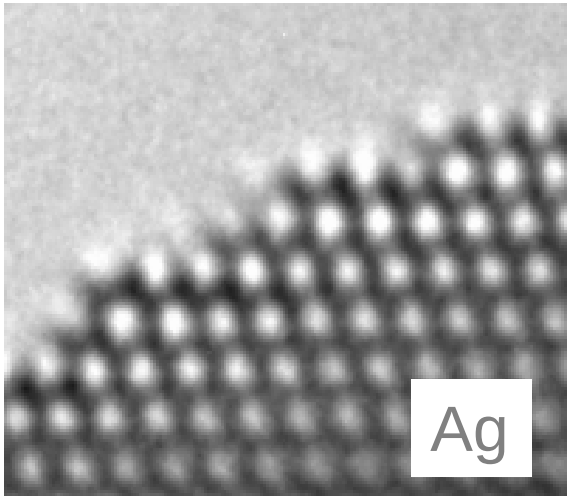
Adsorbed
Adsorbed over sub-surface
Surface oxide
Bulk oxide

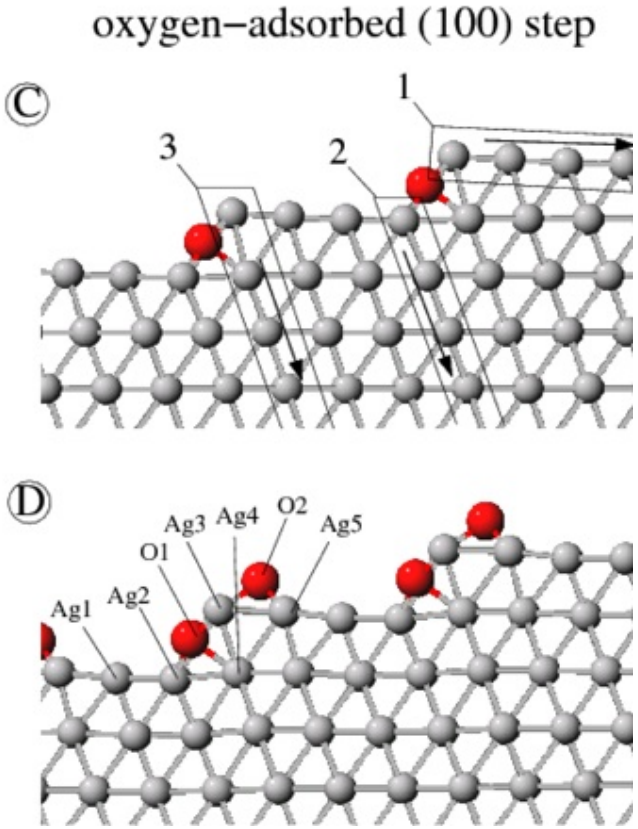


J. Schnadt,1 A. Michaelides,2 J. Knudsen,1 R. T. Vang,1 K. Reuter,2 E. Lægsgaard,1
M. Scheffler,2 and F. Besenbacher1 PRL 2006

Defects: Oxo-philicity







T. Jakob
M. Scheffler

Department of Inorganic Chemistry
www: fhi-berlin.mpg.de

Mo-V compounds for C3,C4 oxidation