Fritz Haber Institut der MPG

R. Schlögl

- D. Su
- A. Knop-Gericke
- M. Hävecker
- T. Hansen
- T. Jakob (TH)
- M. Scheffler (TH)
- T. Ressler (TUB)

DFG

IDECAT
Integrated Design of Catalytic Nanomaterials for a Sustainable Production

BESSY

unicat

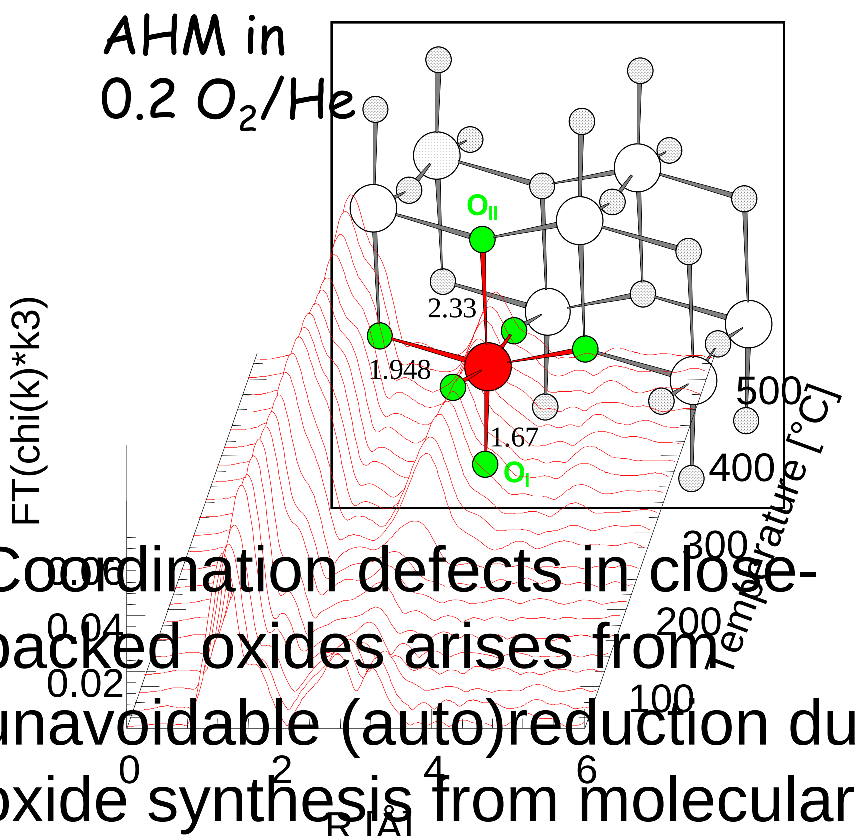
www: fhi-berlin.mpg.de

AC FHI

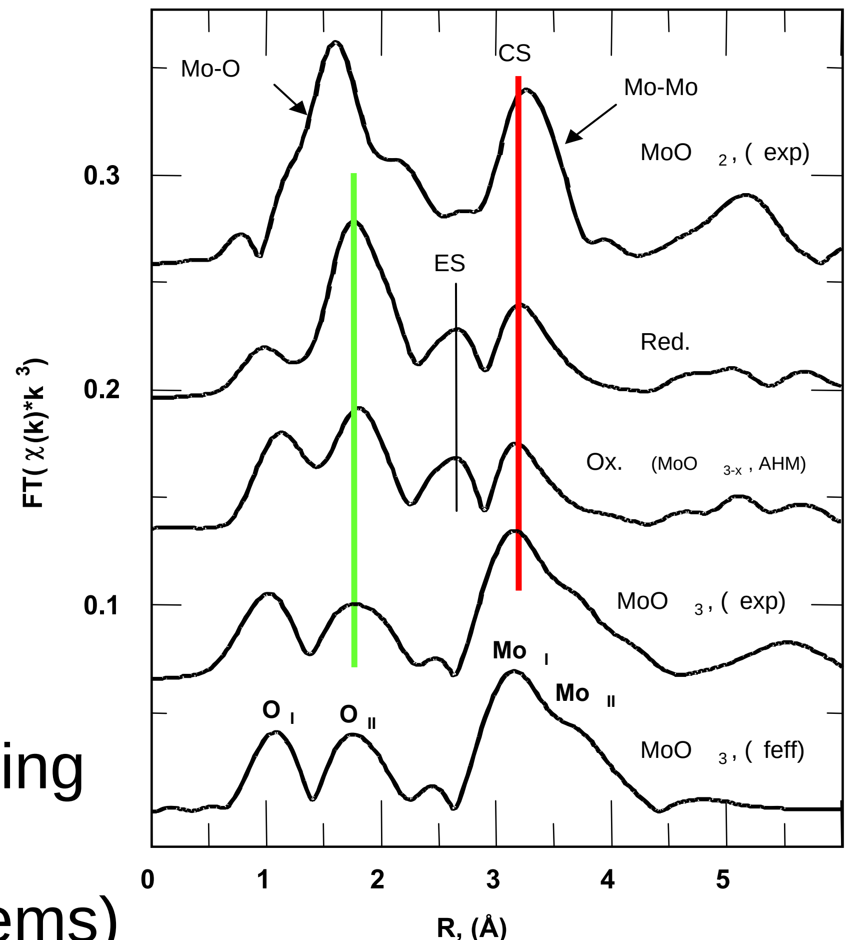
Catalytic Materials

- Catalysts are dynamically behaving matrices containing metastable minority structural elements called “active sites” (Taylor).
- Most of it is not active (bulk).
- Even most of the surface (Langmuir) is not active.
- Active are high energy structures deviating from the equlibrium system: “defects”.
- There are many types of defects besides the surface (complexity).

Identification of defects in polycryst. MoO_3



Coordination defects in close-packed oxides arises from unavoidable (auto)reduction during oxide synthesis from molecular precursors (absent in PVD systems)



The function of a catalyst: The single crystal approach (G. Ertl)

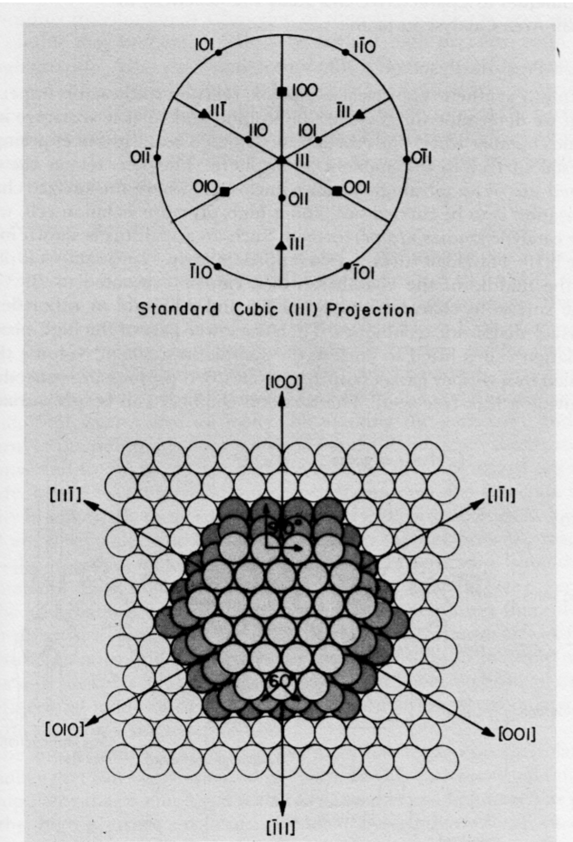
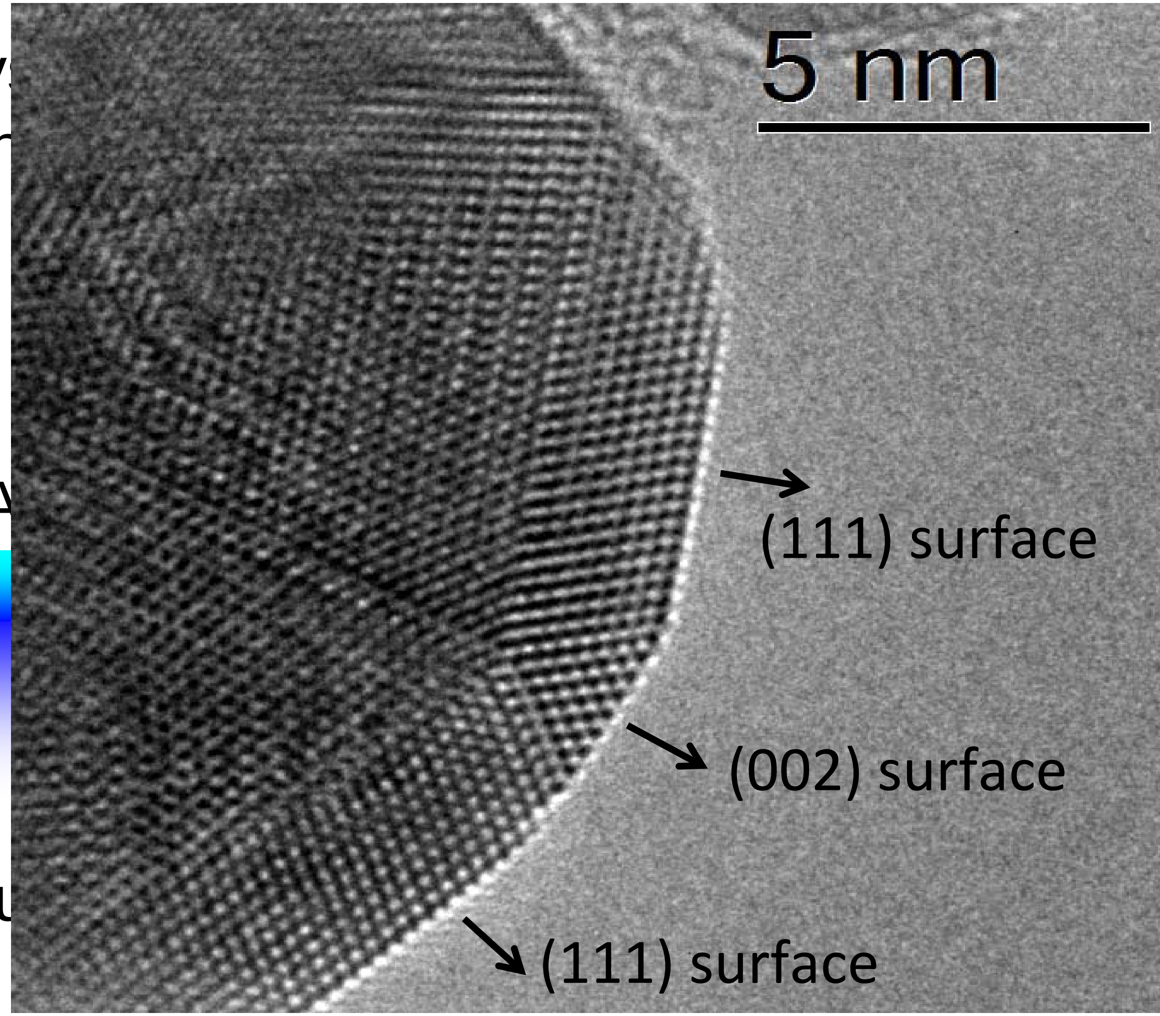


Figure 8.9. Catalyst particle viewed as a crystallite, composed of well-defined atomic planes.

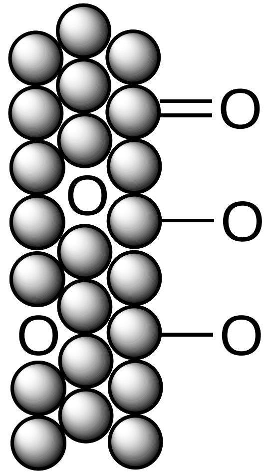
Somorjai 1981



Bulk is “irrelevant”,

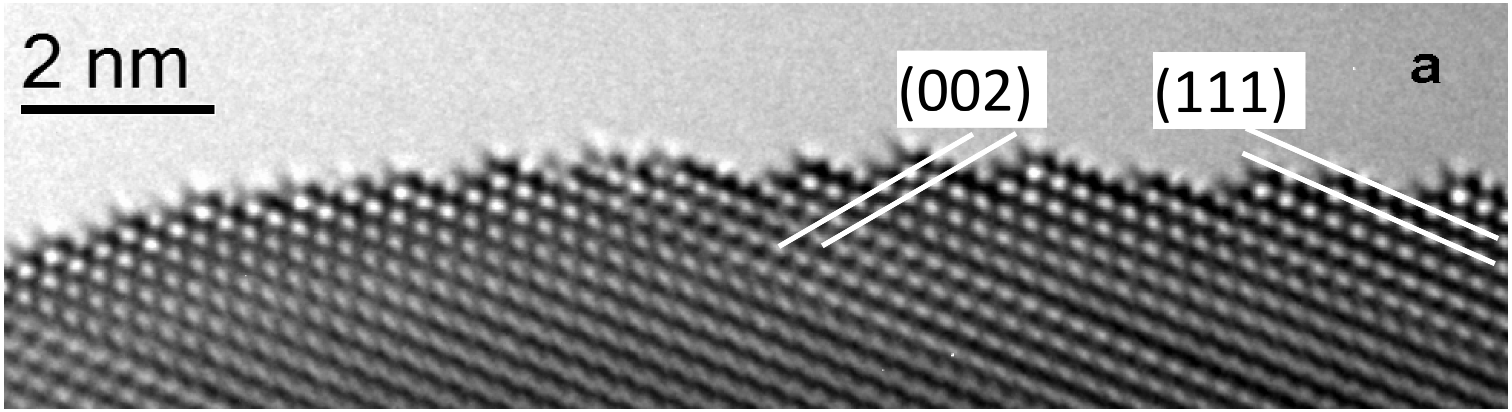
Di-oxygen as oxidant

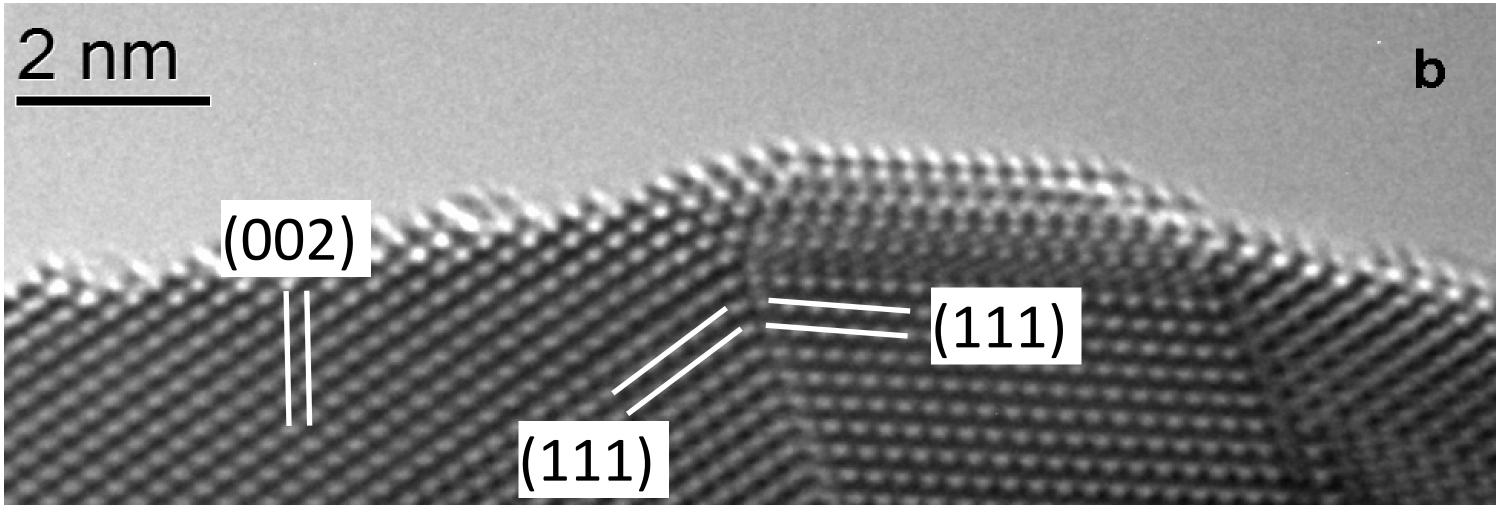
- Atomic chemisorbed oxygen (created typically in UHV) is amphoteric in redox properties: at “virtual pressure” $\rightarrow$ sub-surface
- Sub-surface oxygen is not reactive but
  - Polarizes the surface for adsorption
  - Restructures the surface by incorporation (autocatalytic)
  - Segregates to the 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)
  - Protonates via OH oxygenates



With metals

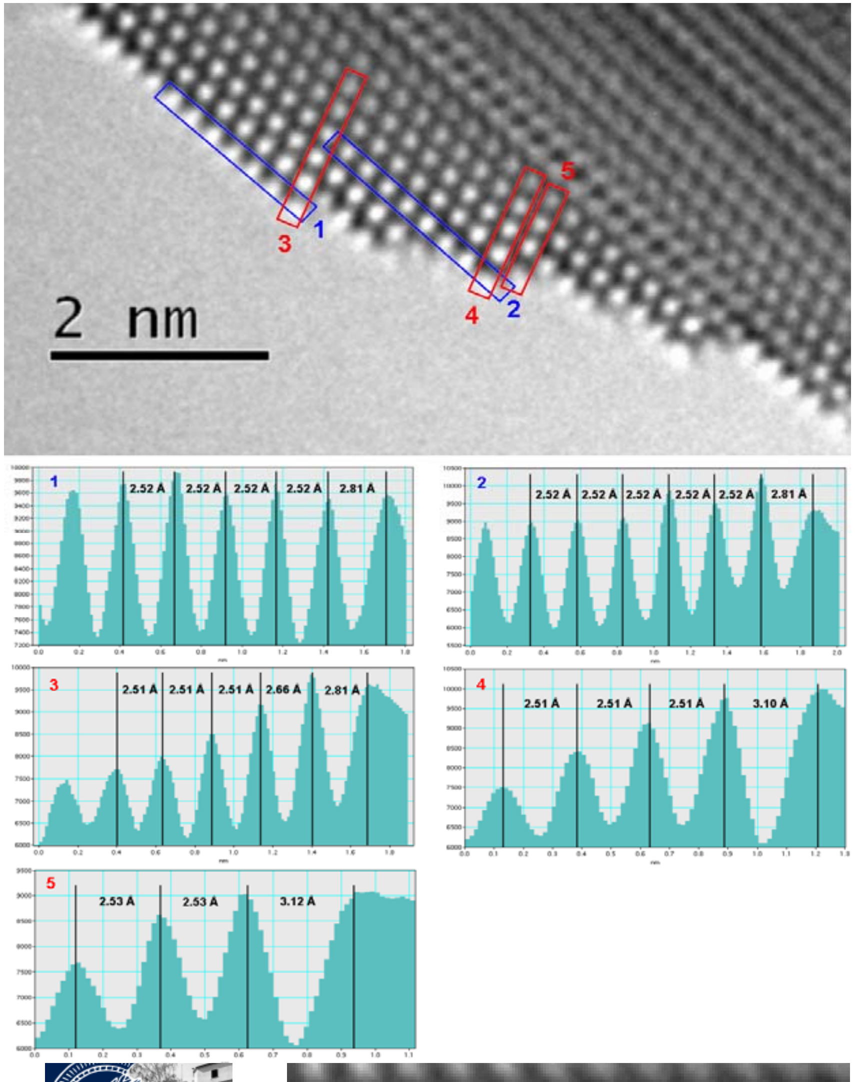
Surface termination: Ag $_{nano}$

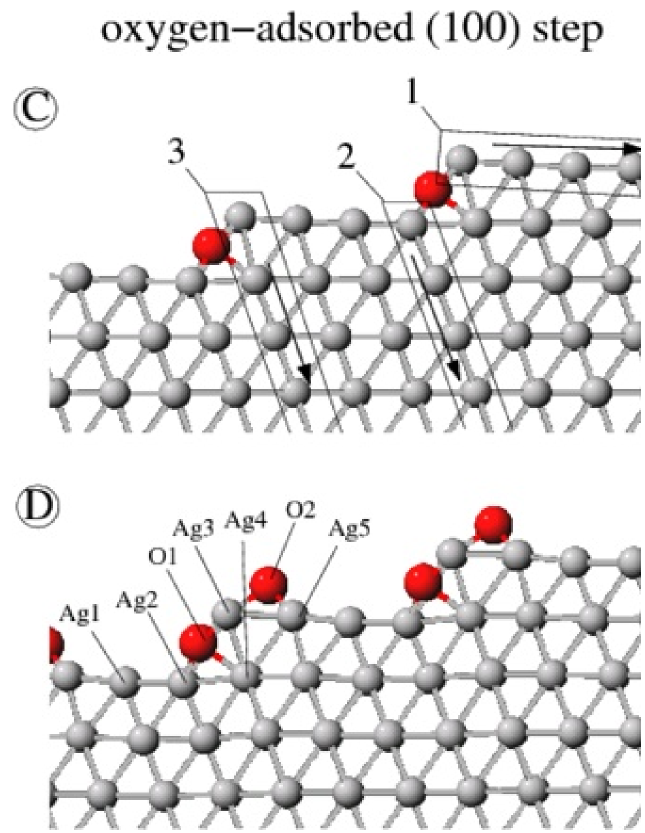




Two strategies relating to good (a) and poor (b) catalysts

Ultrastructure





T. Jakob
M. Scheffler

www: fhi-berlin.mpg.de

Propylene oxide: A demanding oxidation

473 - 523 K

$2\ CH_2CHCH_3$ + O_2 → $2\ CH_2(O)CHCH_3$

electrophilic

excess nucleophilic oxygen needed for adsorption of substrate (rate)

$2\ CH_2CHCH_3$ + $9\ O_2$ → $6\ CO_2 + 6\ H_2O$

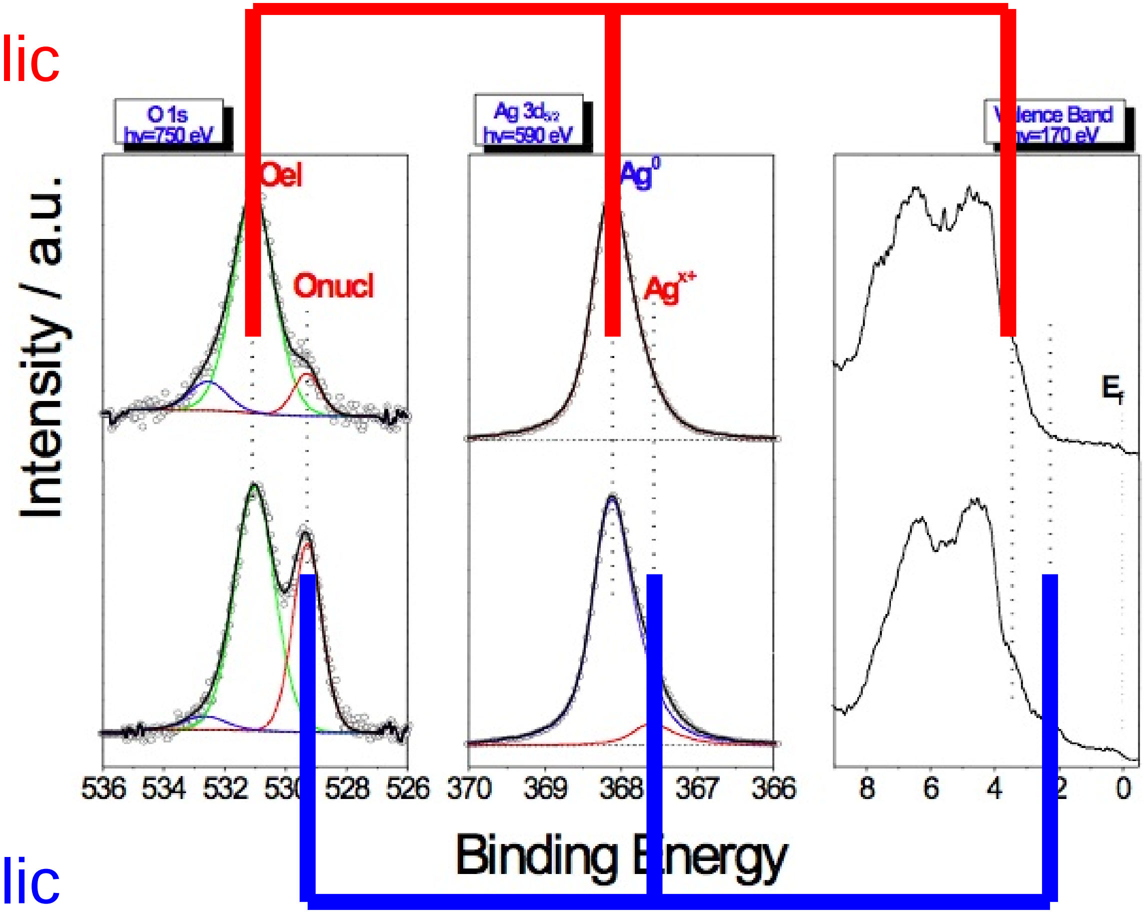
nucleophilic, electrophilic

Ag, promotion by chlorine

Structurally labile system, instable performance

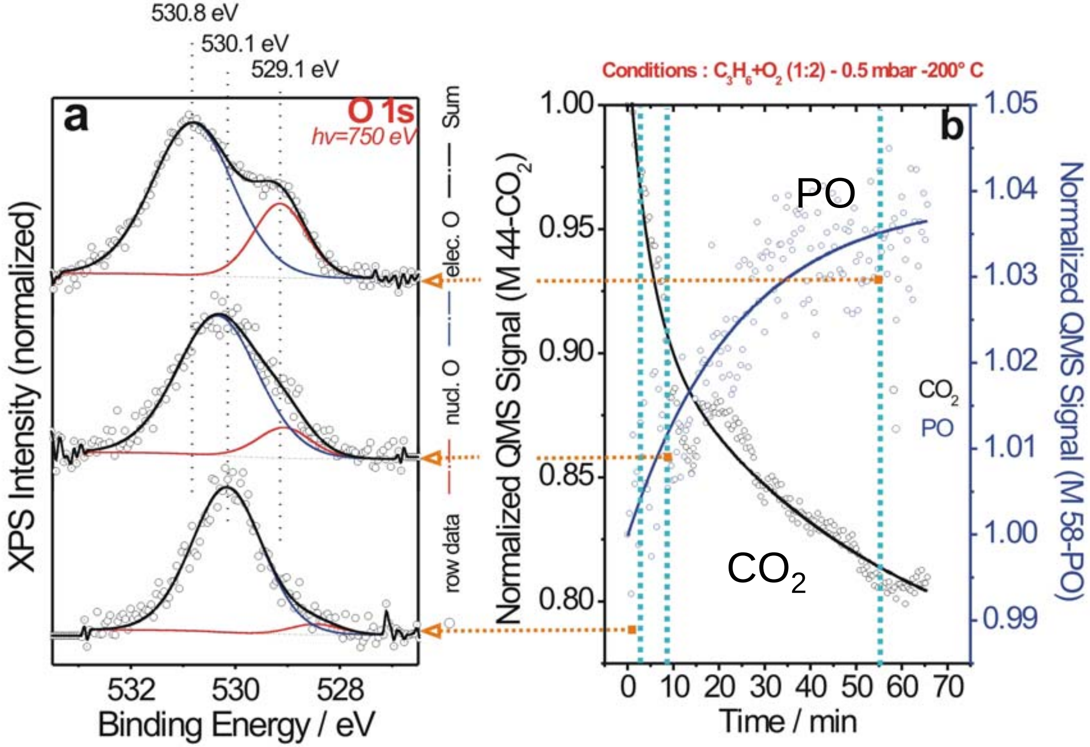
Multifunctional oxygen

electrophilic



nucleophilic

Structure-function correlation in Ag: PO formation



Auto-formation of selective electrophilic oxygen by gradual intercalation of sub-surface oxygen in Ag

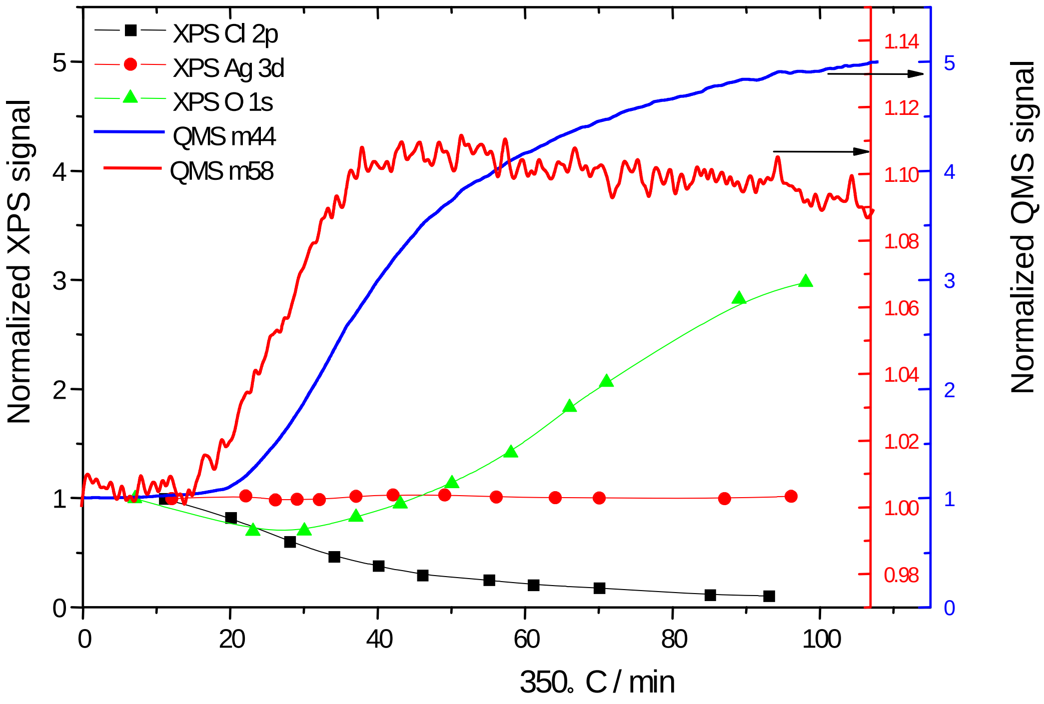
Ag nano, 473 K, 0.5 mbar, 1:2 C_3H_8:O_2
Total oxygen content “0.2 ML”

www: fhi-berlin.mpg.de

The function of a promoter

Chlorine is an effective but not sustained promoter

Chlorine is covered under fresh Ag surface: after 45 min tos: loss of promotion

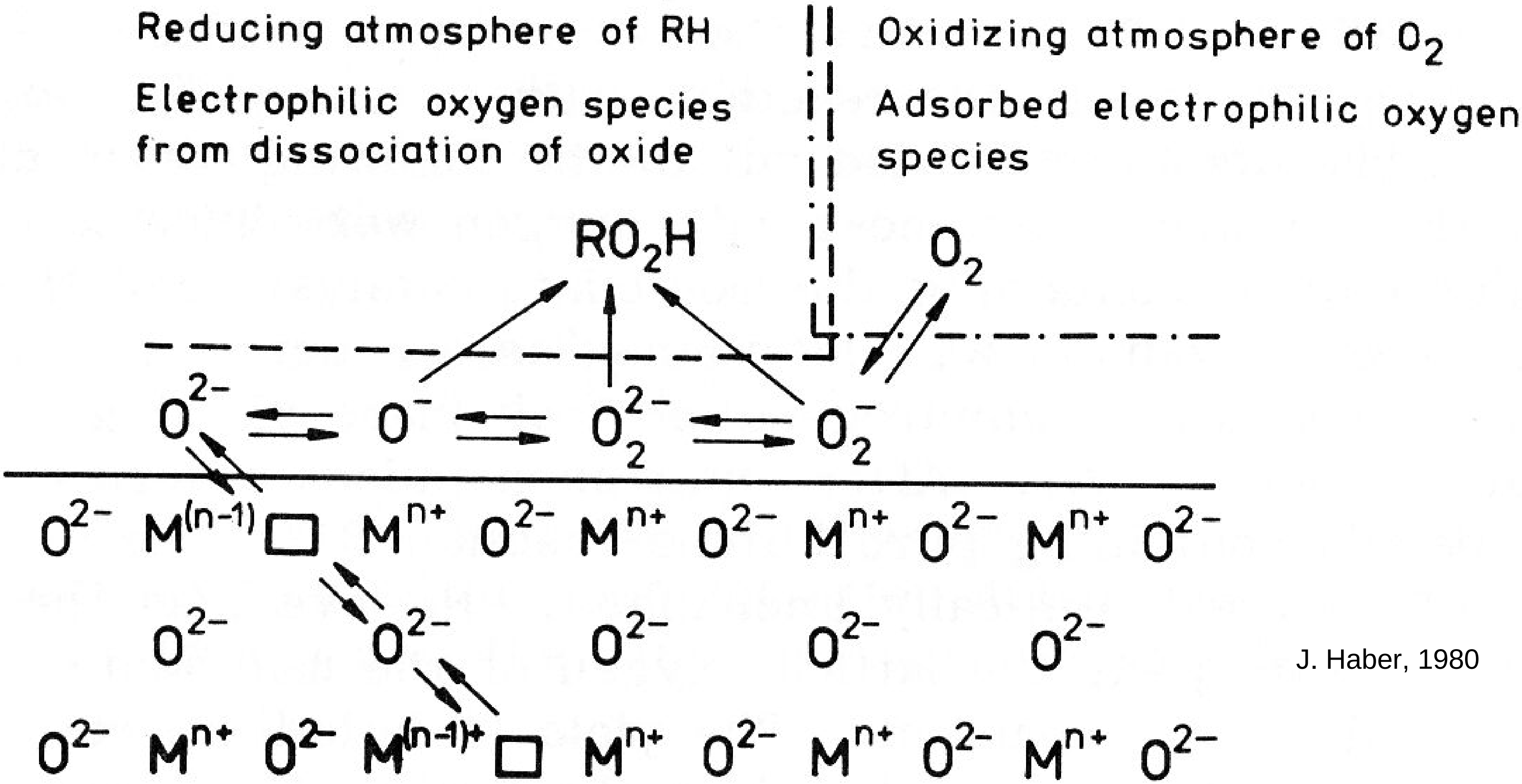


www: fhi-berlin.mpg.de

Limits of the single crystal approach: the selectivity challenge

- In selective oxidation the traditional “Mars van Krevelen” mechanism assumes participation of lattice oxygen (Haber et al.)
- Structural desactivation of metals and oxides (sintering) suggests active bulk
- Equally active surface sites are inconsitent with specific probe counting experiments (Fe/NH_3 4.5%) and disagree with the Taylor model of an active surface (checkerboard)
- Numerous equilibration and activation phenomena of catalysts under operation conditions (also hydrogenation)
- The “living catalyst”(Trifiro, Centi) that “digs its own bed towards activity” (Ertl)

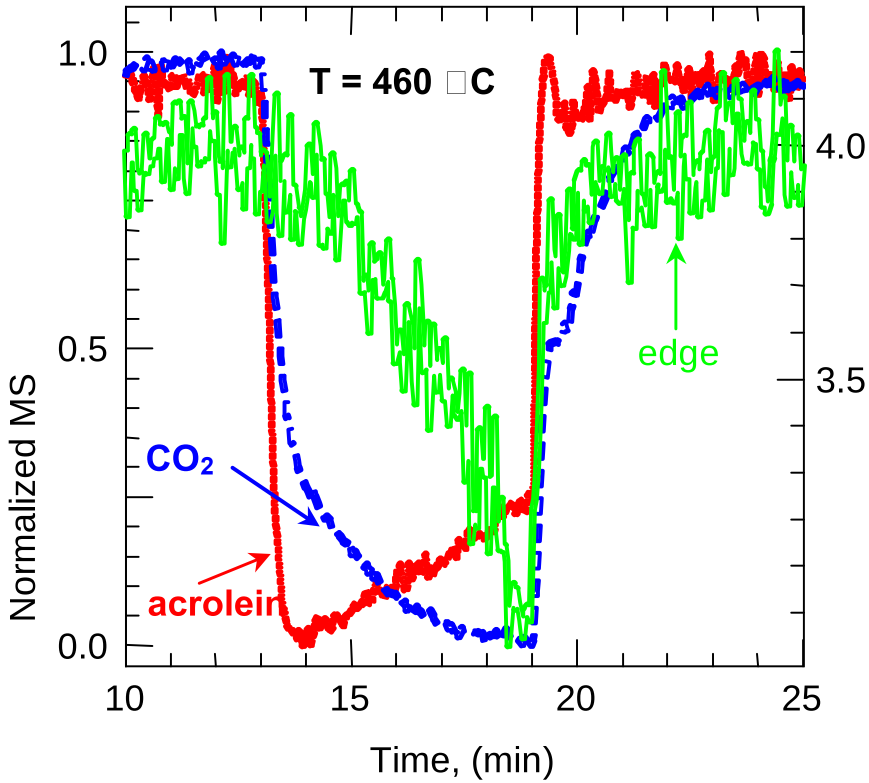
Tutorial: MvK Mechanism



J. Haber, 1980

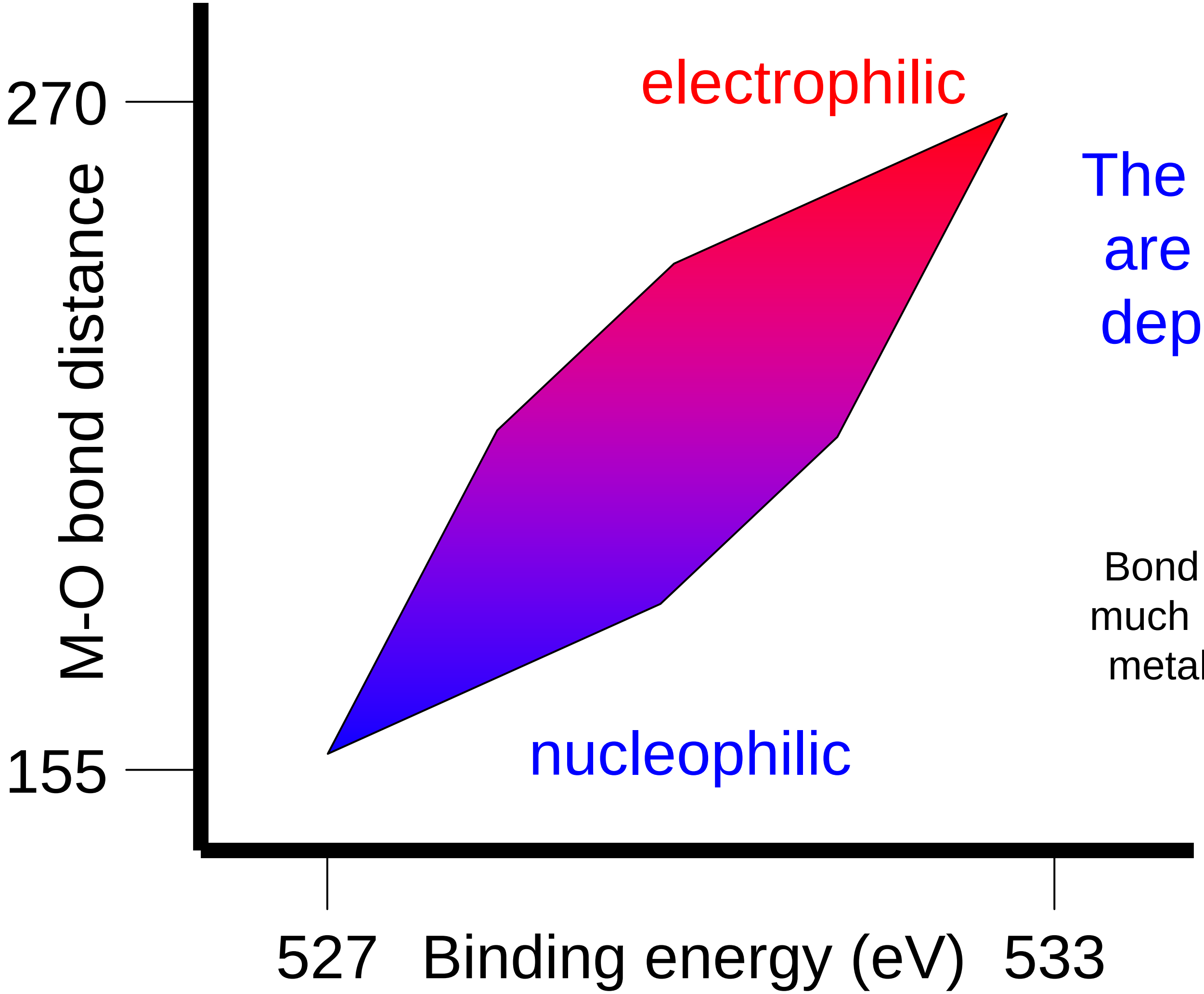
In situ NEXAFS (Mo K-edge) during oxidation of propene

$R\text{-}CH_2R + [(MoO_3)_nMoO_2] = R\text{-}CH^*R + [(MoO_3)_nMoOOH]$	(1)	Activation
$R\text{-}CH^*R + [(MoO_3)_nMoOOH] = R\text{-}CHO + [(MoO_3)_{n-1}(MoOOH)_2]$	(2)	Reaction
$[(MoO_3)_{n-1}(MoOOH)_2] + O_2 = H_2O + [(MoO_3)_nMoO_2]$	(3)	Regeneration



T. Ressler et al.
J. Cat. 1995

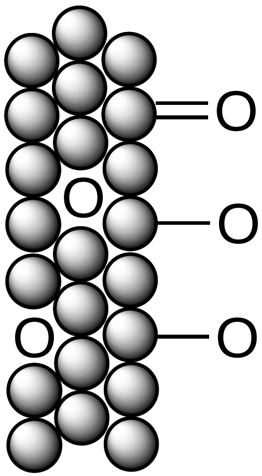
Reactive oxygen



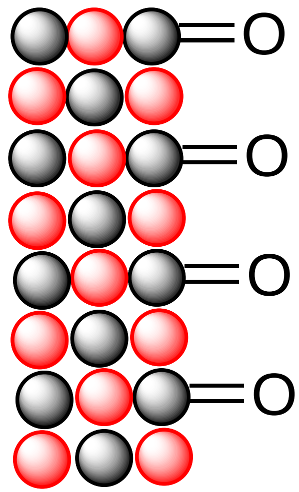
The redox properties are continuous and depend on the M-O polarization

Bond distances in oxides much better known than in metals (with sub-surface states)

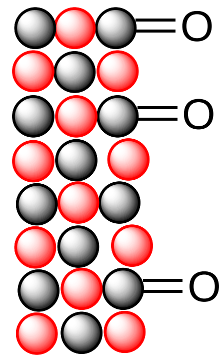
Nucleophilic vs electrophilic oxygen



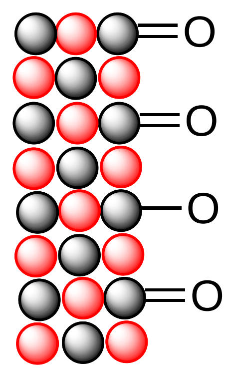
With metals



With oxide



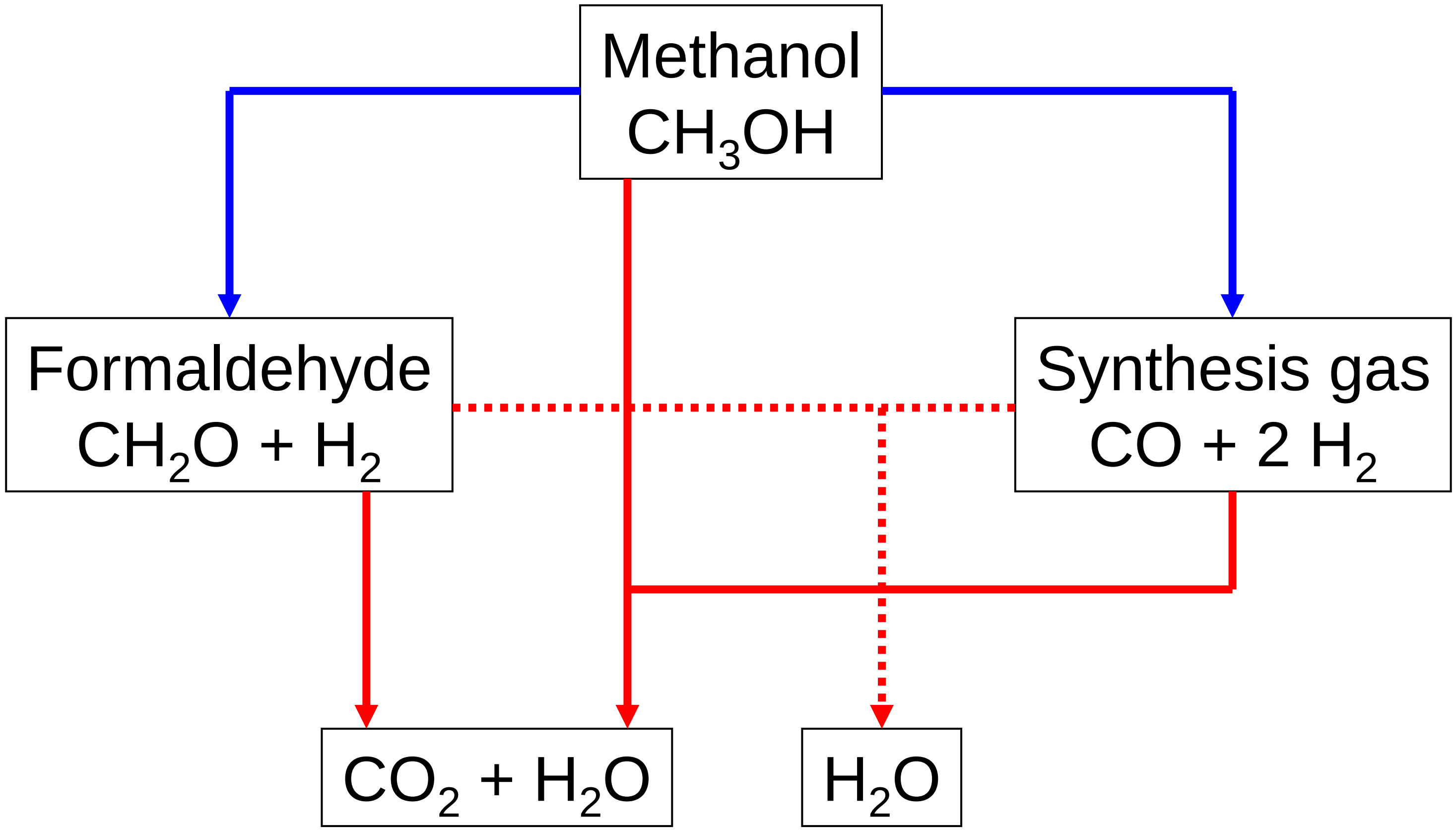
“surface lattice”



“gas phase”

The 0.5 O_2 issue

Reaction network

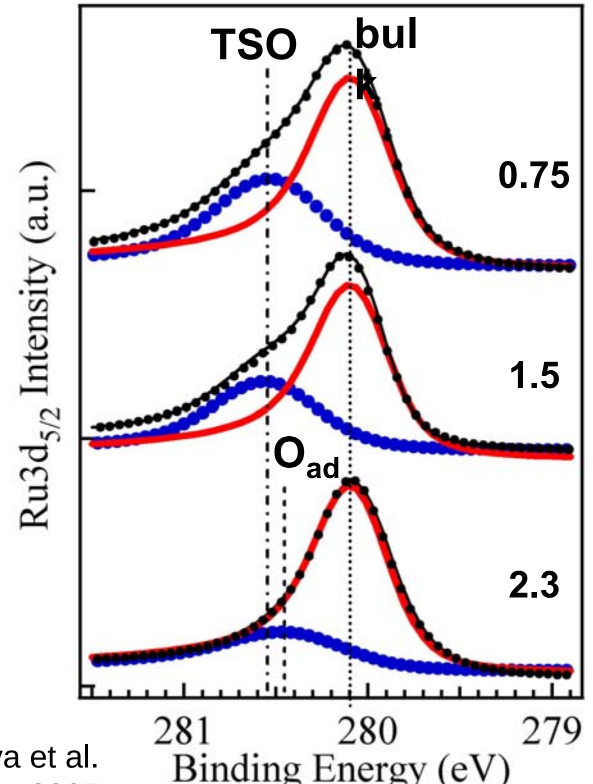


Selectivity: dehydrogenation of MeOH
oxygen addition to C
equilibrium shift by hydrogen oxidation

Multiple reaction control: chemical potential of gasphase: RuO_2

Ru 3d5/2
In-situ PES

$CH_3OH:O_2$ mixing ratios:



M. Kiskinova et al.
Catal. Today 2007

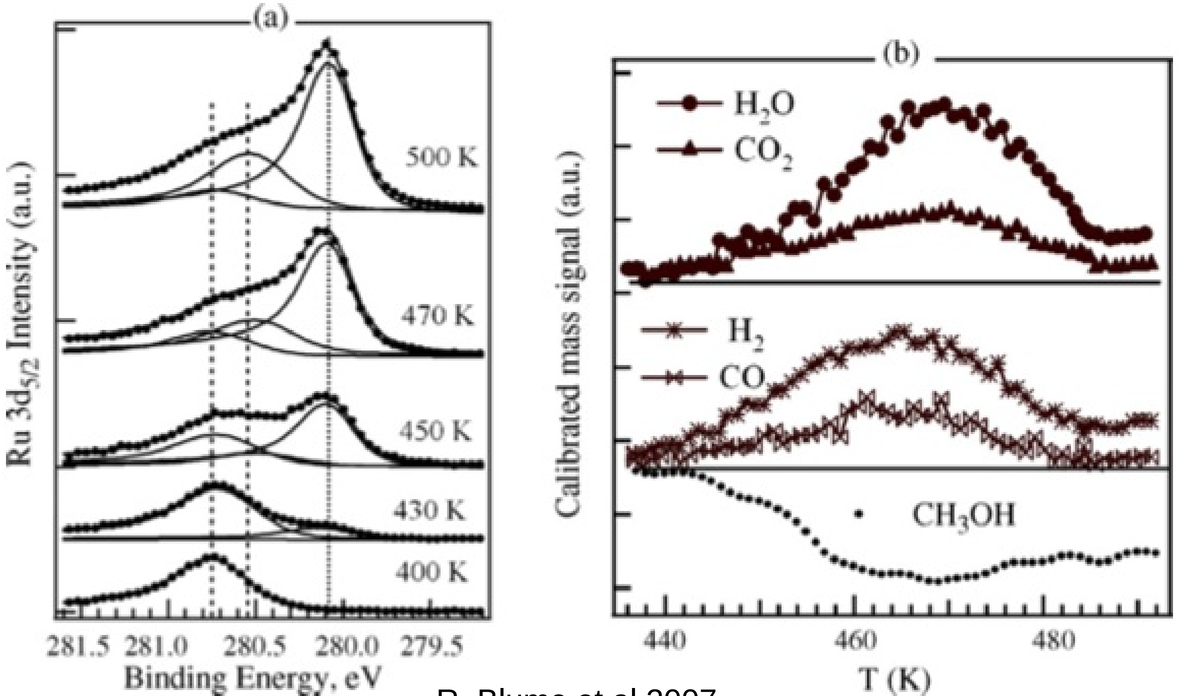
dominant reaction pathway:

$CH_3OH + 3/2 O_2 \rightarrow CO_2 + 2\ H_2O$
nucleo plus electro

$CH_3OH + 1/2 O_2 \rightarrow CH_2O + H_2O$
nucleo plus electro

$CH_3OH \rightarrow H_2 + CO$
nucleo

Muliple reaction control: dynamics of oxidation state

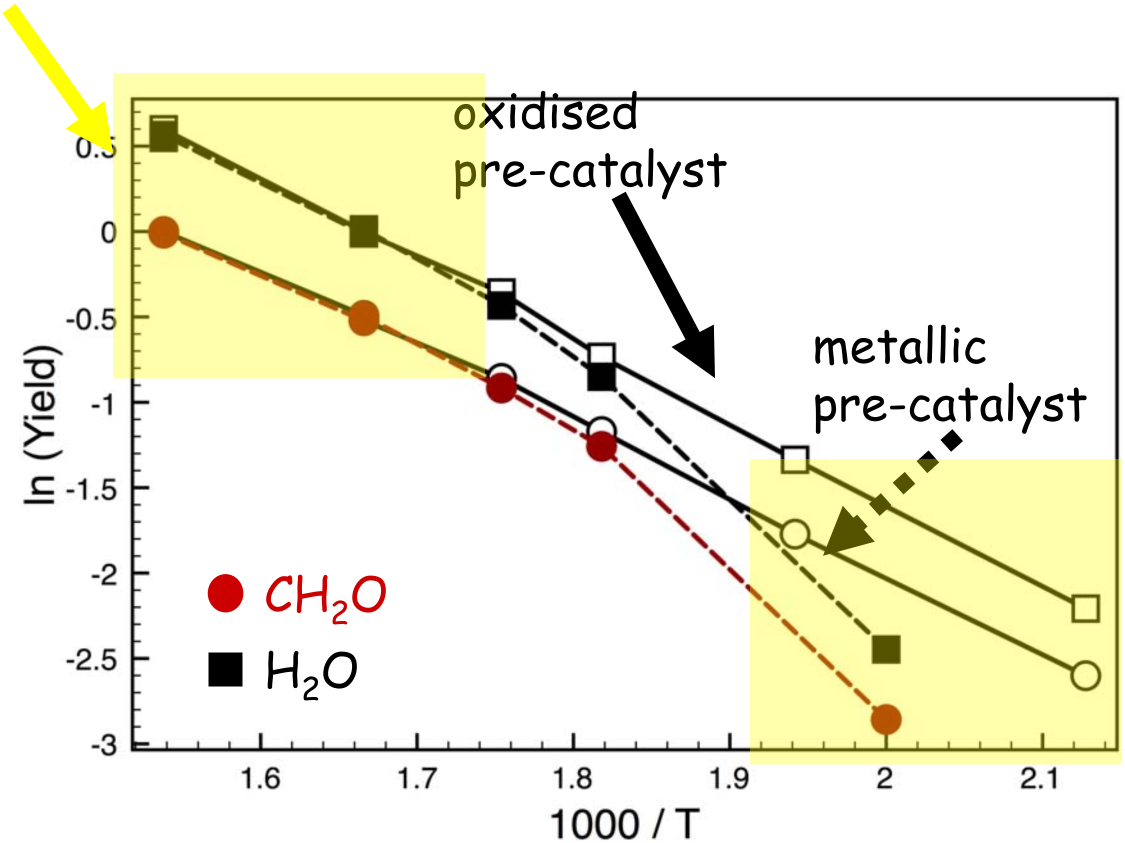


R. Blume et al 2007

Reaction of RuO_2 with MeOH without gas phase oxygen leads to dehydrogenation before activation of lattice oxygen and to combustion ("blast furnace reaction") at higher T

MeOH oxidation over RuxOy

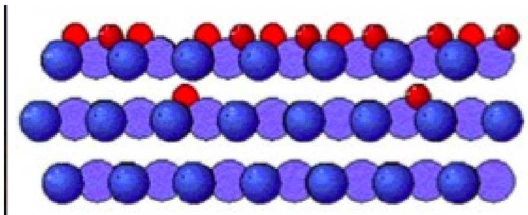
Same catalytic active state
independent of Ru pre-catalyst



Deviation from
straight line for
metallic pre-catalyst:

activation barrier for
oxygen incorporation

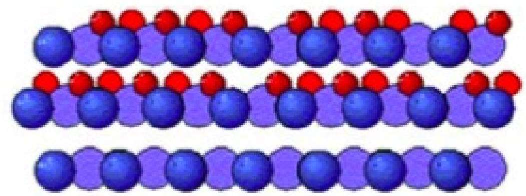
Chemical dynamics: metastability



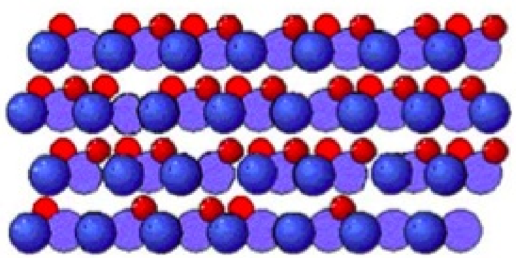
A

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

At slightly elevated potential: “trilayer” (theory)



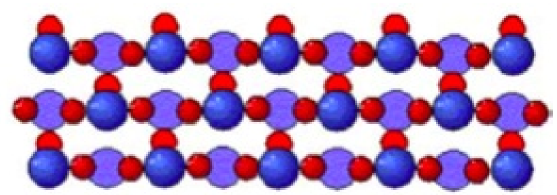
B



C

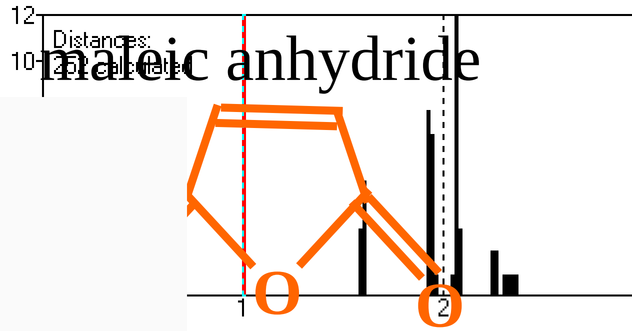
At potentials bejond the “pressure gap”: sub-oxide, sub-surface oxide, TSO (HP-XPS)

At high potential: oxide; when defective nucleo and electrophilic

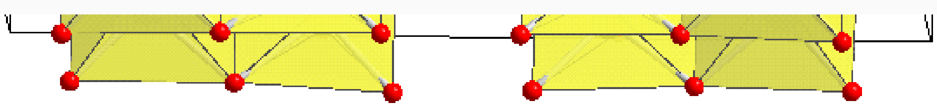


D

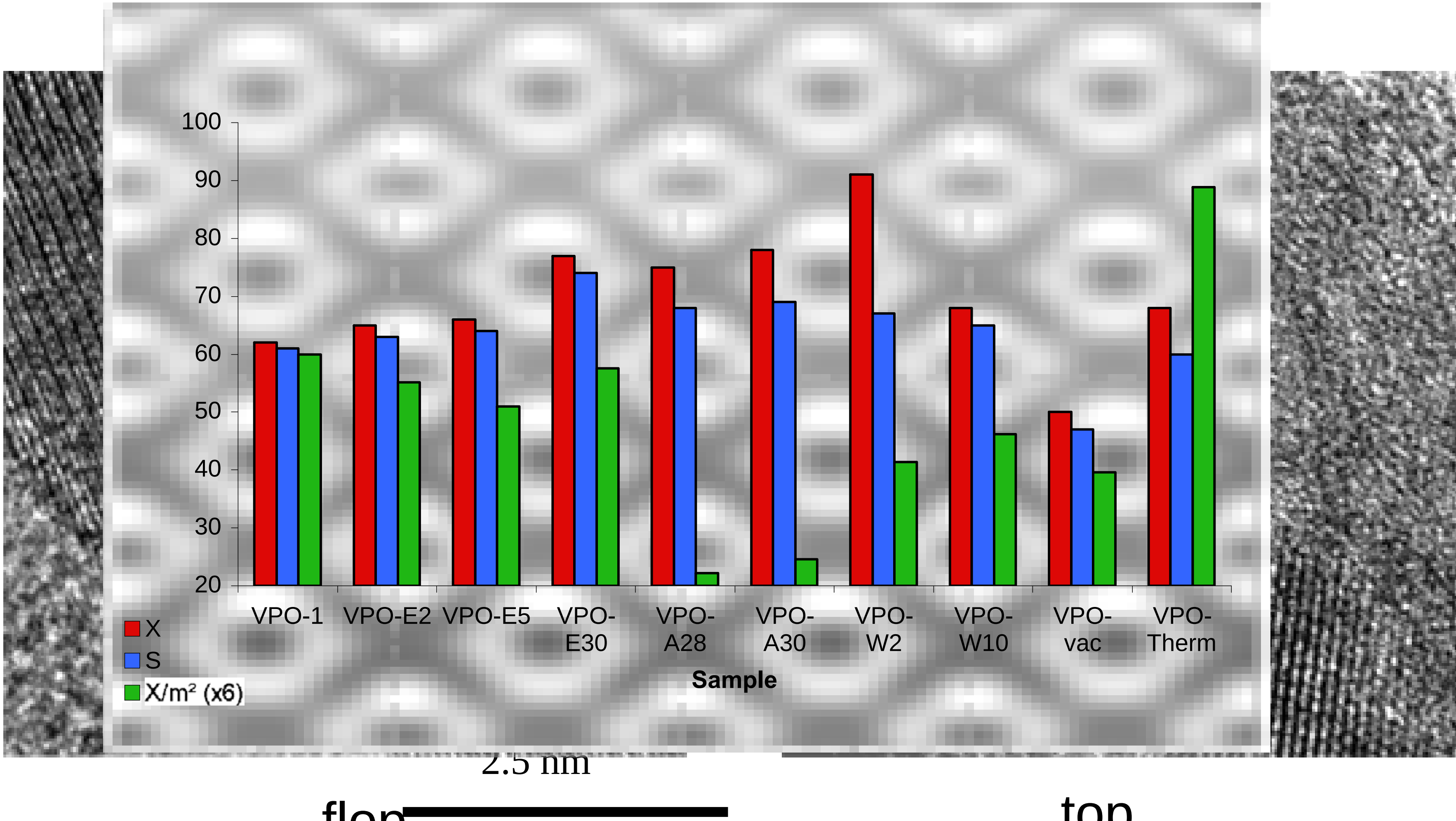
Butane oxidation: VPP structure



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



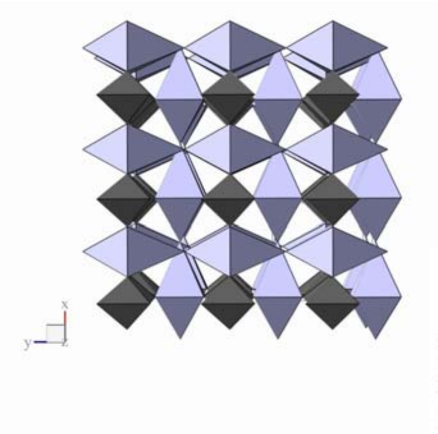
Order and activity

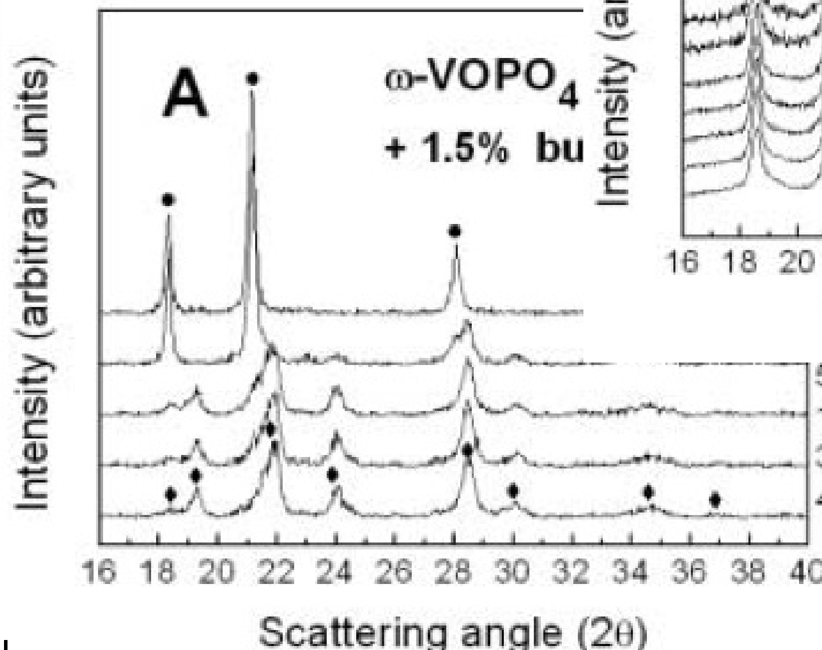


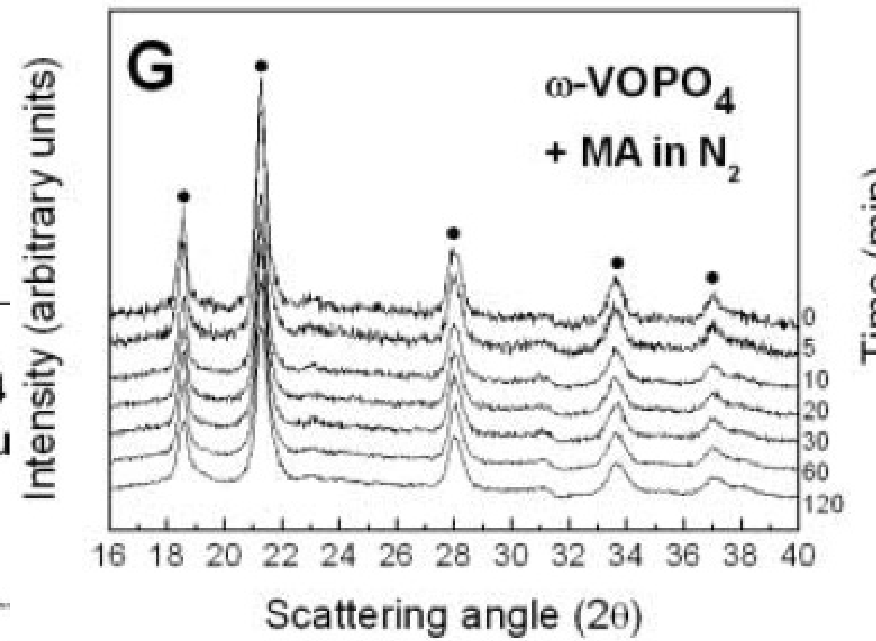
flop

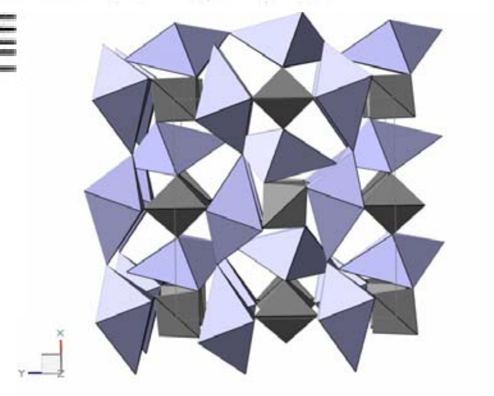
top

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





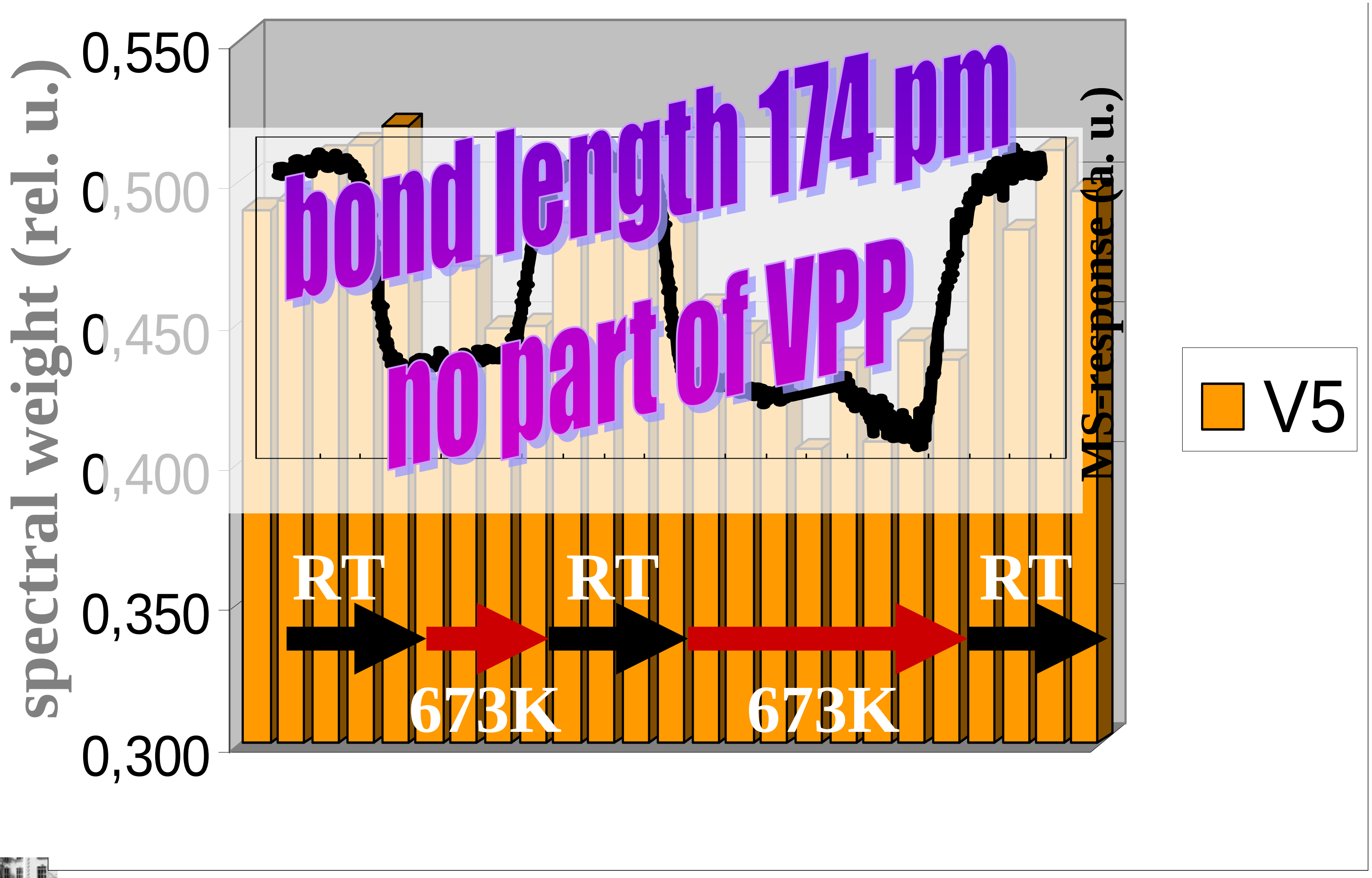




G. Hutchings et al
Science, 2006

Surface: Dynamics of the active phase

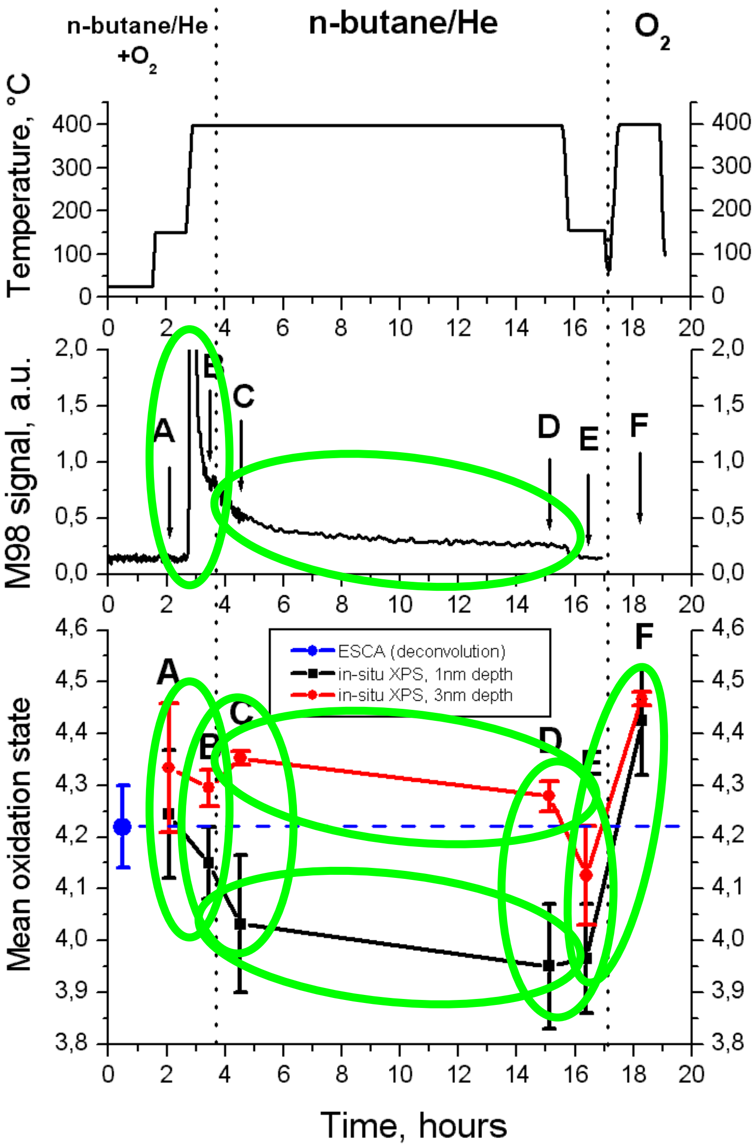
In situ NEXAFS at the V LIII edge in butane oxygen:
Partial yield detetction

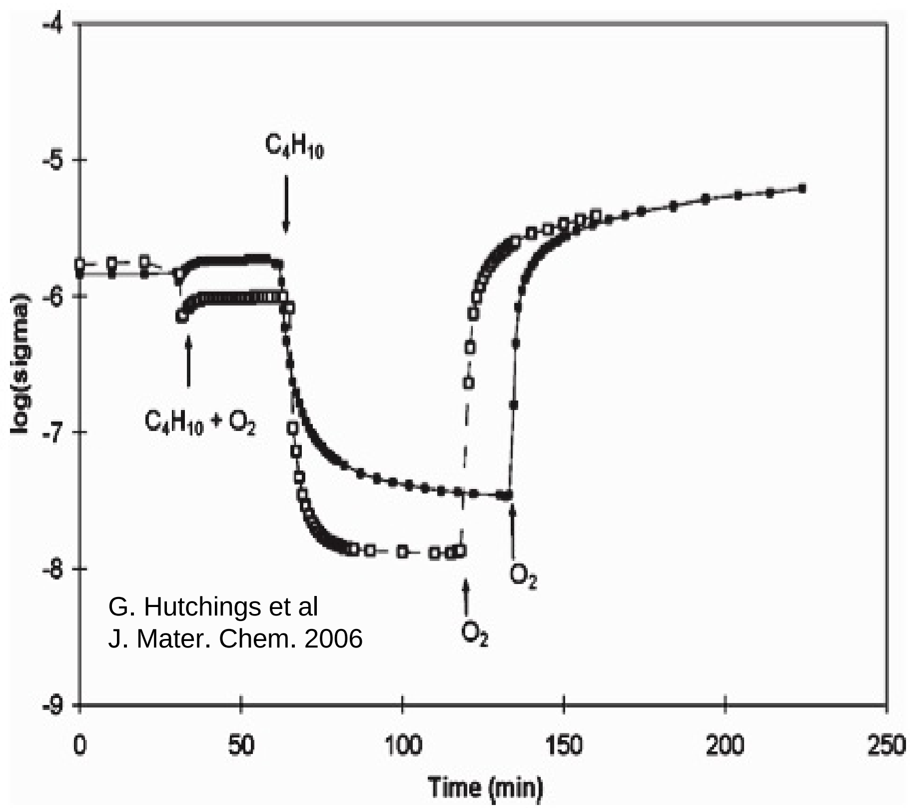


(Formal) oxidation state

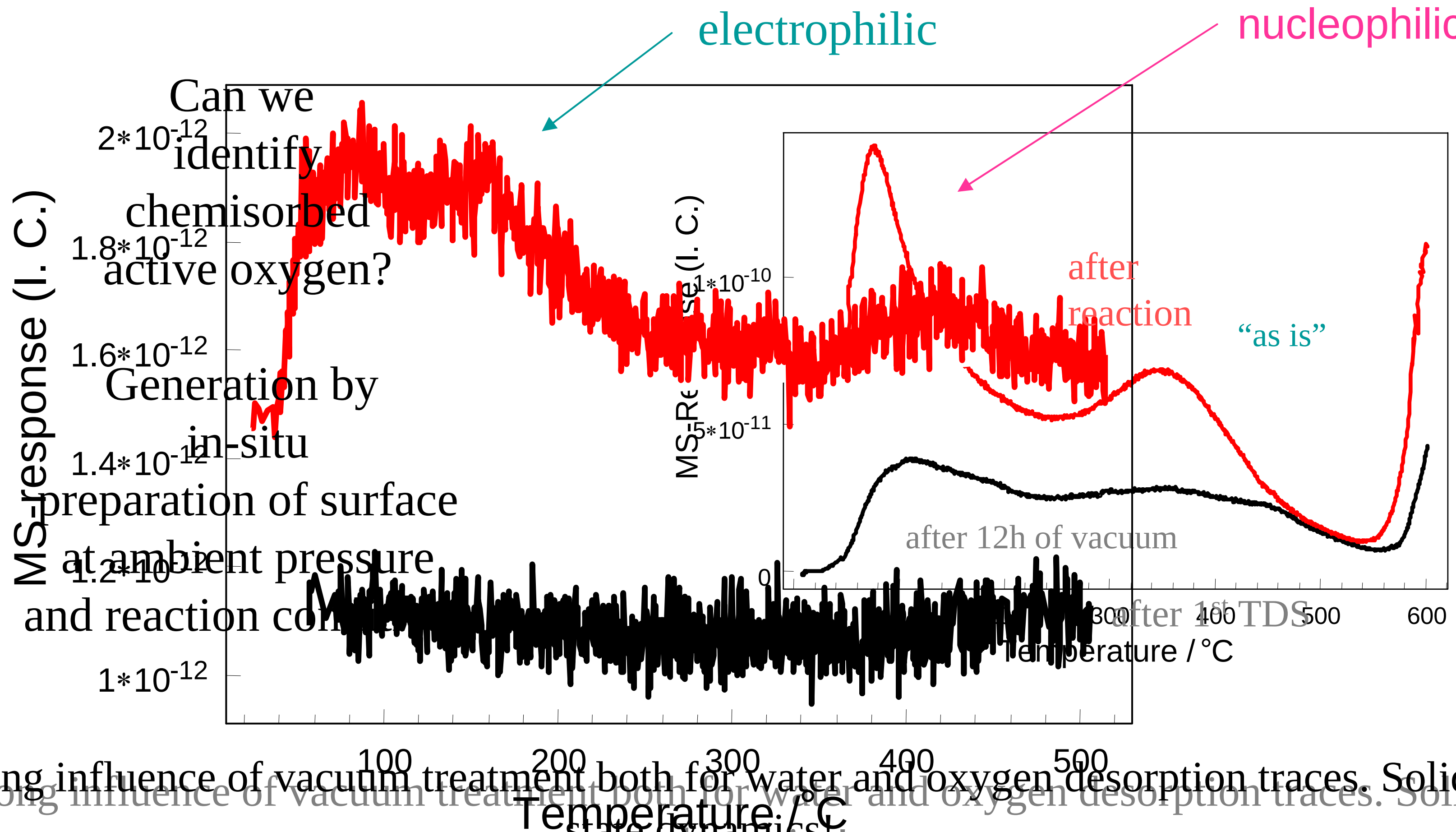
- Chemical concept, in fluid phase reaction as electrochemical redox equivalents in integers countable
- In solids not rigorously defined
- Multiple spectroscopic proxies with uncertainties in “calibration” (shifts)
- Complex structures and phase mixtures yield non-integer values
- Sensitive fingerprint for redox states of solids

In-situ XPS of VPP in Riser Mode





Active oxygen on VPP: TDS

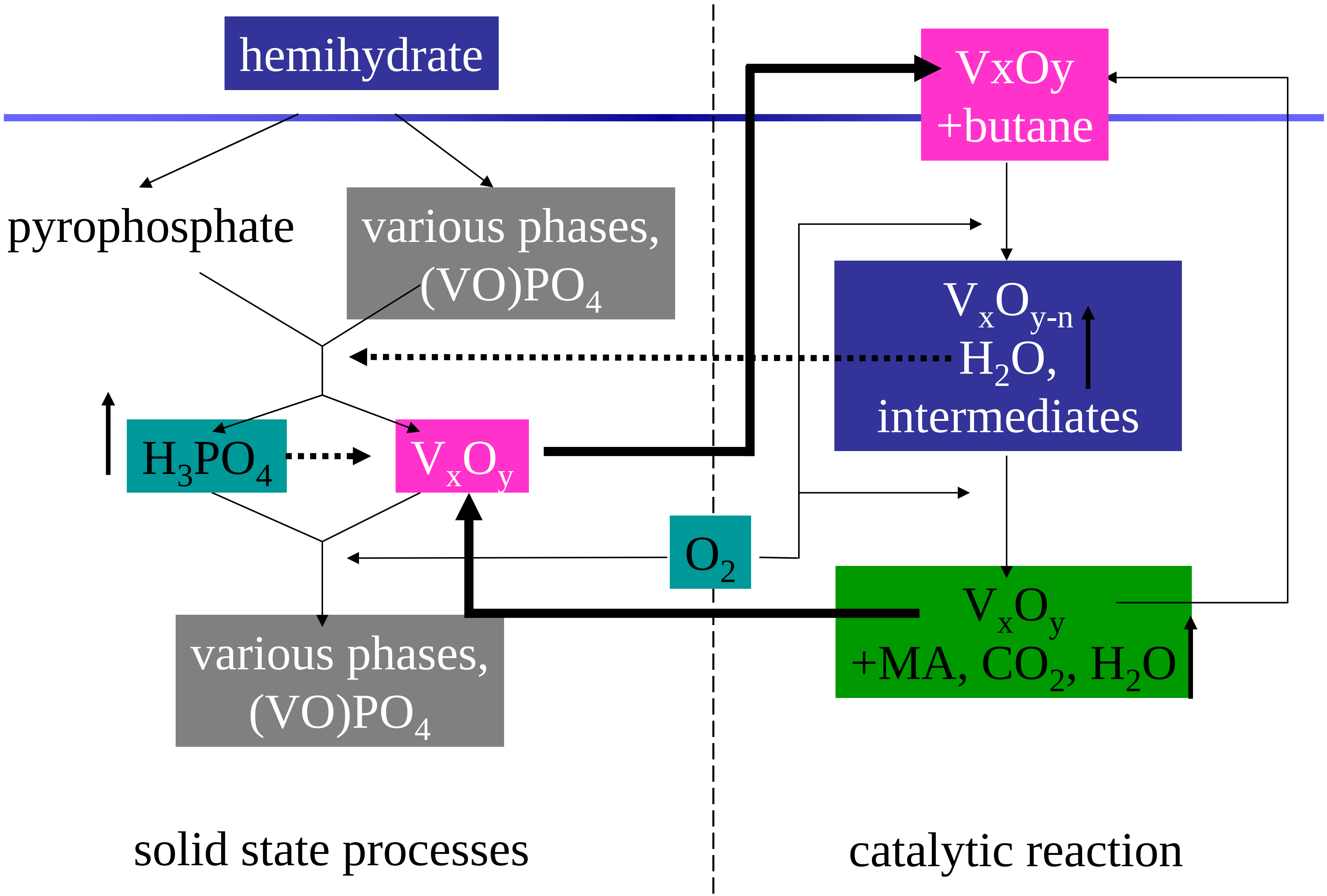


Can we identify chemisorbed active oxygen?

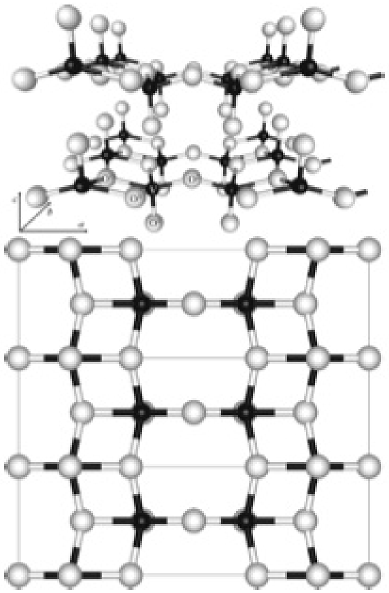
Generation by in-situ preparation of surface at ambient pressure and reaction conditions

Strong influence of vacuum treatment both for water and oxygen desorption traces. Solid state dynamics!

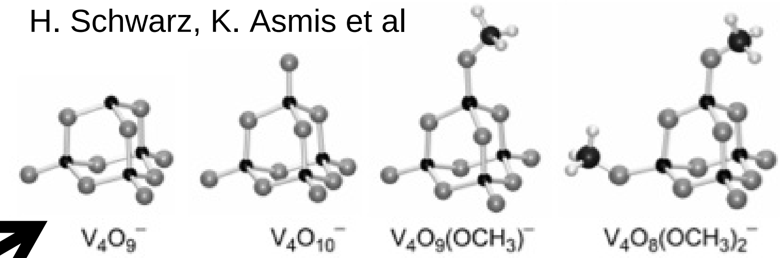
Strong influence of vacuum treatment both for water and oxygen desorption traces. Solid state dynamics!

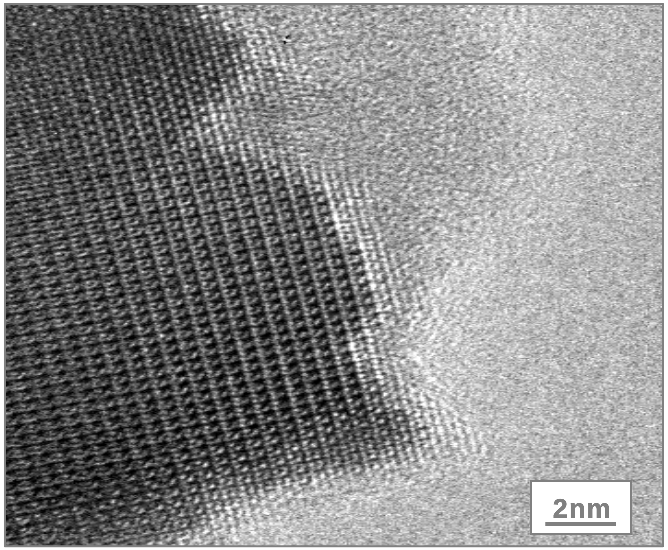

hemihydrate
pyrophosphate
various phases, (VO)PO_4
H_3PO_4
V_xO_y
O_2
various phases, (VO)PO_4
VxOy +butane
V_xO_{y-n} H_2O, intermediates
V_xO_y +MA, CO_2, H_2O
solid state processes
catalytic reaction

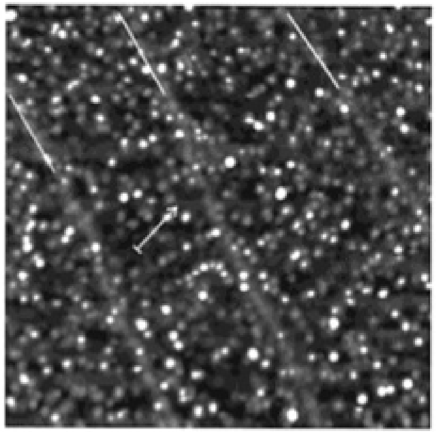
What have we learnt



H. Schwarz, K. Asmis et al



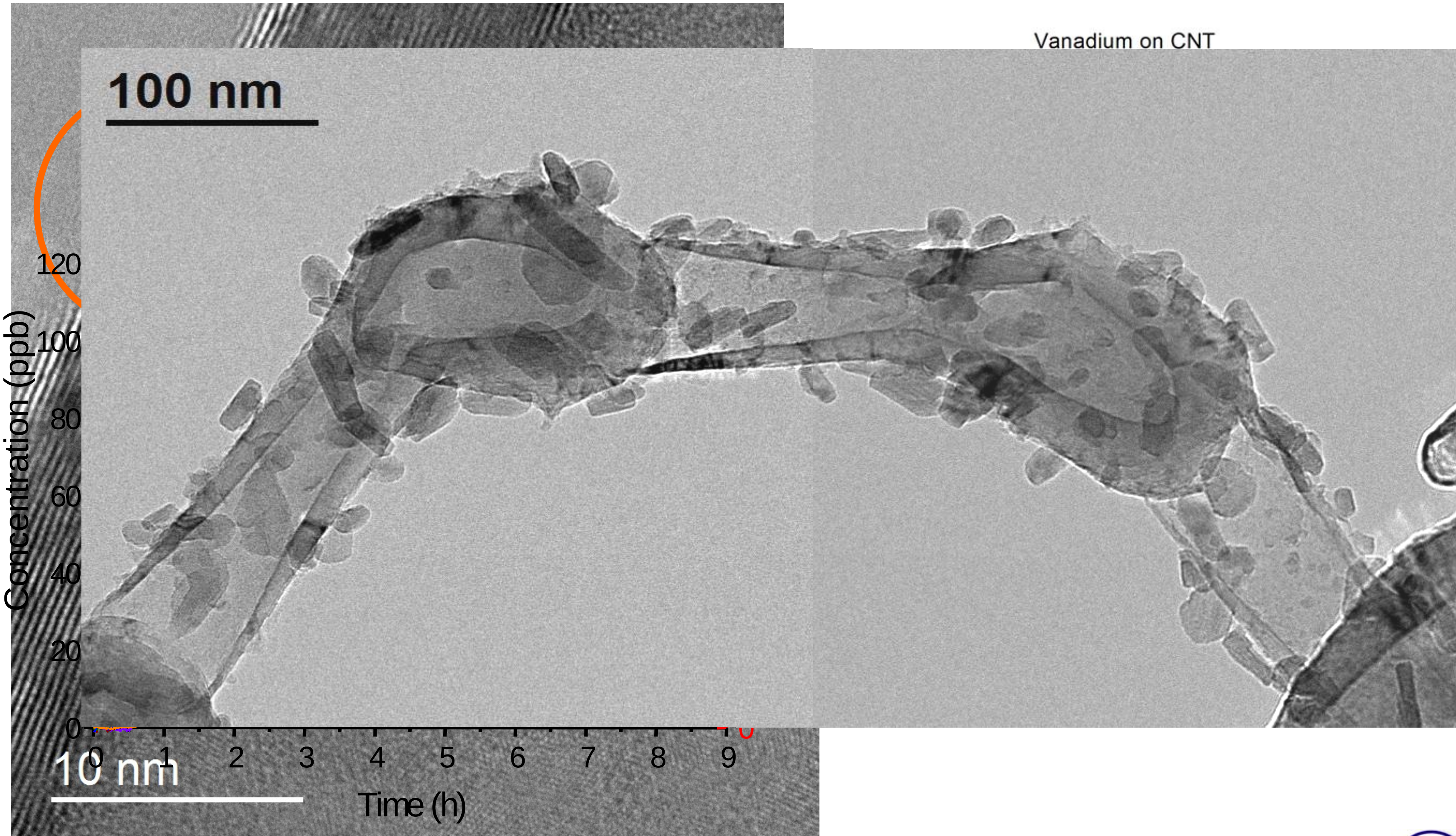




H.J. Freund et al

www: fhi-berlin.mpg.de

Clusters: where the reactive surface ends



Selectivity: An optimization challenge

Sustainable supply?

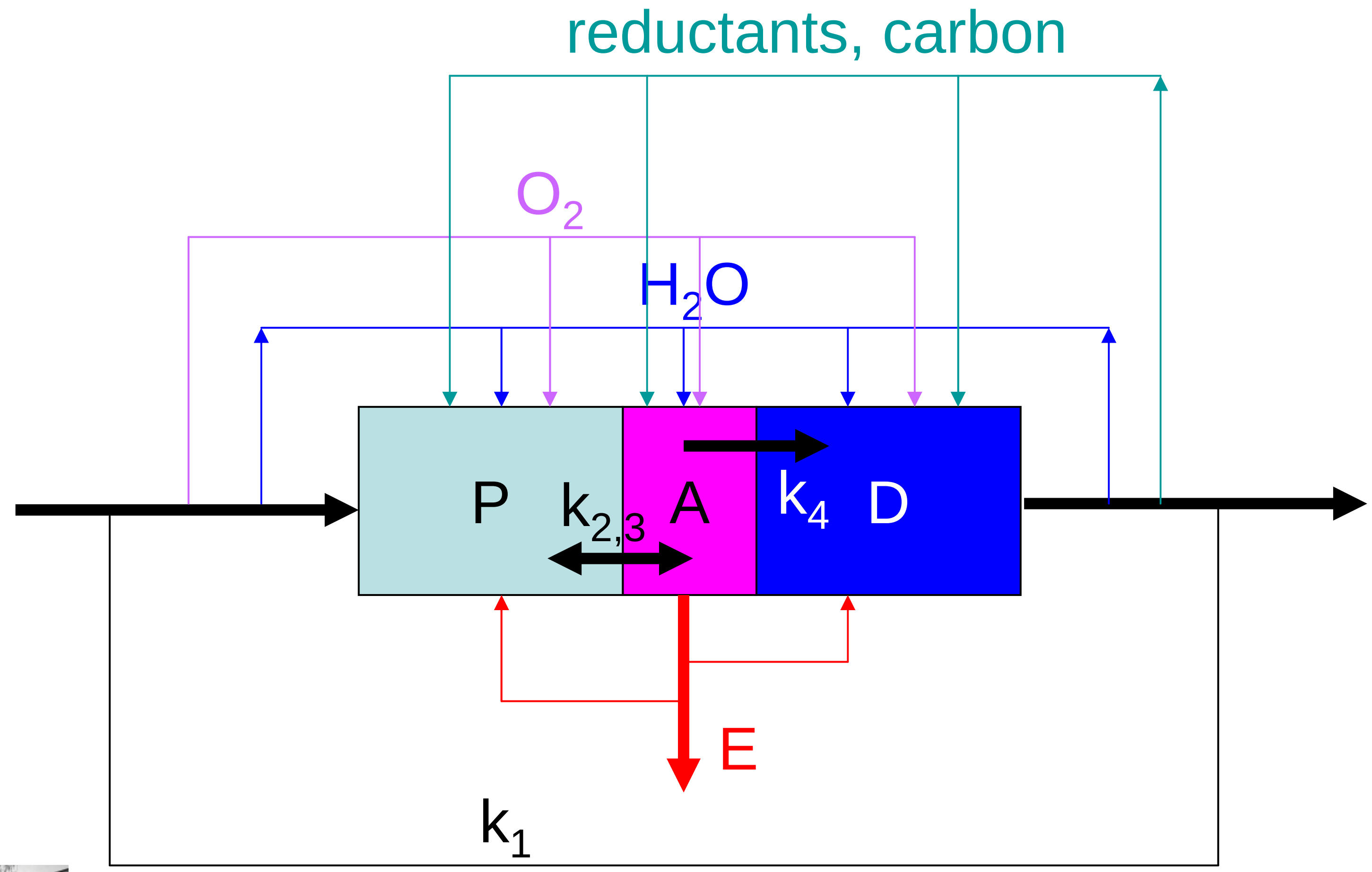
Green chemistry!

Renewables or coal?

The system: Why in situ analysis?

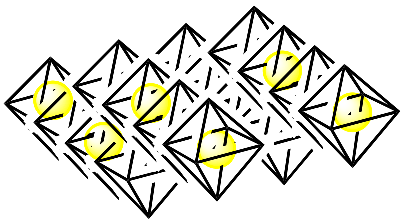
Multiple feedback loops with different effects on different functional parts of the catalyst

Care with reductionistic approach

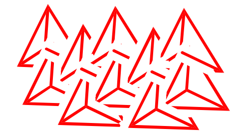


The non-rigid (dynamical) catalyst

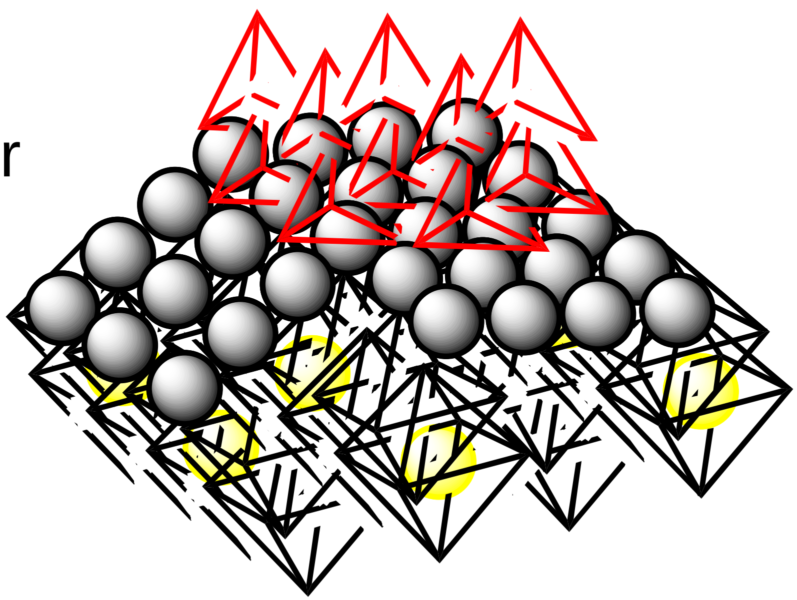
The chemical diversity (in metals)
arises from reactants driving the
dynamics by their reactions

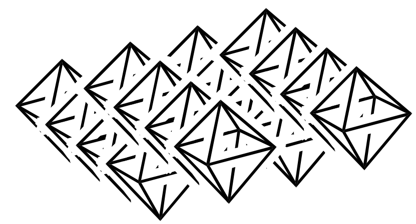


bulk insulator

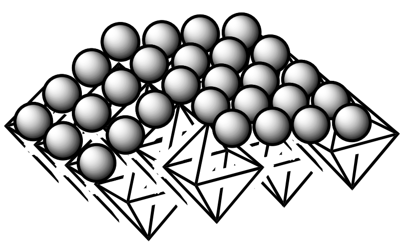


active phase

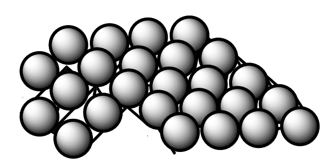




conductor



metal-insuator
assembly

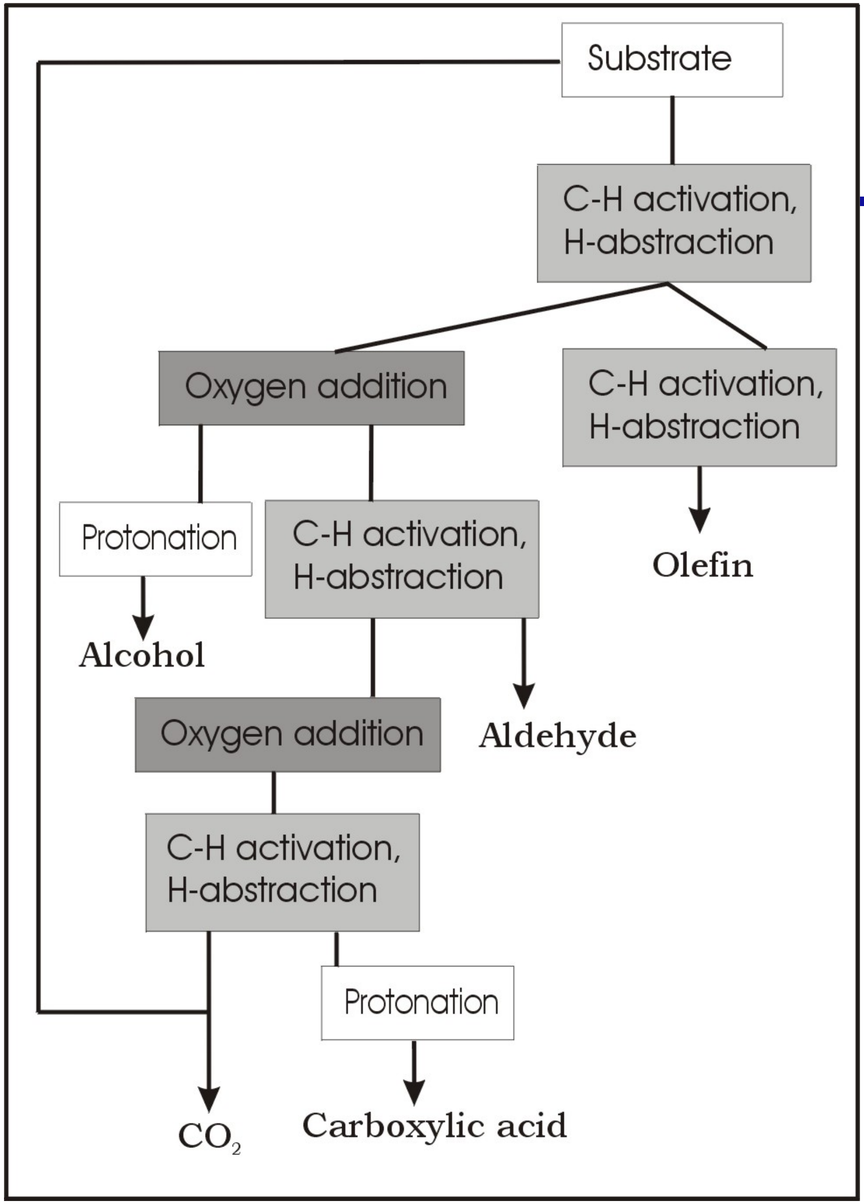


segregate

Make things as simple as possible -
But not simpler
(A. Einstein)

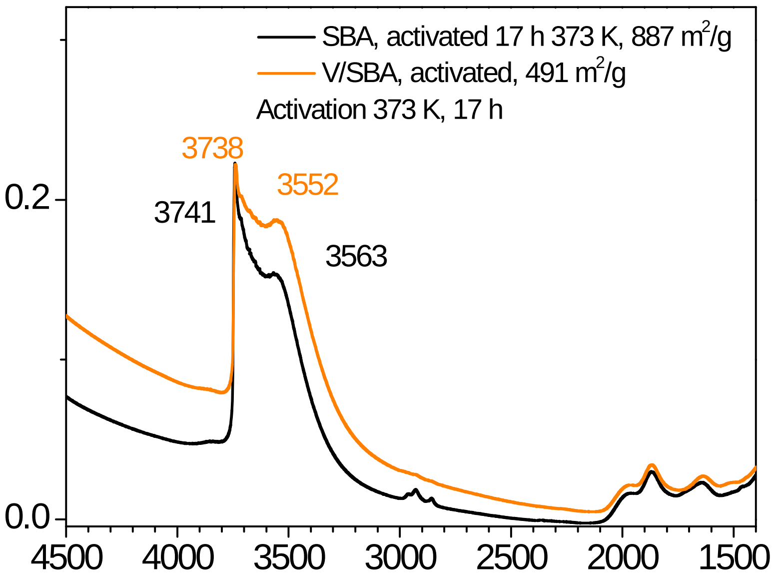
Catalysis is a facinating challenge
and not a “mature technology”

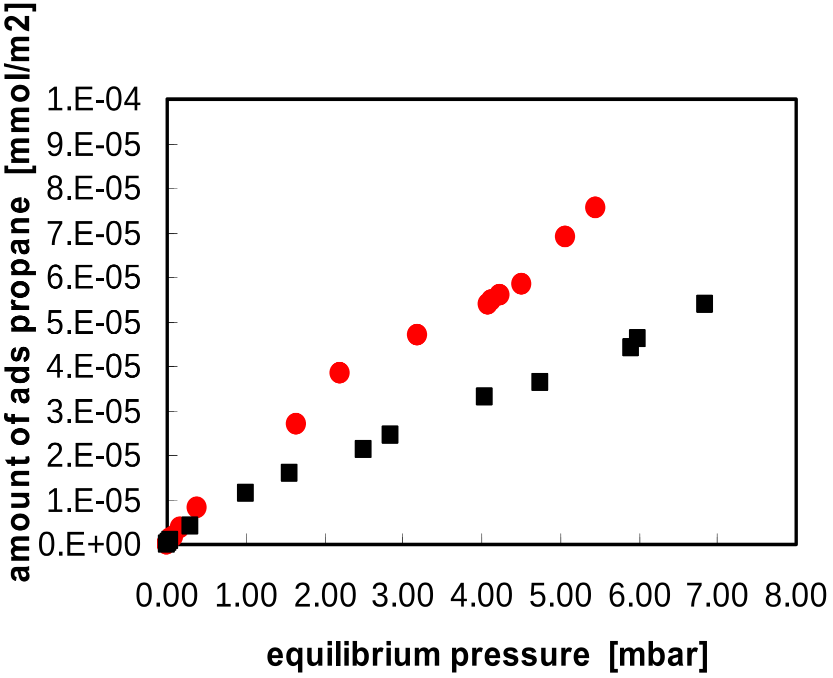
Thank You



A medium-complex scenario: Selective Oxidation

0.8V/SBA 15: propane adsorption





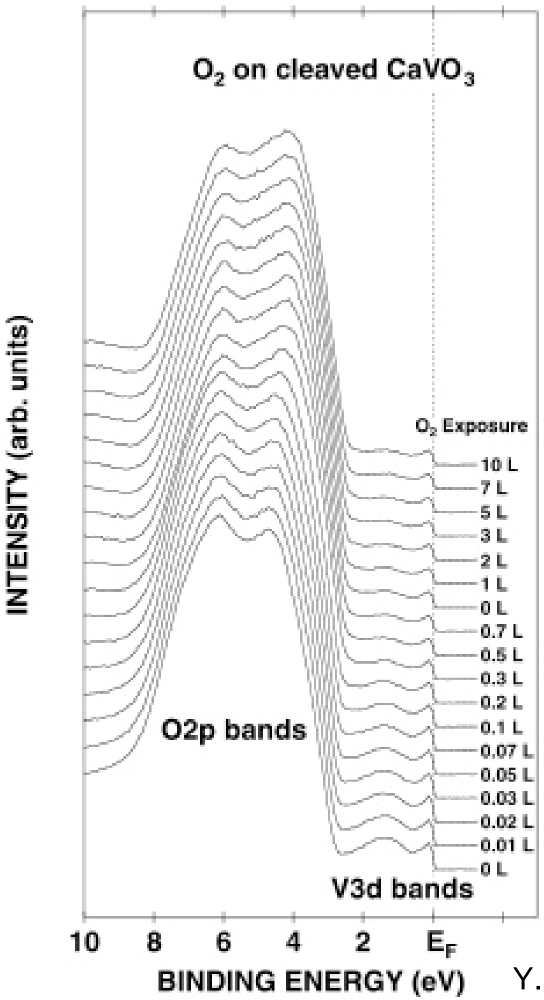
Per surface area, the V-containing catalyst adsorbed more propane.

→ Δn_{ads} ~ 0.5 µmol/m^2 Si-OH + Si-O-V-OH / V-O-V-OH

→ not detectable in the IR spectrum

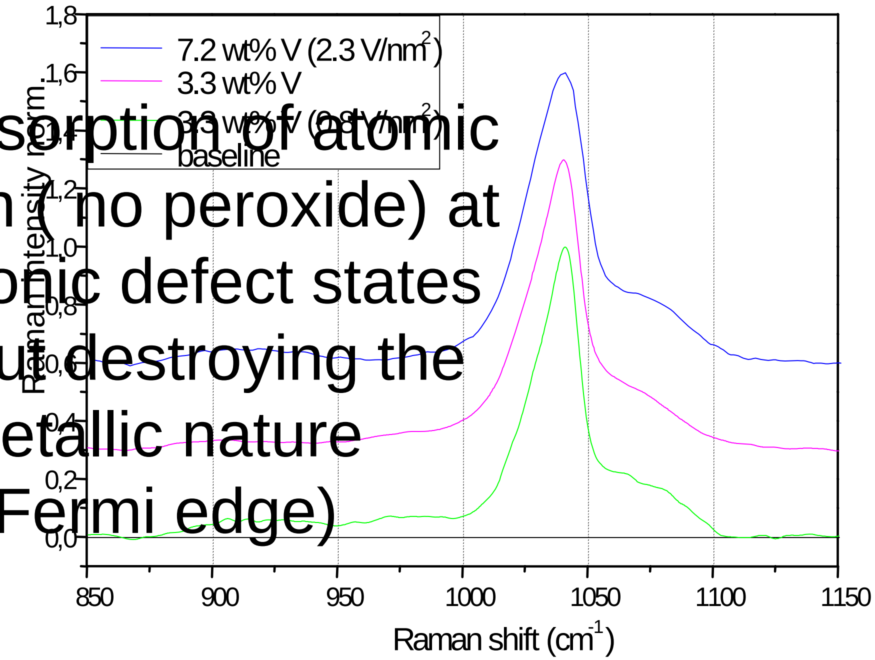
10^{10} sites per mm^2

Nature of the active state



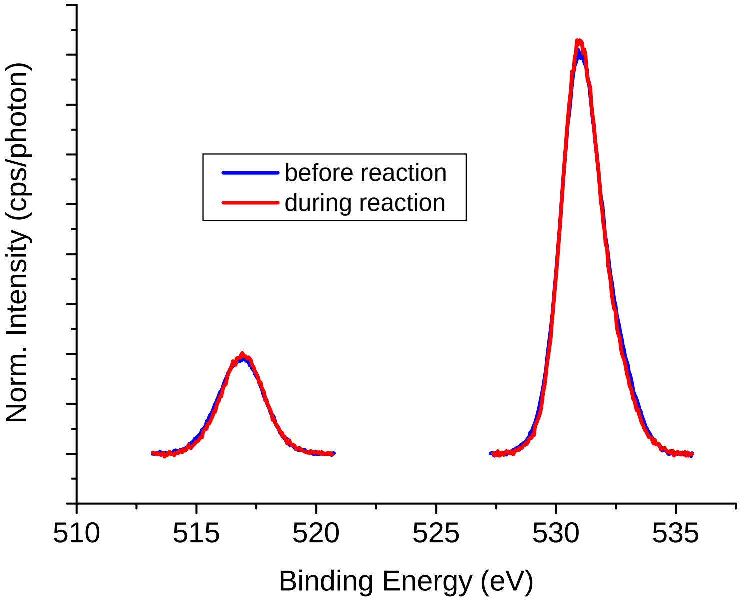
Y. Aiura et al. SS 2001

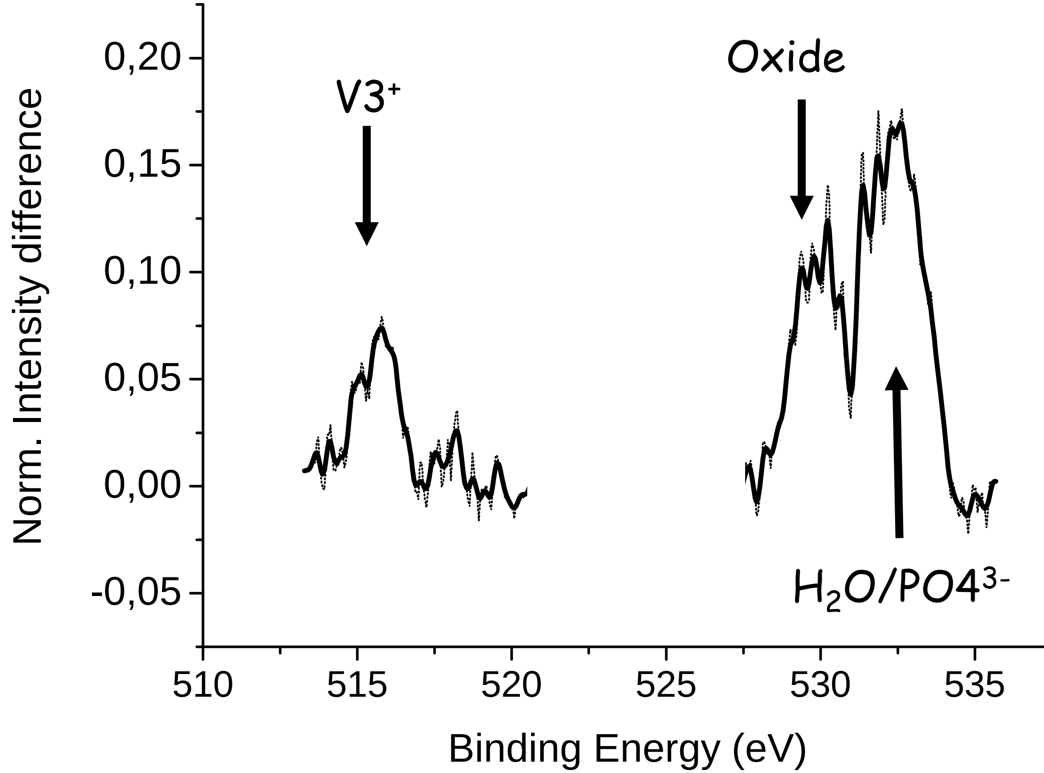
Chemisorption of atomic oxygen (no peroxide) at electronic defect states without destroying the metallic nature (Fermi edge)



Anisotropy of the V=O groups

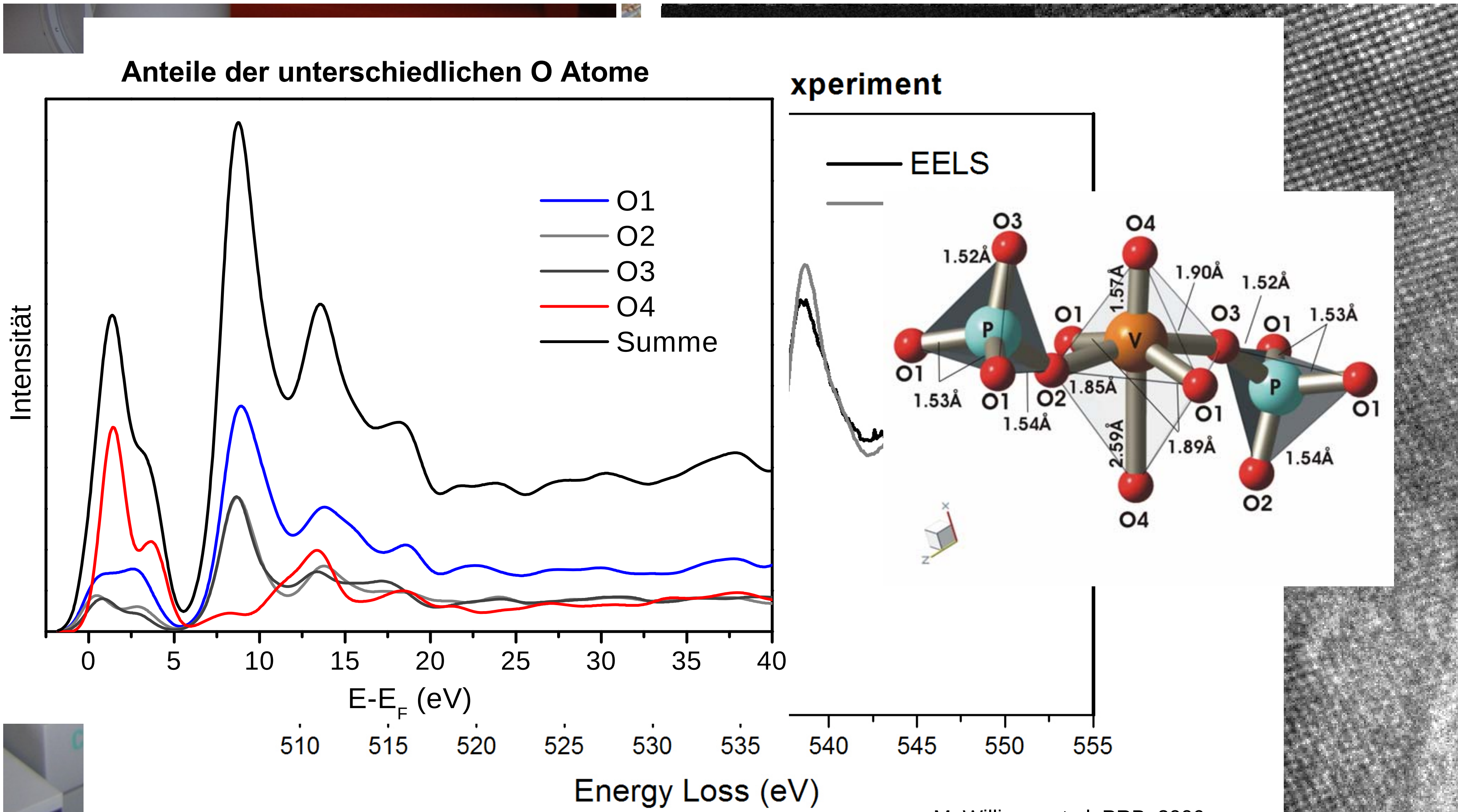
How much of a catalyst is "active" in steady state ?





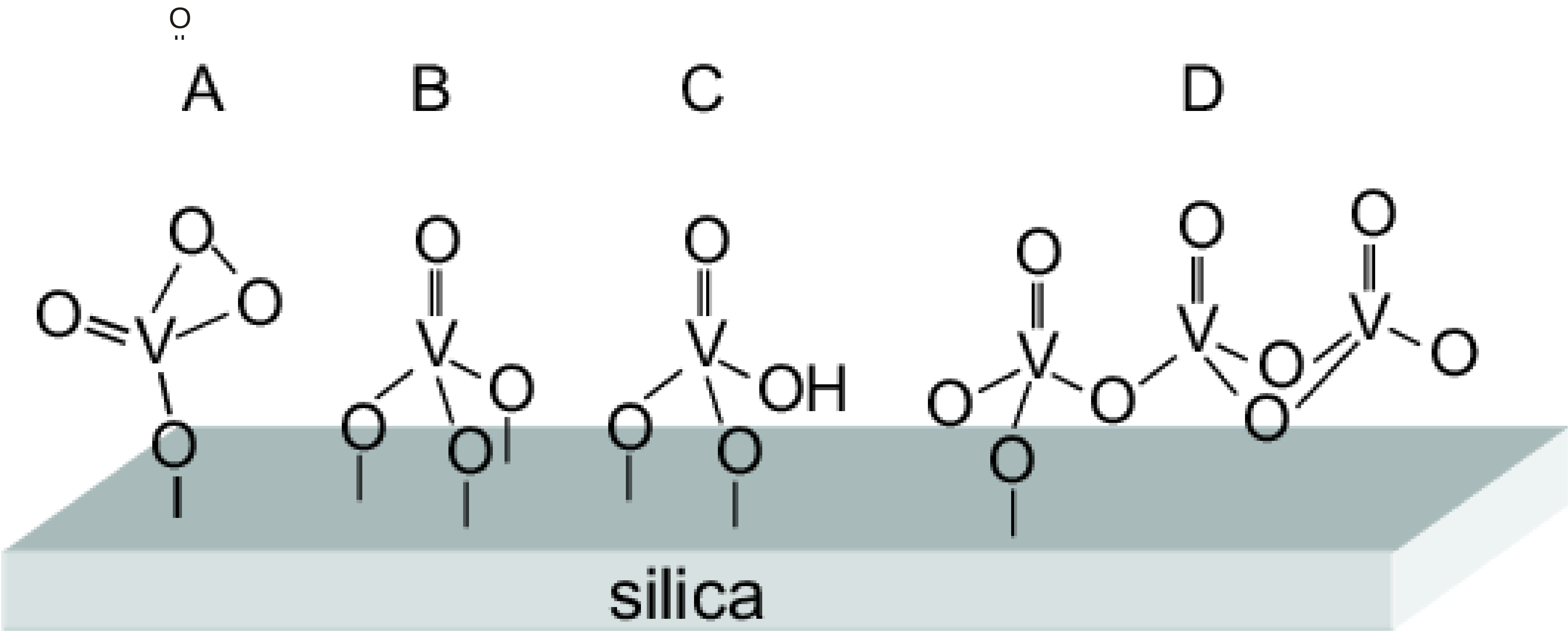
Reversible modifications of a fraction of the surface

Electronic Structure: EELS vs NEXAFS
Spatial vs surface sensitivity



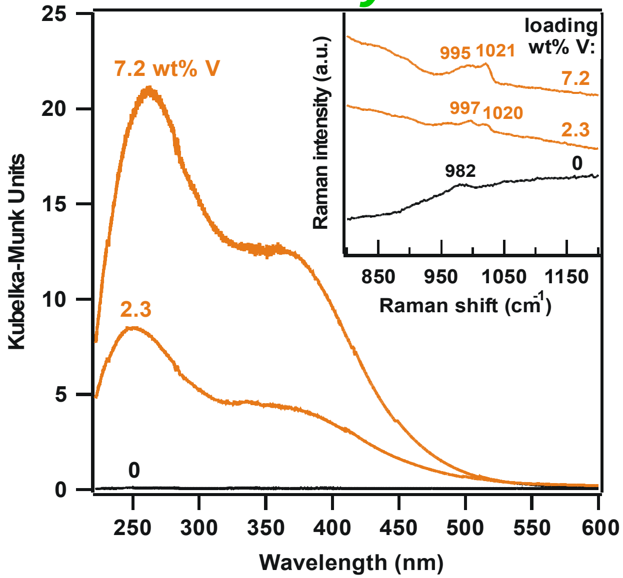
M. Willinger et al. PRB, 2006

What is active

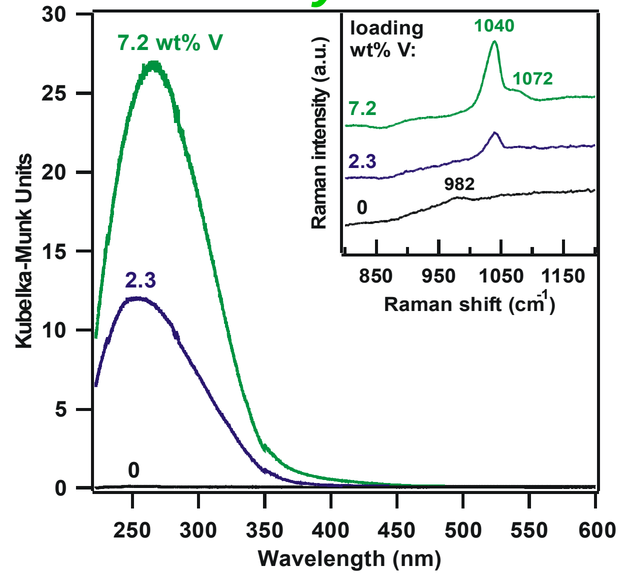


V_XO_Y-SBA 15 “Activation” generation of active sites

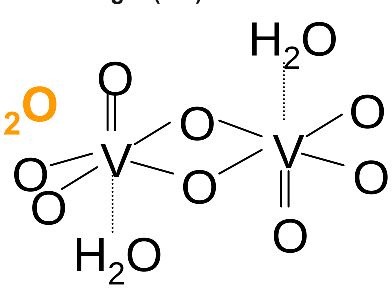
‘as is’: hydrated

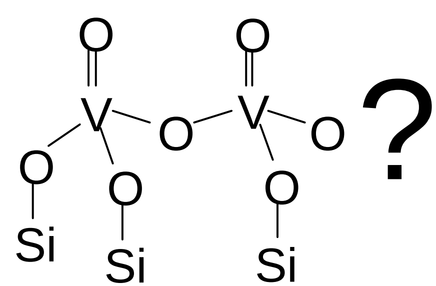


dehydrated

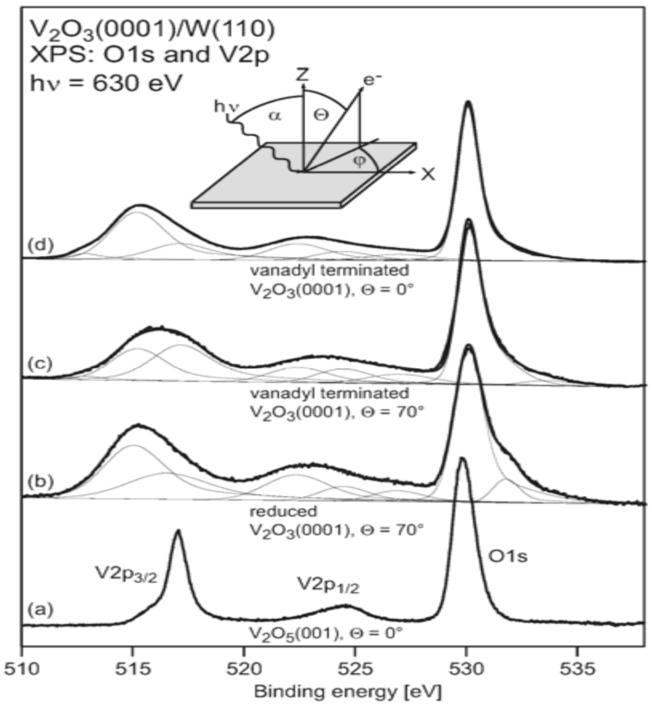


$V_2O_5 \bullet n\ H_2O$

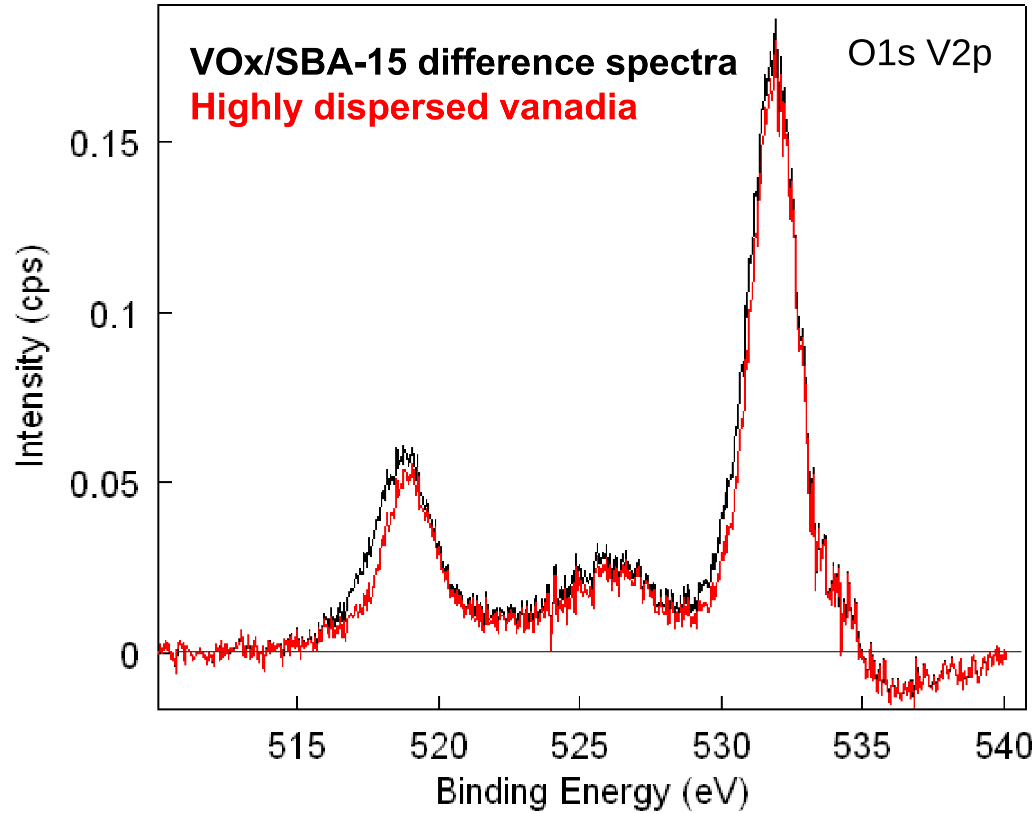




The activated state



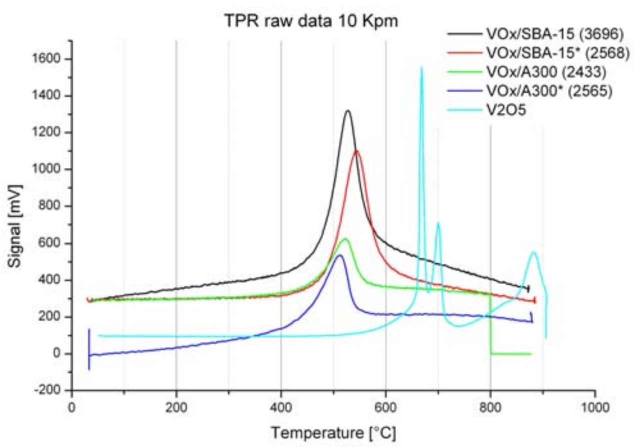
Freund et al., Surf. Sci. 2003



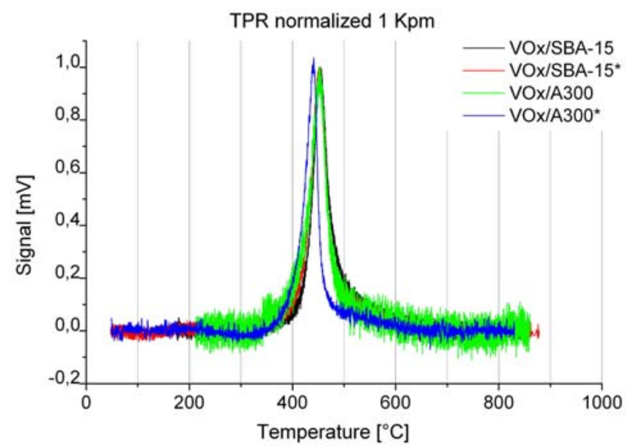
XPS sees a local coordination similar to pyramidal
Electronically isolated from common Fermi edge
Modified oxygen atoms at support intrecace (?)

Propane ODH V-SBA

500ºC	C_3H_8 Conversion (%)	Time on stream (min)	GHSV (h^{-1})	Selectivity (%) C_3H_6	acrolein	acetone	CO_x
SBA-15	0	120/240	18000-6000	0	0	0	0
VOx/SBA-15 (3wt% V)	**1**	120/240	18000	**90**	10	0	**0**
	4	120/240	12000	**81**	12	7	**0**
	11	120/240	6000	**47**	11	6	**36**

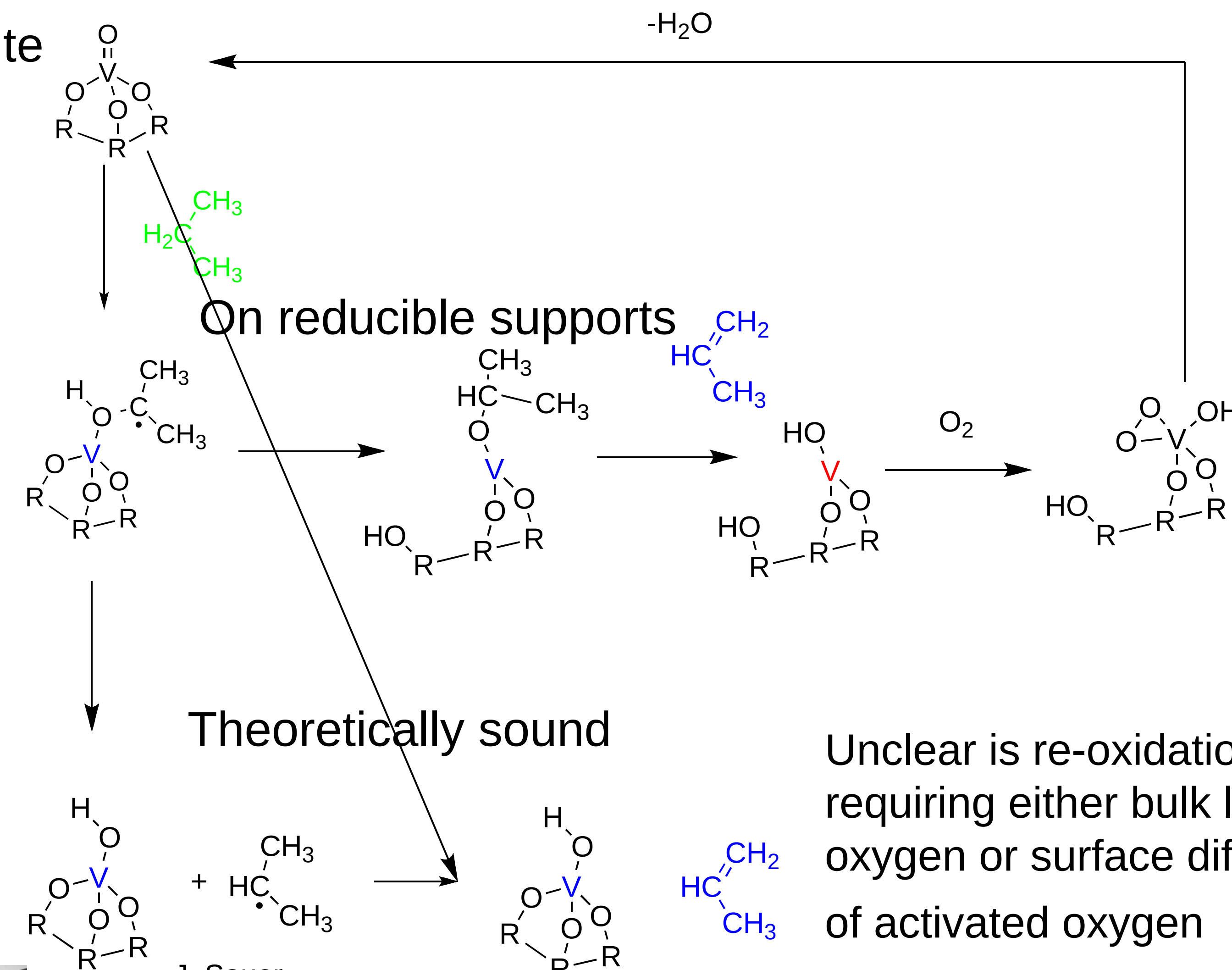


R. Schomäcker et al



Reaction sequences I

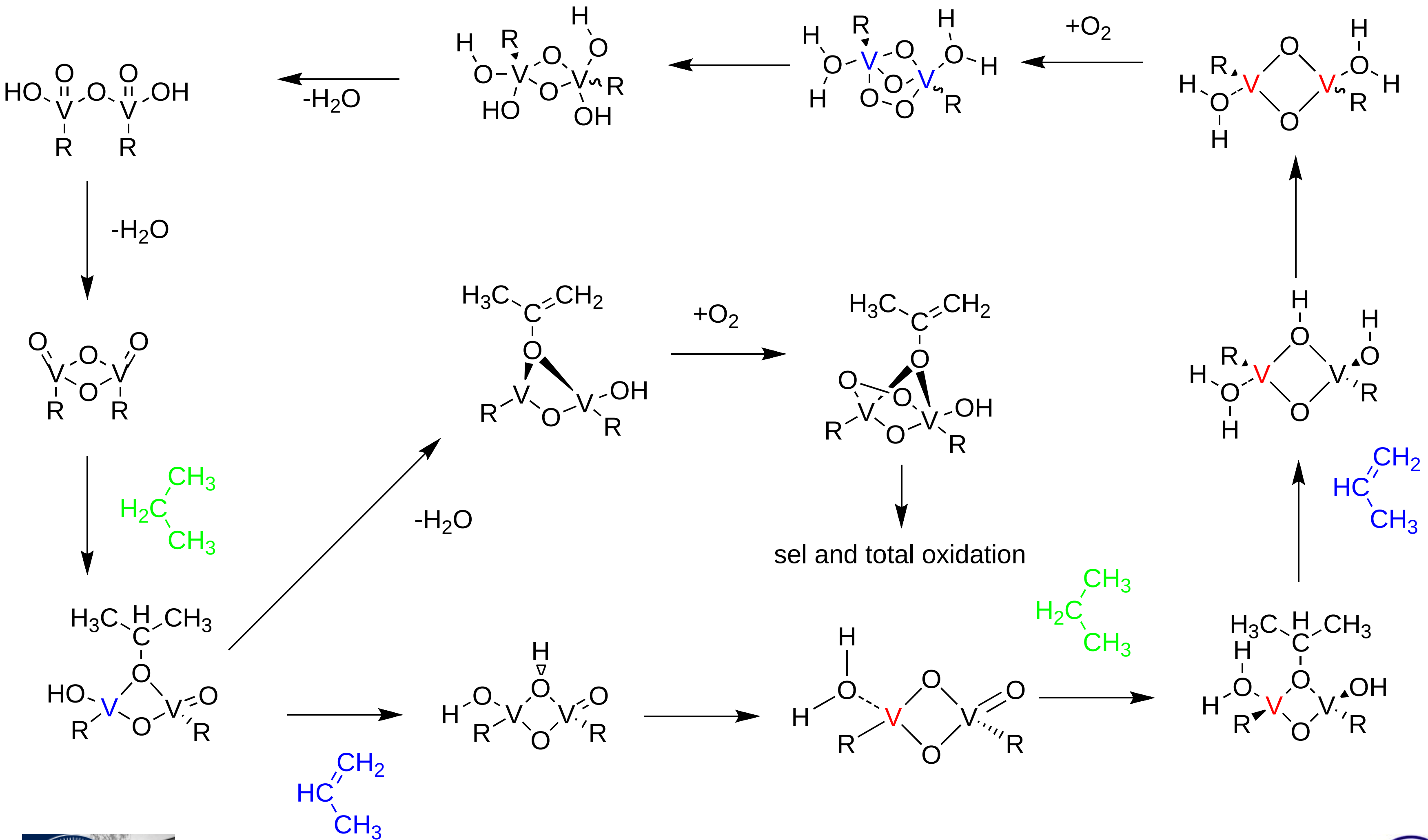
Single site



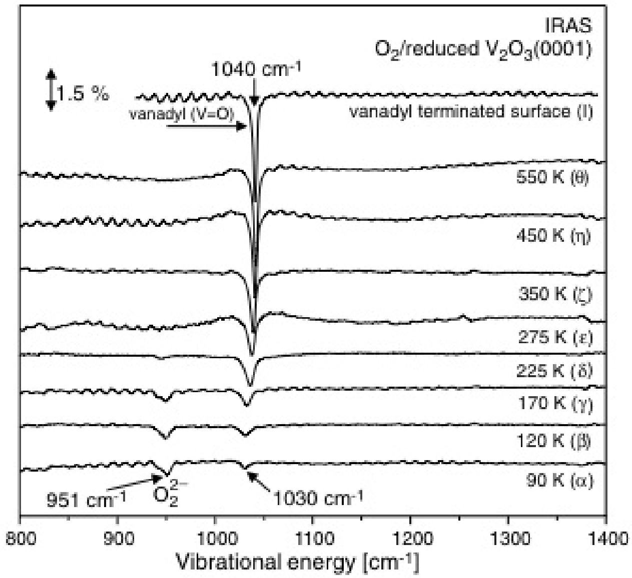
Unclear is re-oxidation requiring either bulk lattice oxygen or surface diffusion of activated oxygen

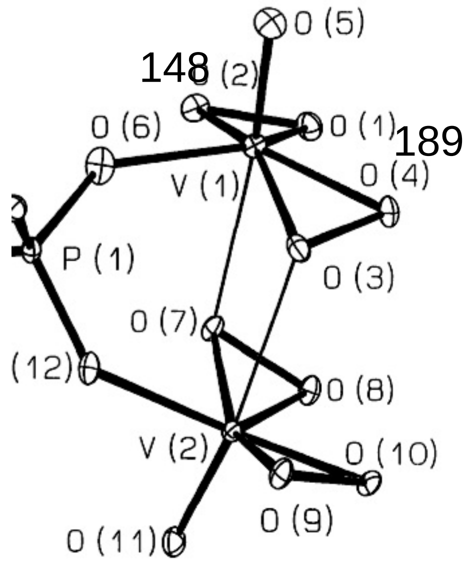
J. Sauer
J. Phys. Chem 2007

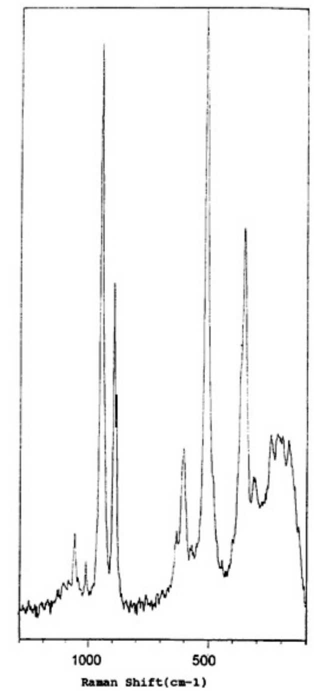
Reaction sequences II



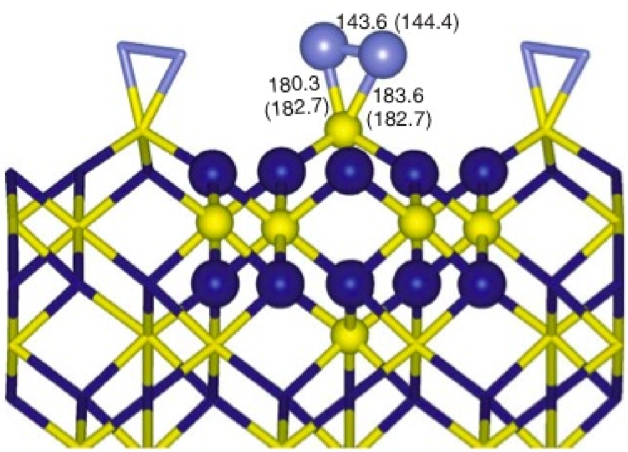
The peroxo species in reference data







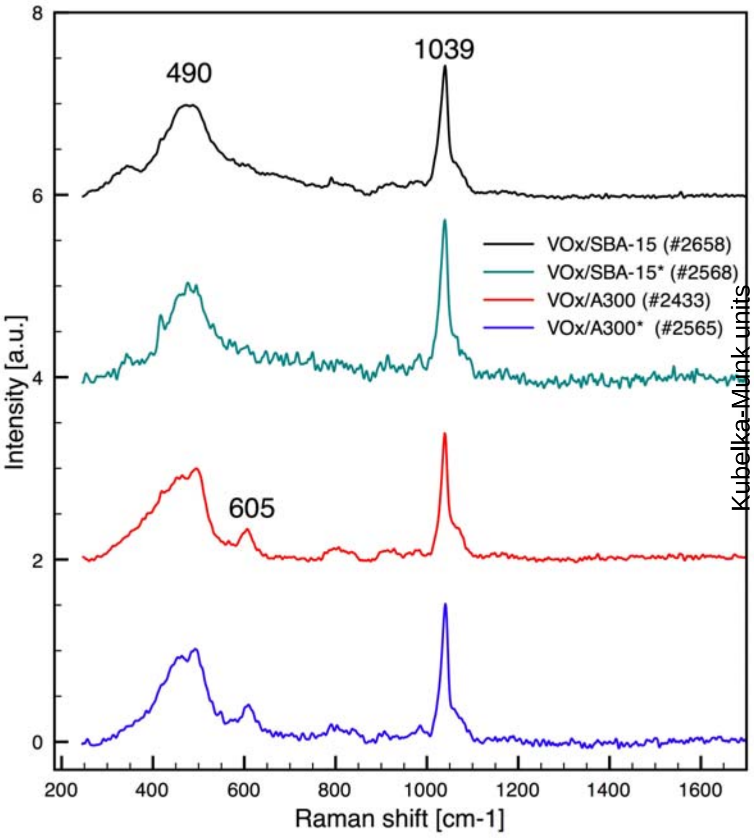
P. Schwendt e al
Poyhedron, 1996

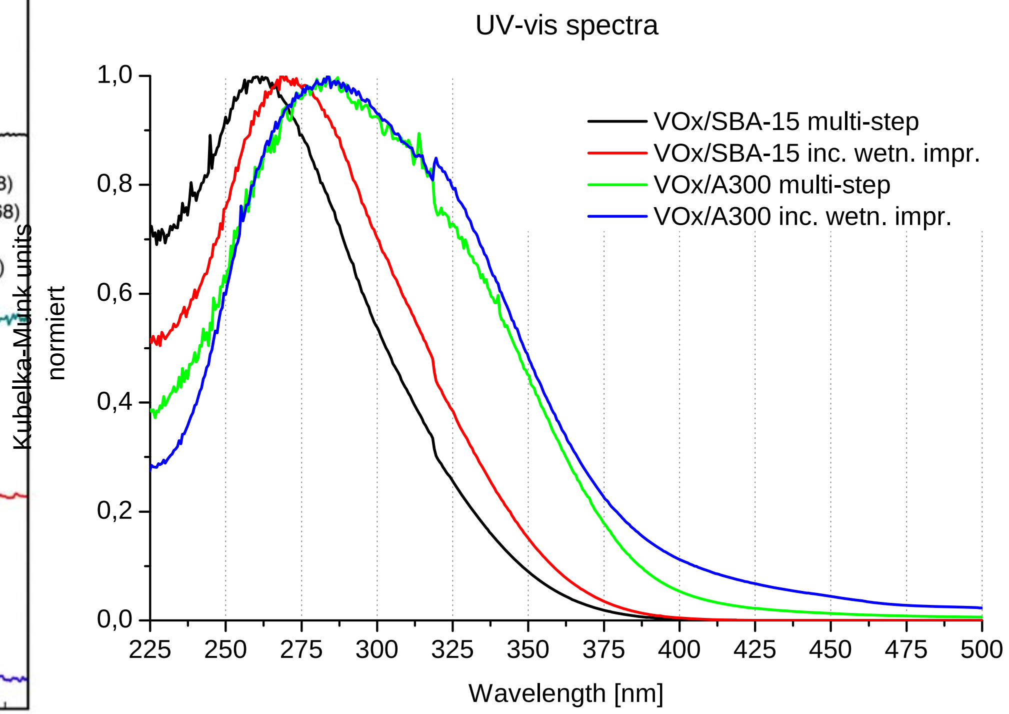


Freund, Sauer et al
Surf. Sci 2006

Vanadyl-peroxoide is a well-characaterised reactive species

Support effects: "silica"
How sensitive are detection methods?





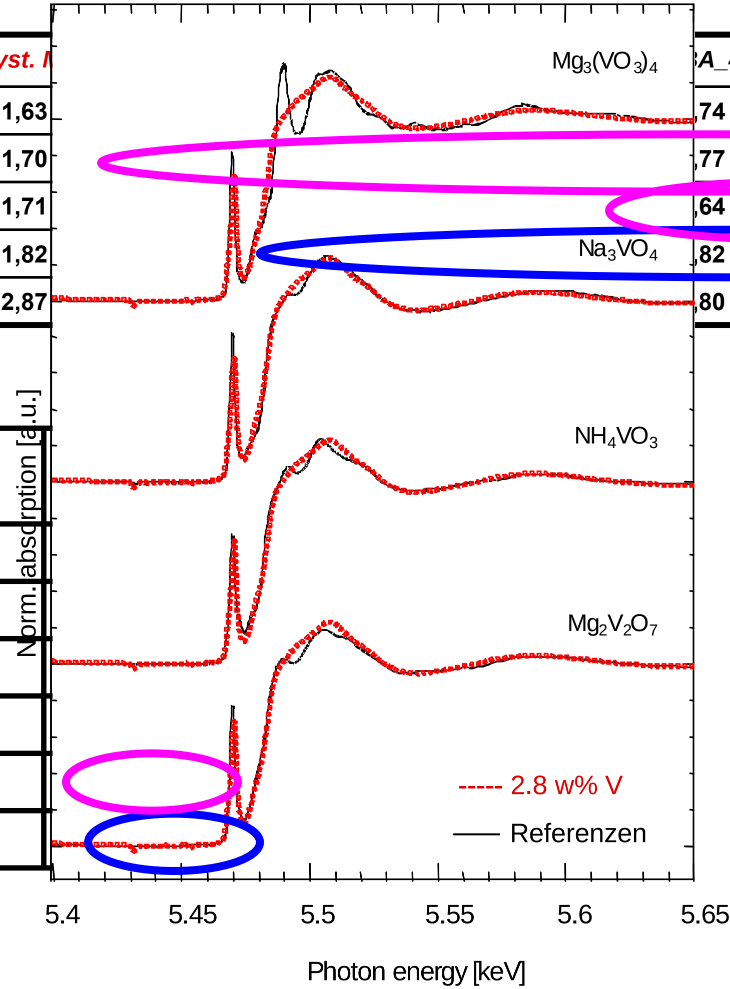
Two impregantion methods on powder and mesoporous silica

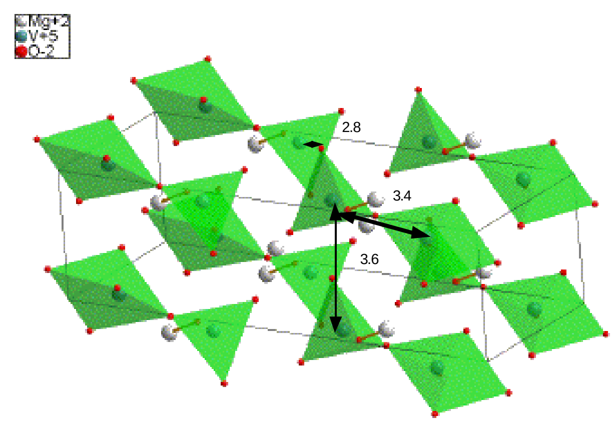
EXAFS what can we learn about oligomerisation?

A. Walter, T. Ressler, TUB

SS-PATH	CN	Cryst. M	A_49	VSBA_100	VSBA_108	NH4VO3
V-O	1	1,63	,74	1,75	1,78	1,68
V-O	1	1,70	,77	1,76	1,72	1,71
V-O	1	1,71	,64	1,66	1,70	1,83
V-O	1	1,82	,82	1,83	1,84	1,79
V-O	1	2,87	,80	2,79	2,77	2,75

Bond	Kind of Bond
A	V - V
B	V - V
C	V - V
D	V - V
E	V - O
F	V - O

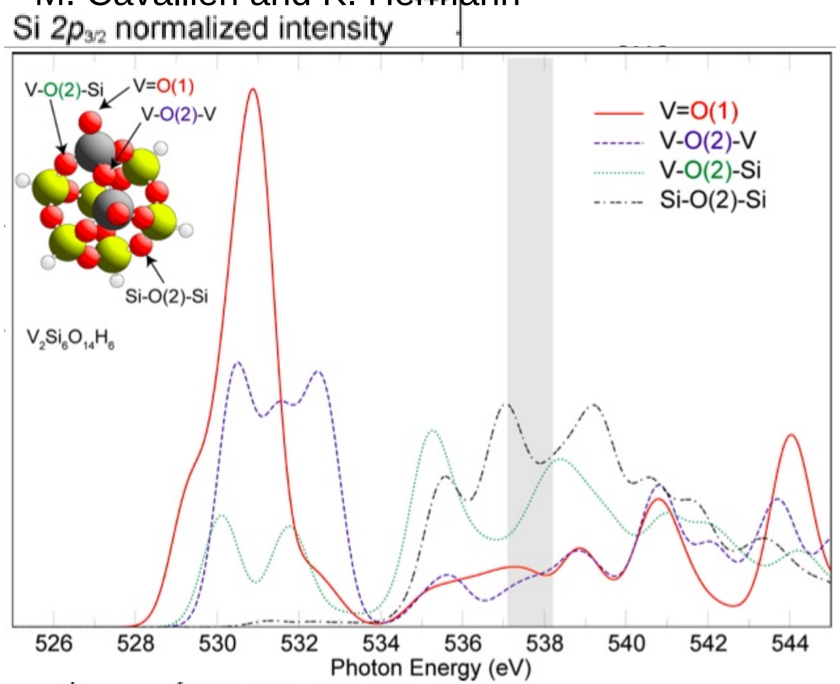


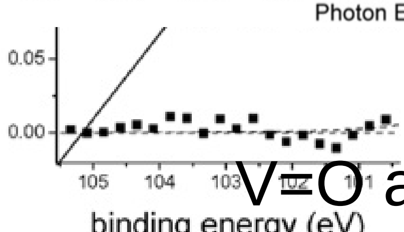


$Mg_2V_2O_7$ ICSD-2321

OK-NEXAFS: theory and experiment

M. Cavallieri and K. Hermann

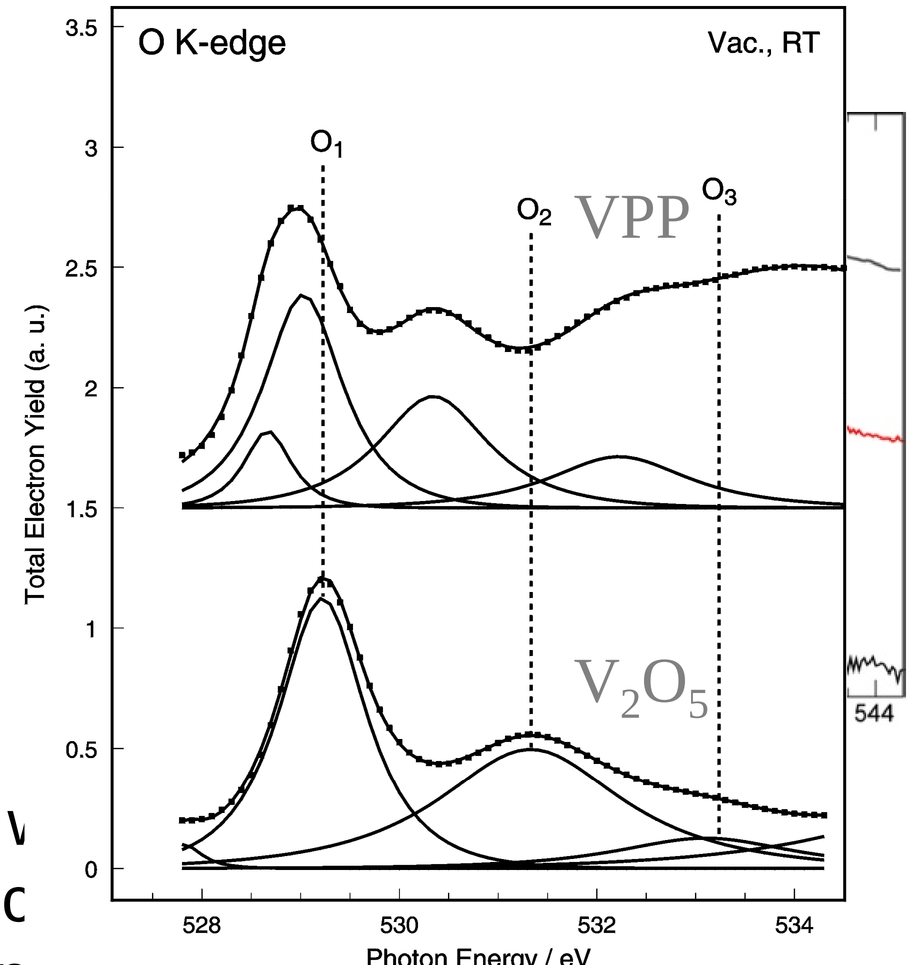




Si-O and V-O w

Gerofolini et al.
Appl Phys A, 2003

V=O and V-O-V also c



Peak shape strongly dependent on V-O-V bond angle

Red-Ox Chemistry and XPS

$$O_2 + 4\,e^- \rightarrow 2\,O^{2-}$$

$$4\,M \rightarrow 4\,M^+ + 4\,e^-$$

$$4\,Cu + O_2 \rightarrow 2\,Cu_2O$$

$$2\,(RCH_2)_2 \rightarrow 2\,(RCH)_2 + 4\,H^+ + 4\,e^-$$

$$2\,(RCH_2)_2 + O_2 \rightarrow 2\,(RCH)_2 + 2\,H_2O$$

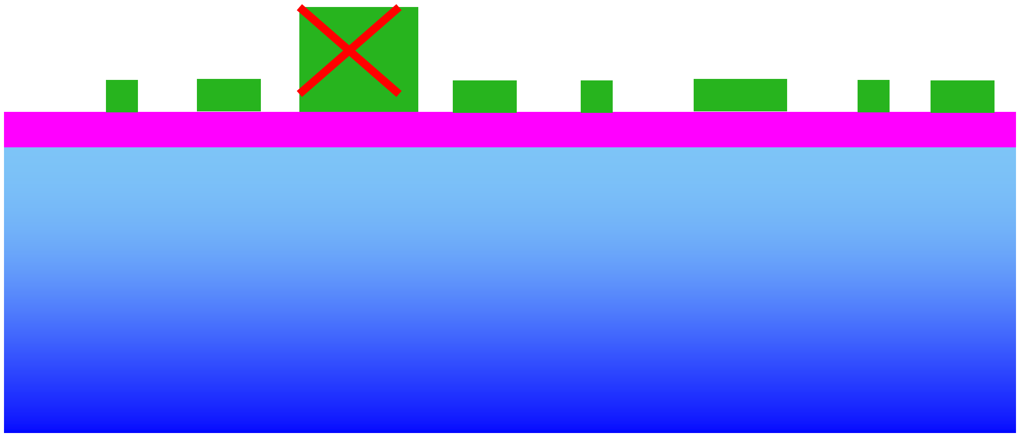
$$2\,(RCH)_2 + O_2 \rightarrow 2\,(RCH)_2O$$

O(C,H) | O electro | O nucleo

H_2O | $O^{2-} \rightarrow (M^+)_2$ | $O^{2-} \leftrightarrow (M^+)_2$ | $O^{2-} \leftarrow (M^+)_2$

534 | 532 | 530 | 528

Functional elements of a sel ox cat



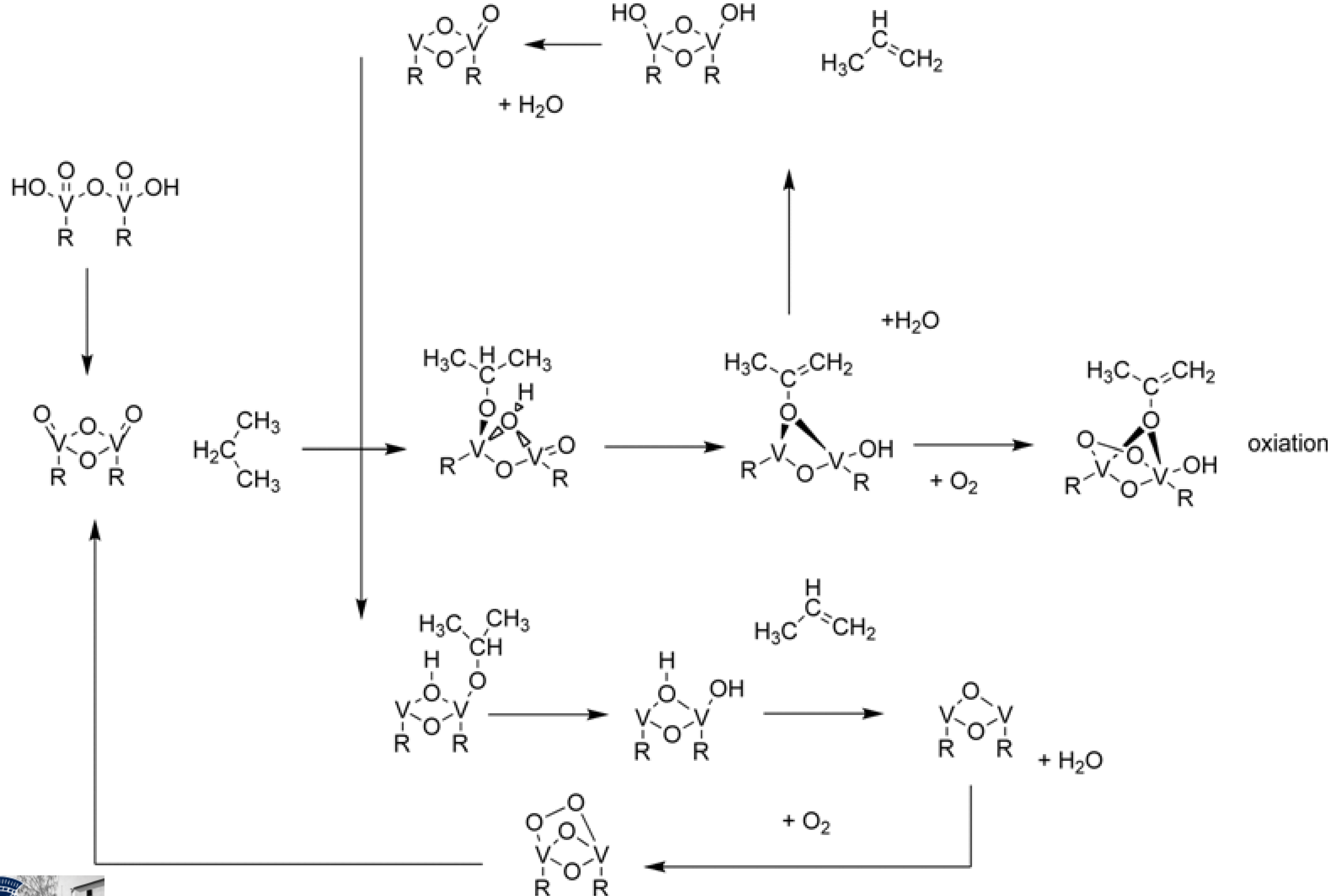
Distribution of active species
Oligomeric, clusters
No lattice, site isolation

Separation layer
Terminates bulk, segregation kinetics
Surfactant for active species
Controls stability of the active species

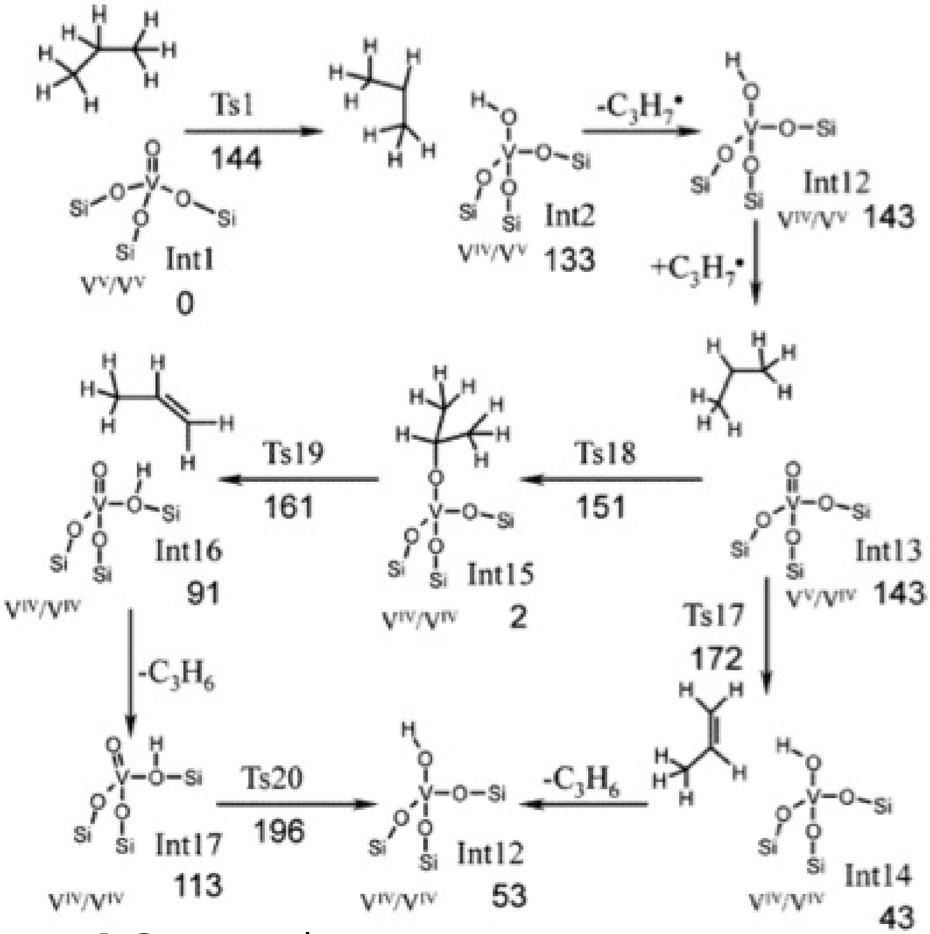
Bulk with complex structure
Dynamics, self repair
Reservoir for active species
Adjusts the reactivity of cations

only the microscopic level is considered
supramolecular assembly forming under reaction conditions

Reaction pathway dual site propane ODH



Model studies

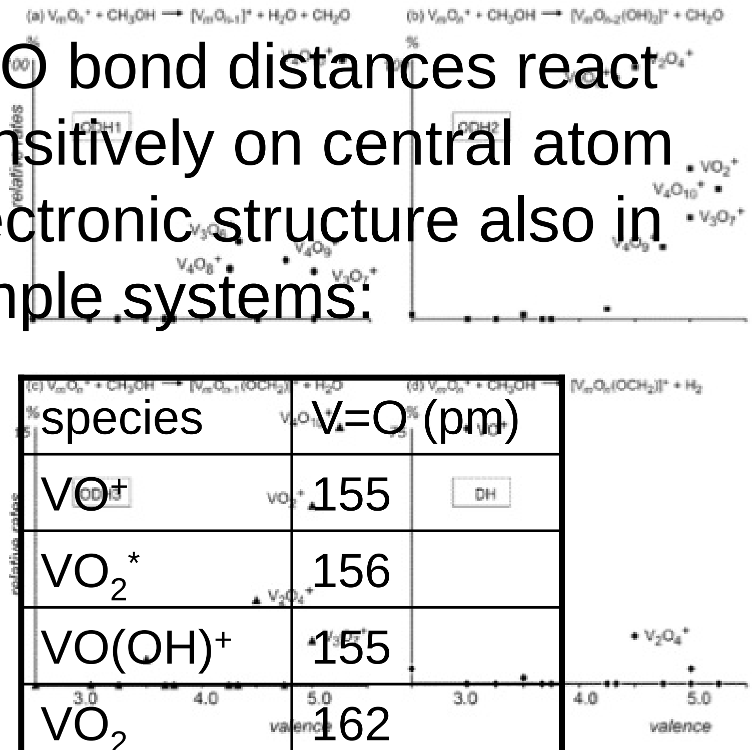


J. Sauer et al
J. Phys. Chem. 2007

Theory gives us a compete reaction scenario of the ODH of propane;
The concept of independent single sites and exchange of radicals is used;
The re-oxidation is not yet described and will create probelms with a single site (4 electrons per oxygen; also transfer of activated molecular oxygen?

Model studies

V=O bond distances react sensitively on central atom electronic structure also in simple systems:



species	V=O (pm)
VO^+	155
VO_2^*	156
$VO(OH)^+$	155
VO_2	162
VO(OH)	161

H. Schwarz et al.
J. Phys. Chem., 2007

H. Schwarz et al, Eur. J. Chem., 2007

Reactivity of gas phase clusters in MeOH ODH critically depends on oxidation state:
high oxidation states favour this reaction,
low oxidation states activate whole molecule, non-selective processes

V3+ most stable reactive species

Dynamics of heterogeneous catalysts

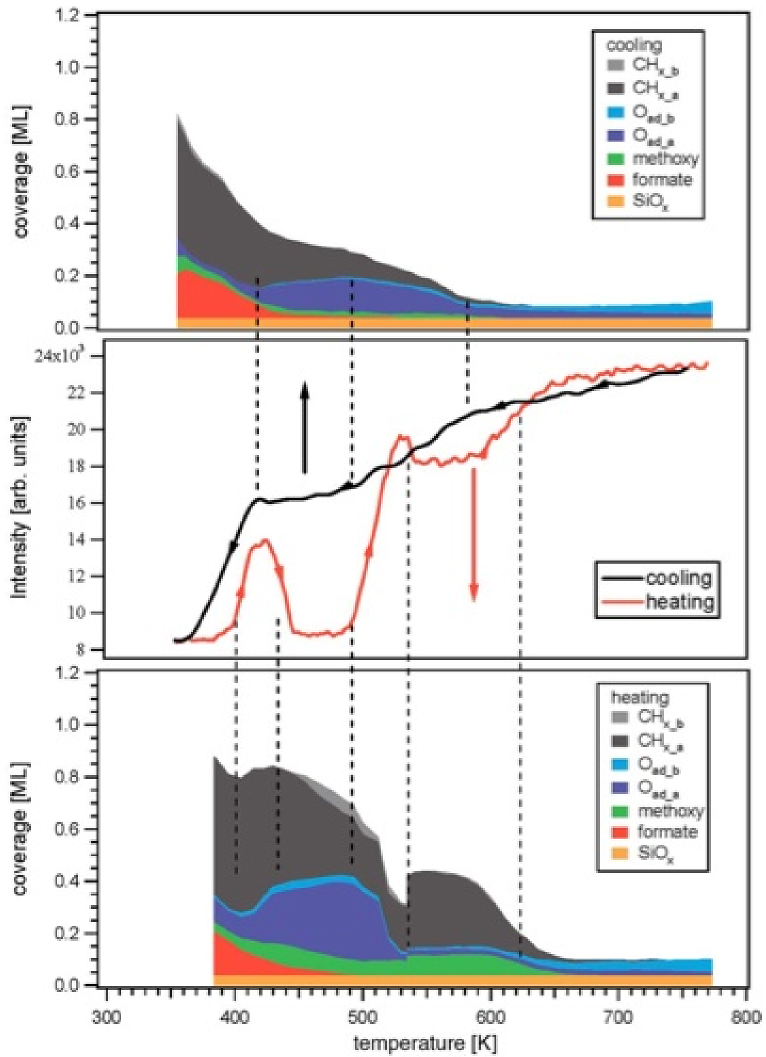
- Catalysts modify the rates of chemical reactions by
  - Pressure-dependent spatio-temporal decoupling of elementary reactions (pressure gap)
  - Enhancement of metastable species (intermediates) above thermodynamic abundance
- Require metastable material for adaptive sites emerging from reactant-catalyst interaction
- Isolation of the material only leaves accidential sites at “defects” for residual activity (material gap)

Catalysis and coverage: Cu/O system

In situ monitoring of surface species during methanol oxidation to FA:

Power of speciation of XPS (from C1s and O1s data)

S. Günther, R. Imbihl



Under highly reactive conditions no hydrocarbon or active oxygen at the surface in detectable quantities but O-modified Cu (111) surface: no “oxide”

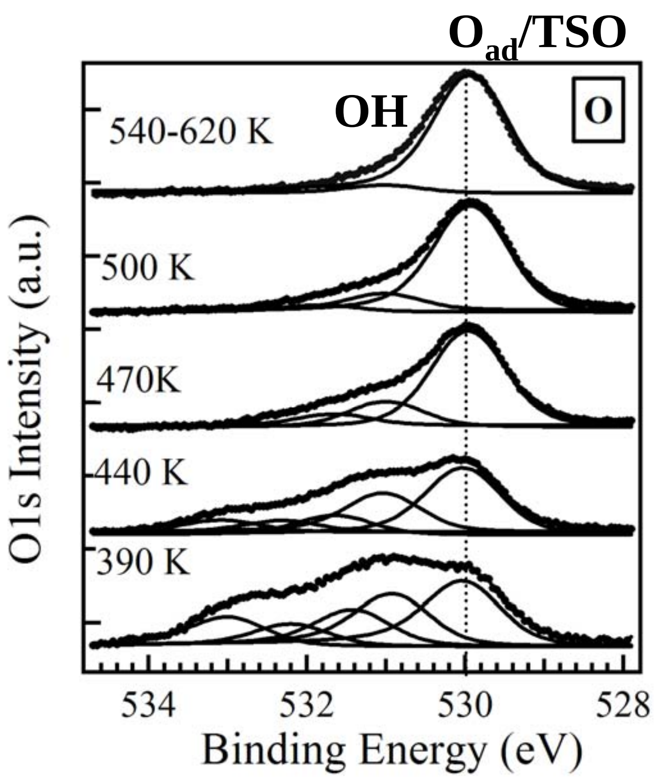
Note hysteresis and oxide formation as inhibiting process during cool-down

Di-oxygen as oxidant

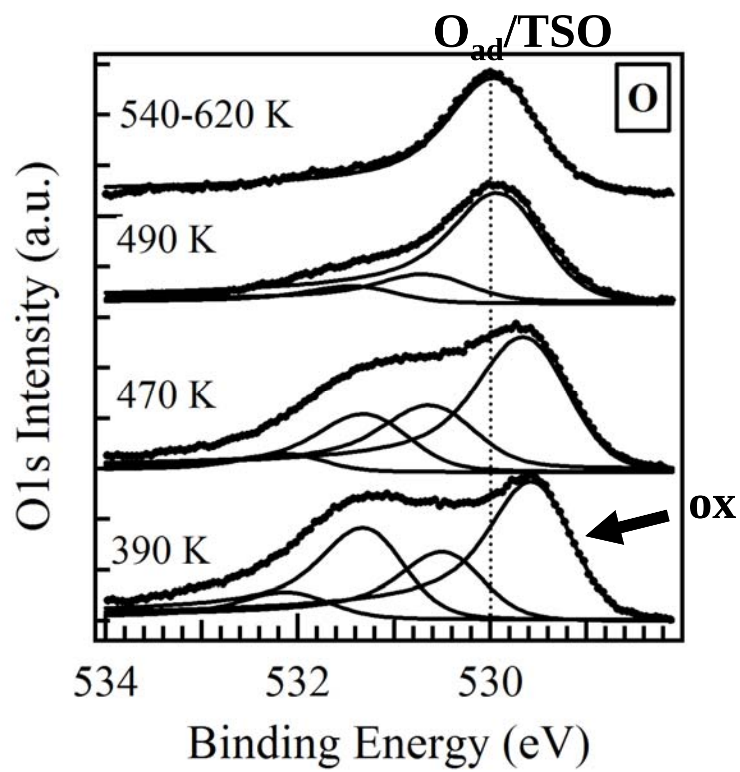
- Atomic chemisorbed oxygen (created typically in UHV) is amphoteric in redox properties: at "virtual pressure" $\rightarrow$ sub-surface
- Sub-surface oxygen is not reactive but
  - Polarizes the surface for adsorption
  - Restructures the surface by incorporation (autocatalytic)
  - Segregates to the 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)
  - Protonates via OH oxygenates

O1 s in-situ spectral responses

pre-catalyst: metallic Ru(10$\bar{1}$0)

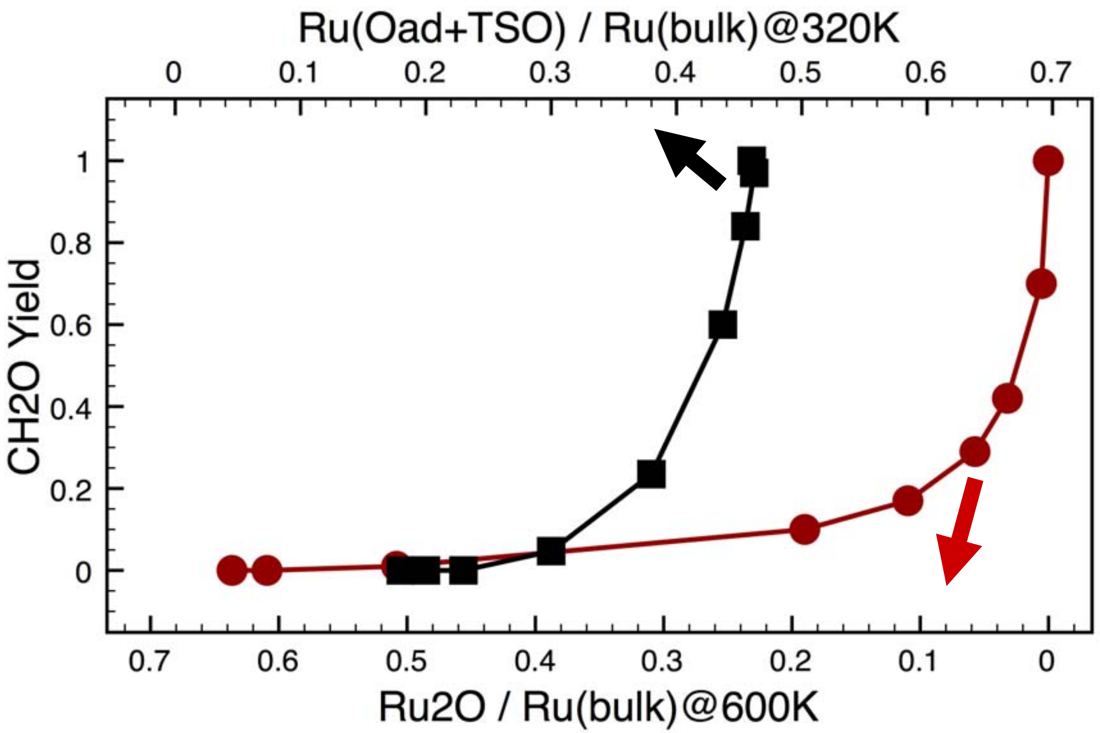


pre-catalyst: oxidized Ru(10$\bar{1}$0)



Quantitative structure function relation

Accumulation of Ru(TSO)

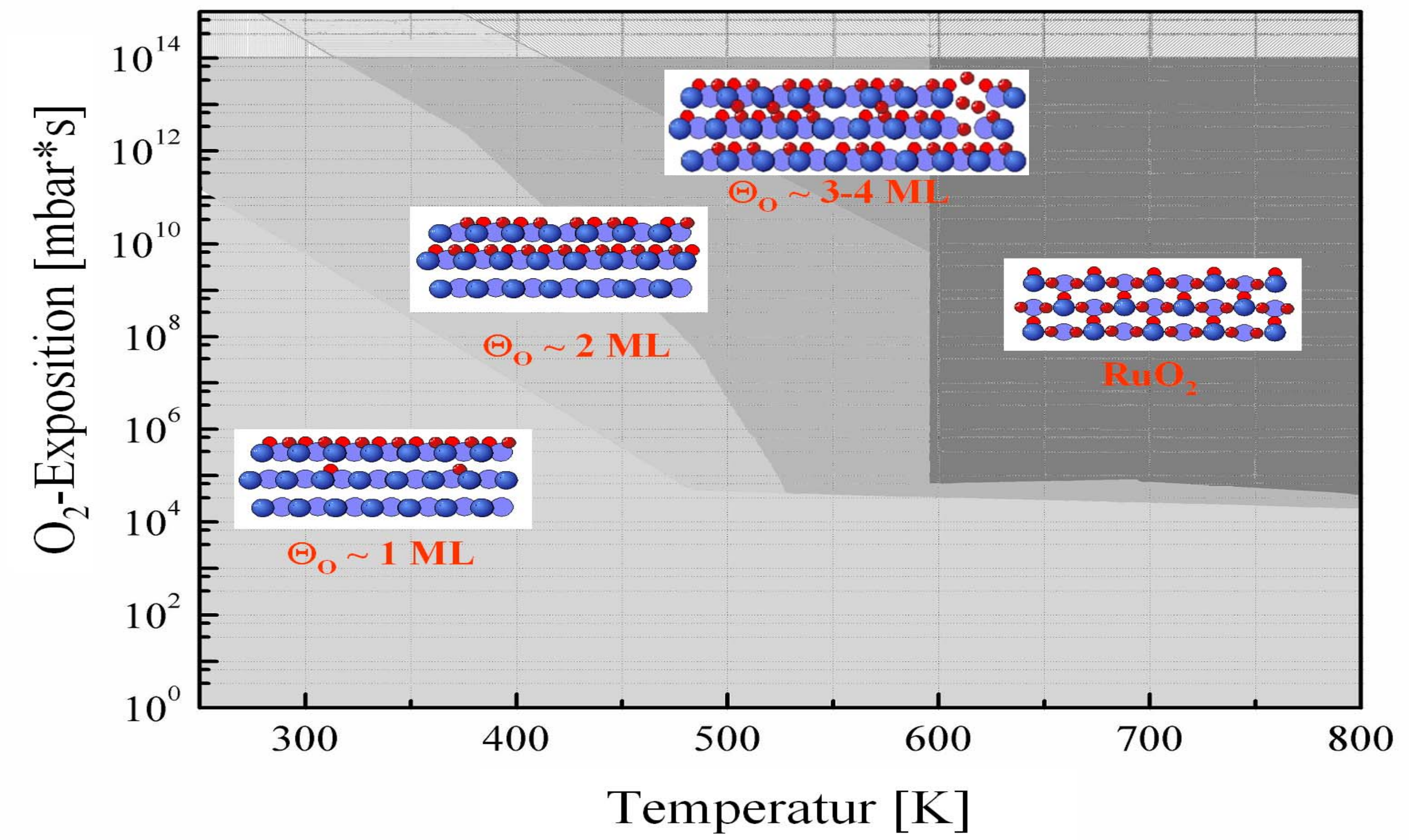


Reduction

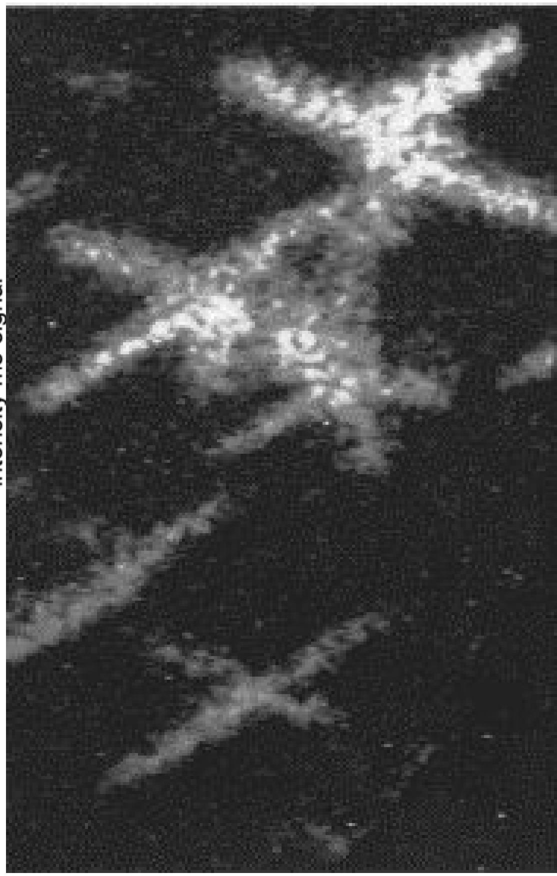
Oxide is inhibiting

TSO forms from oxide and is active state

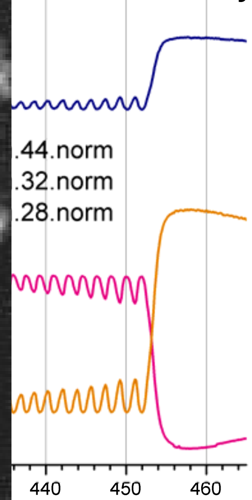
Metastable sub-surface species



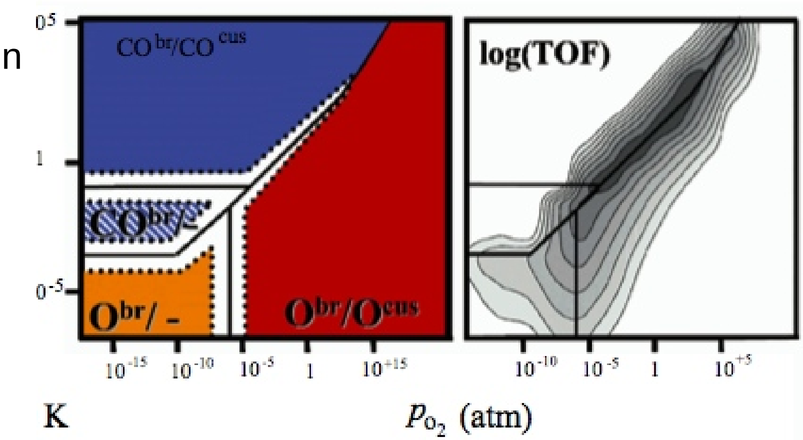
Comparison with CO oxidation over Ru



RuO_2 powder
488 K
excess of oxygen



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



two surface states
kJ/mol) reactivation

Niehus , Böttcher et al

Theory predicts in agreement with surf sci studies rate maximum where several phases are iso-energetic: metastable

Challenge in catalysis

- Enormous sucess in understanding of individual elementary steps (surface science).
- Was enabled by excluding complexity (model systems).
- Assembly of elementary steps to working cataysts in reactions with kinetic demands not successful.
- Reduction of complexity (Langmuir instead of Taylor models) was too drastic.

Function of a catalyst: dynamical limit