Complex Metal Oxides as Heterogeneous Catalysts

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Scope and Acknowledgements

Function of catalysts and structure-function correlations as basis for rational design efforts.

Full analysis of structural complexity by in-situ observation with complementary techniques.

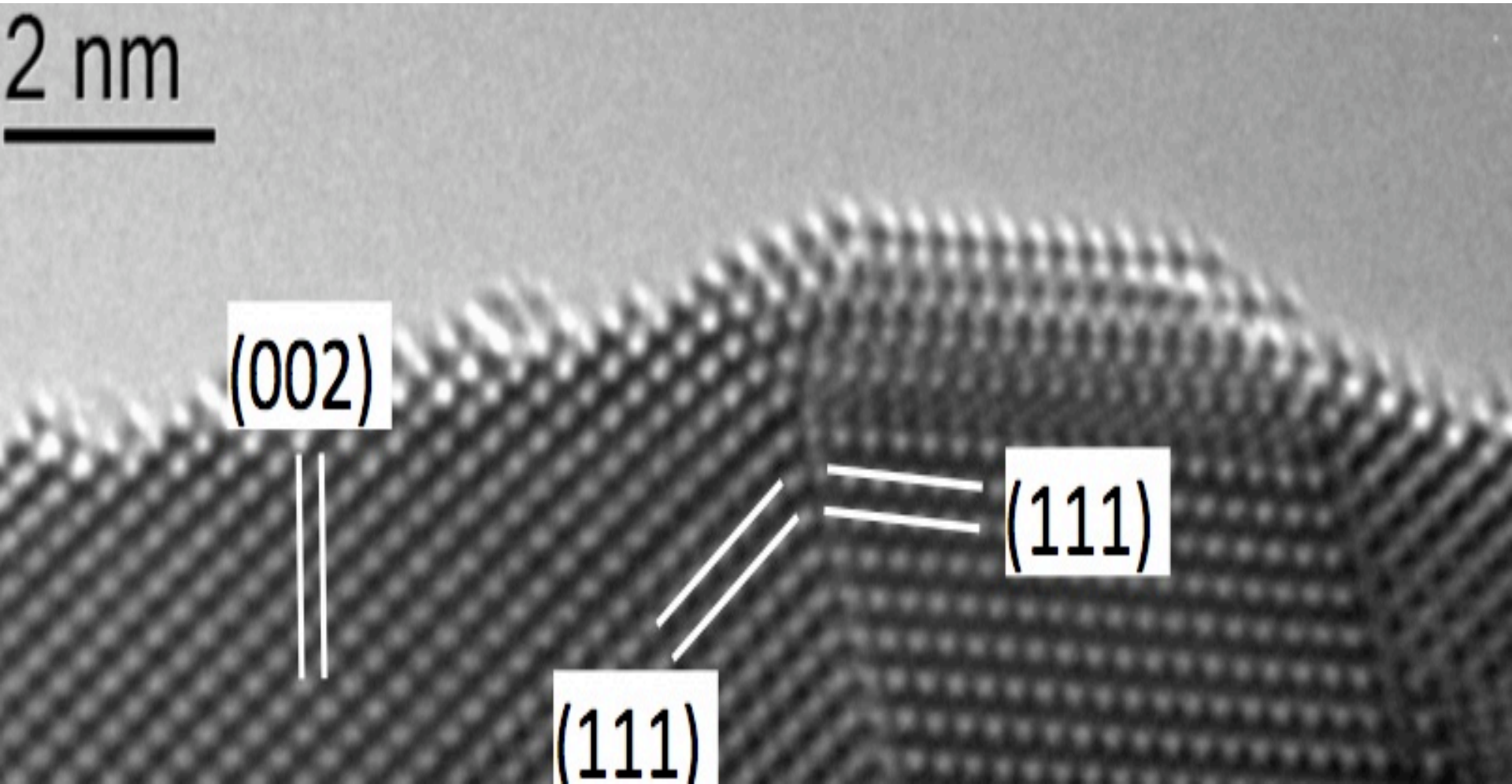
Thanks to the group leaders:
M. Behrens, (R. Horn), A. Knop-Gericke, J. Tornow, A. Trunschke, M. Willinger

Taylor model

The ordinary general, inorganic, and organic chemistry of substances is concerned with the reactions and properties of many million millions of examples of such atoms or molecules, and the result given is a statistical average covering all the cases. The properties of the contact agent, especially in catalytic reactions difficultly achieved, are those of the aristocracy of the atomic or molecular species concerned, and are as different from the statistical average behavior of the crowd as the actions of an educated minority of people should be different from that of an indiscriminately collected mob.

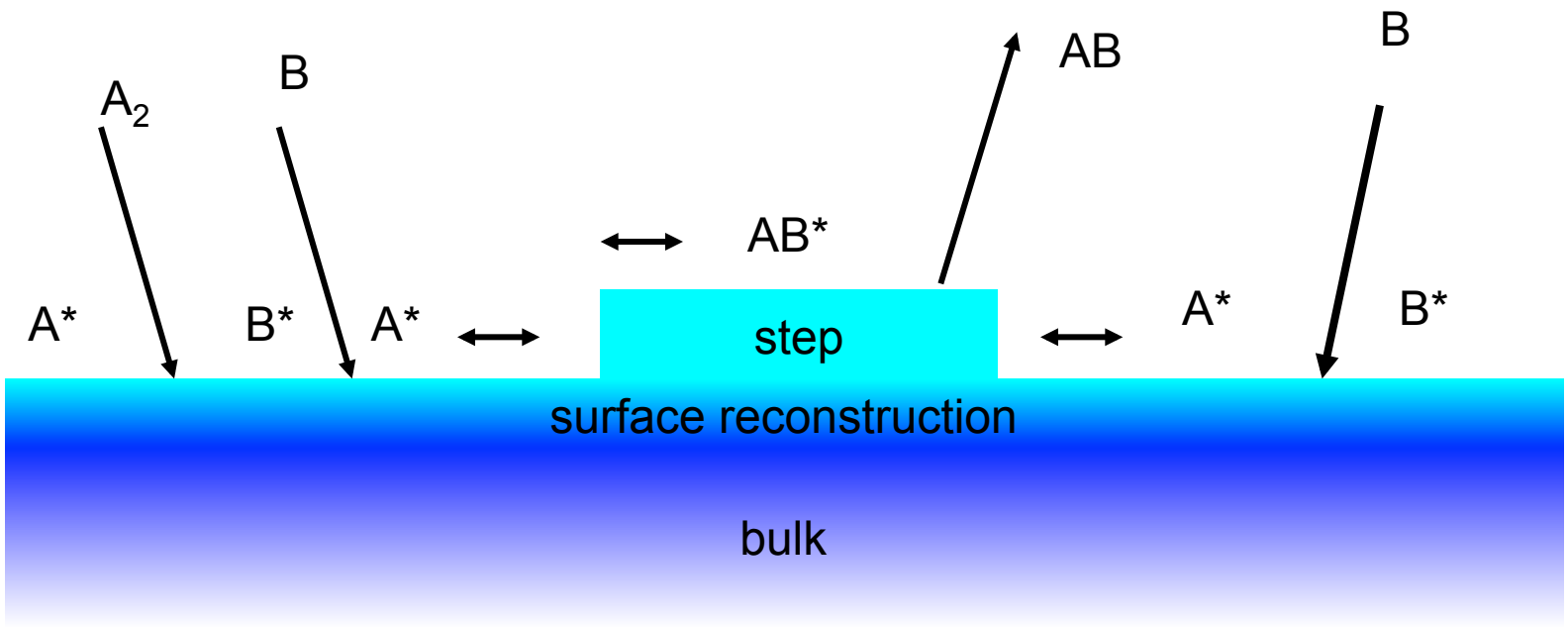
J. Phys. Chem, Vol 30, (1926)

Taylor model



Standard model of heterogeneous catalysis
deep understanding, limited function

system is close to equilibrium
theory finds minimal energy configurations



Adsorbate structures dynamical (chemical waves)
Bulk is “irrelevant”, no chemical transformations sub-surface

Works well for adsorbate-controlled reactions (are only few)

Standard model of heterogeneous catalysis deep understanding, limited function

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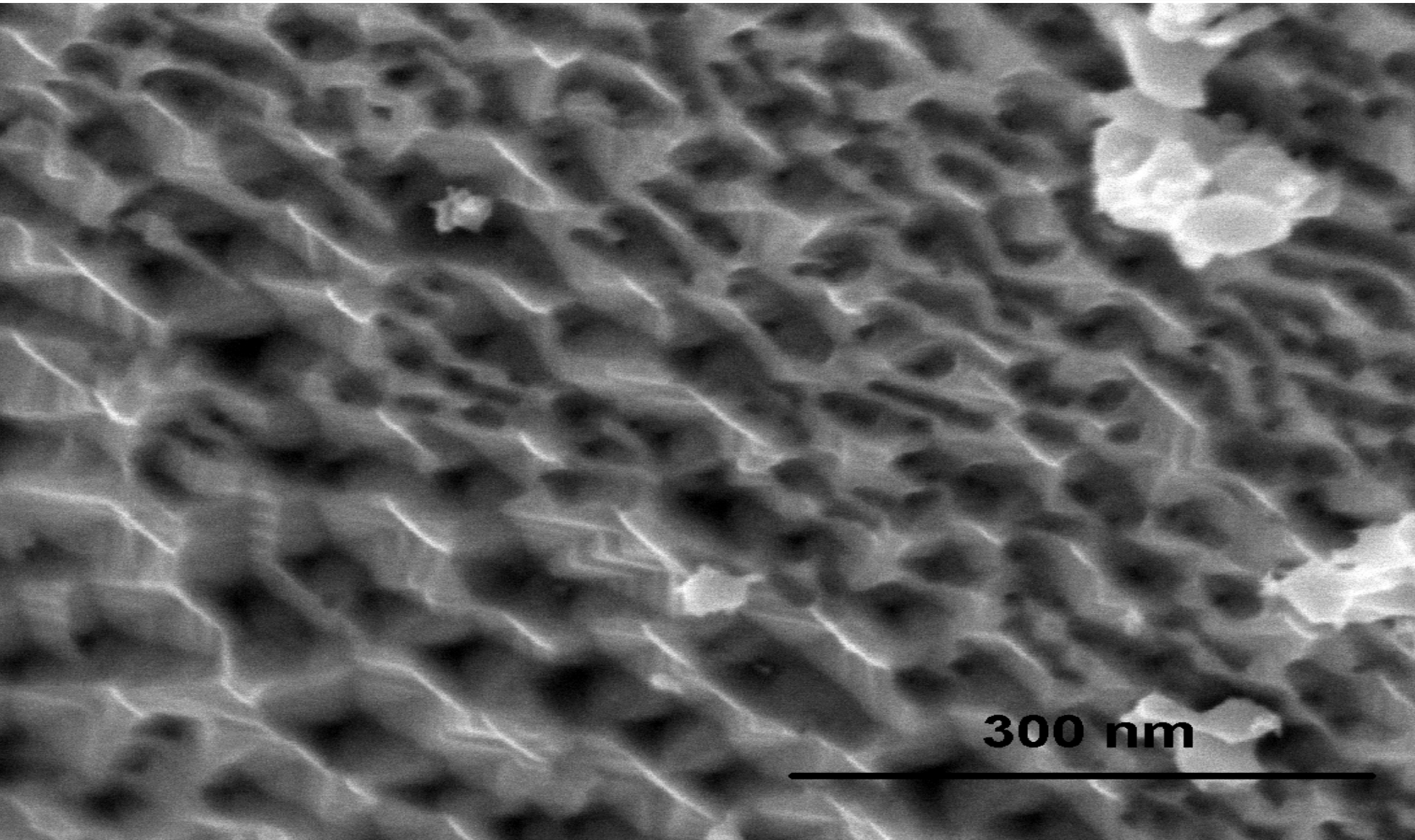

More complexity: Active sites
In-situ analysis

- 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.

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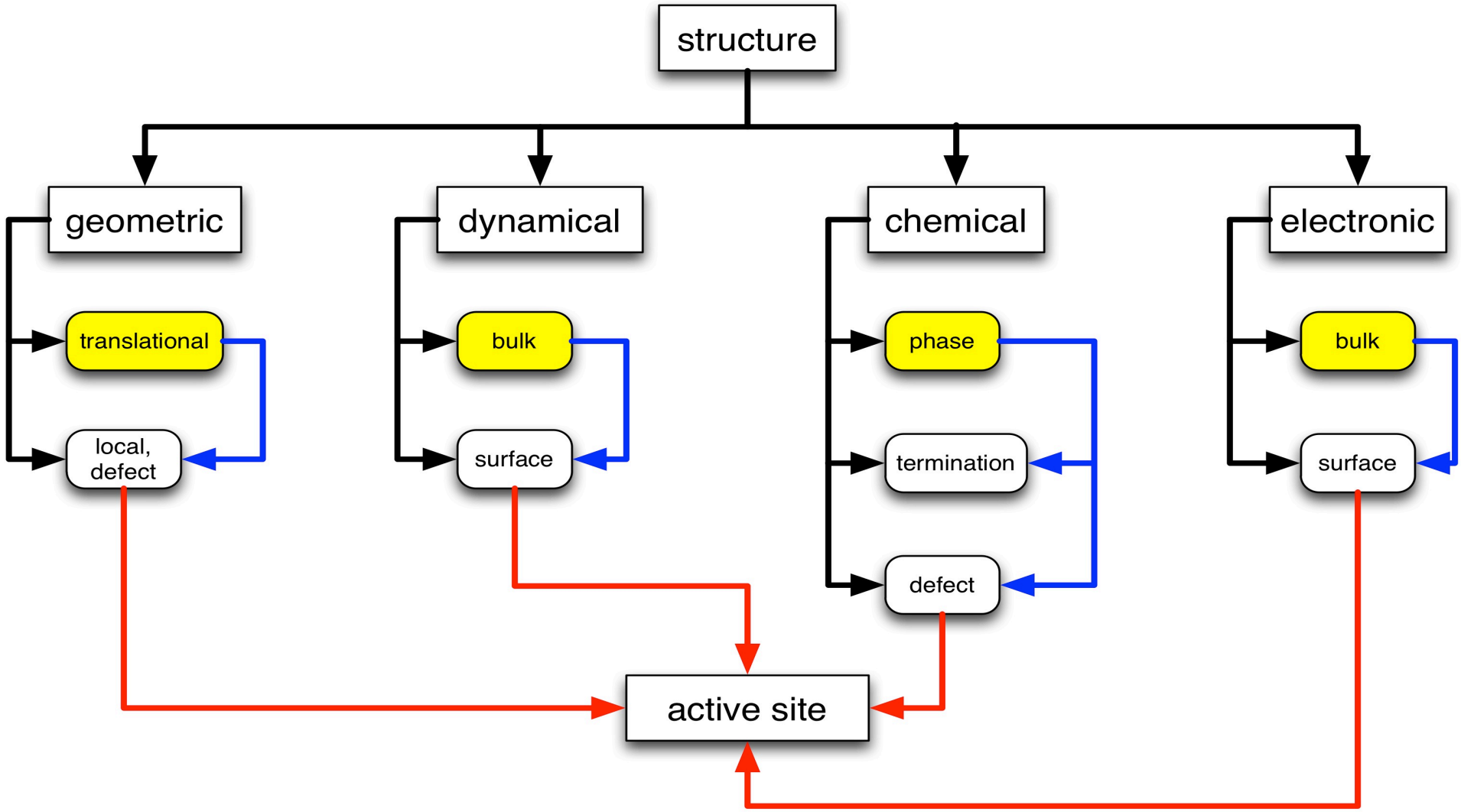
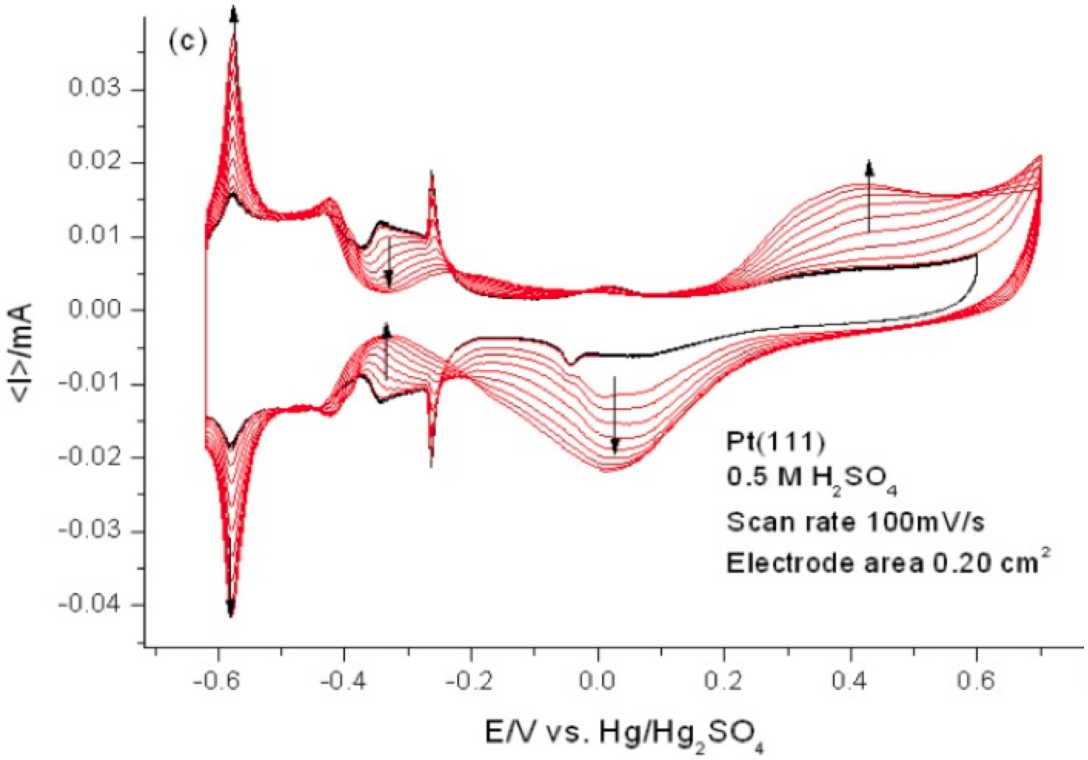
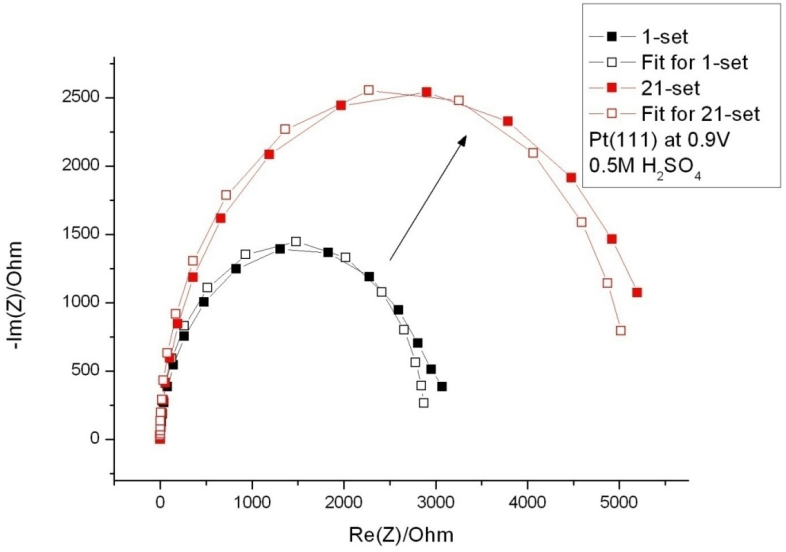
Catalyst structure: A variable target



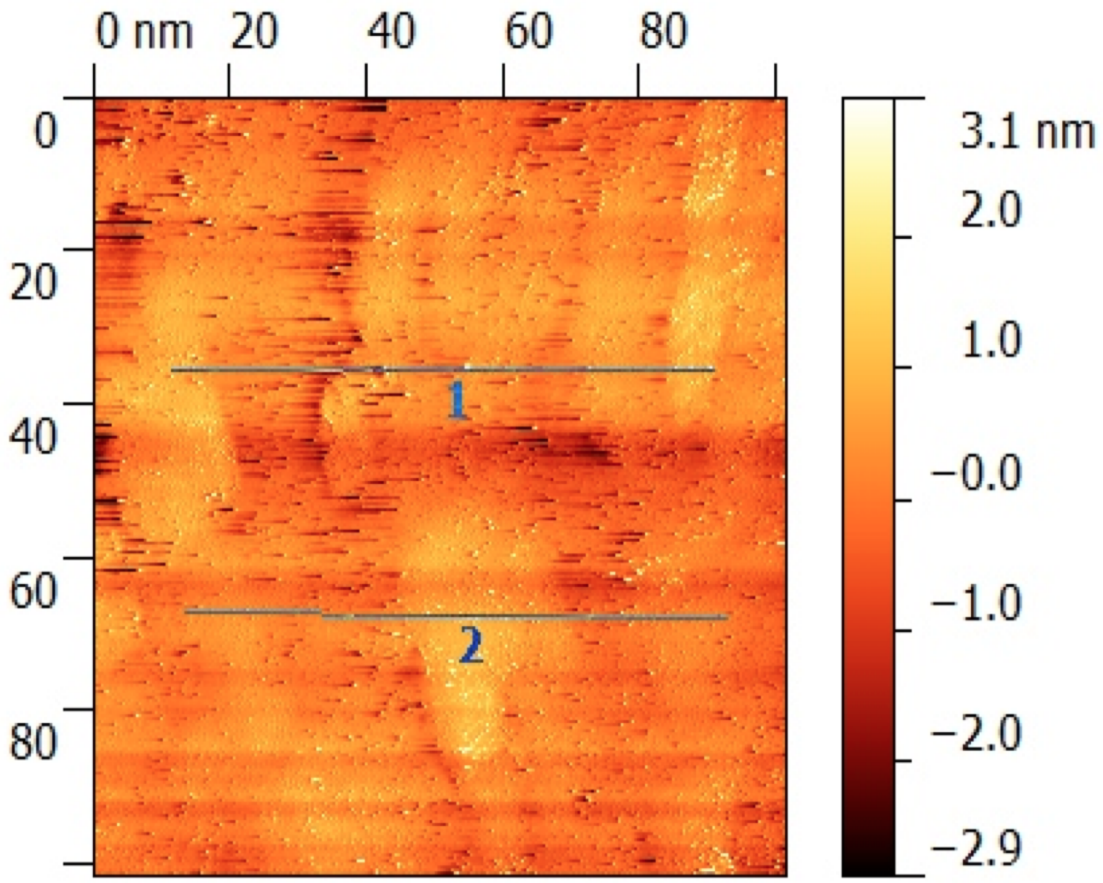
Excursion: Dynamics of Pt in OER



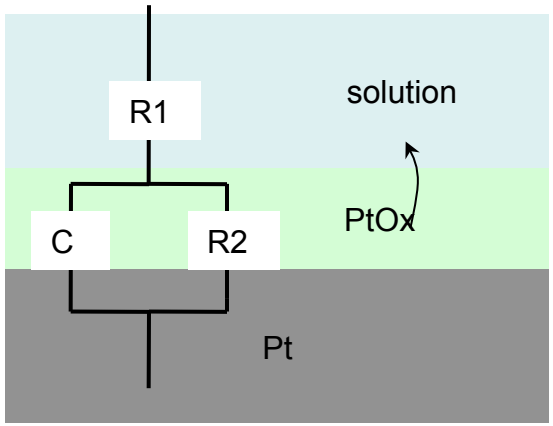


Irreversible roughening
Enhanced hydrogen production
Oxidic overlayer pre-requisite for OER

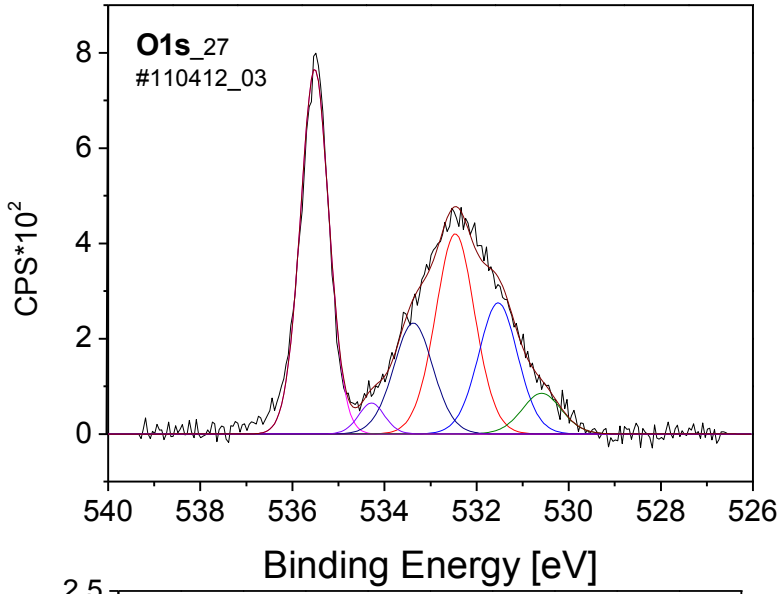
Excursion: Dynamics of Pt in OER

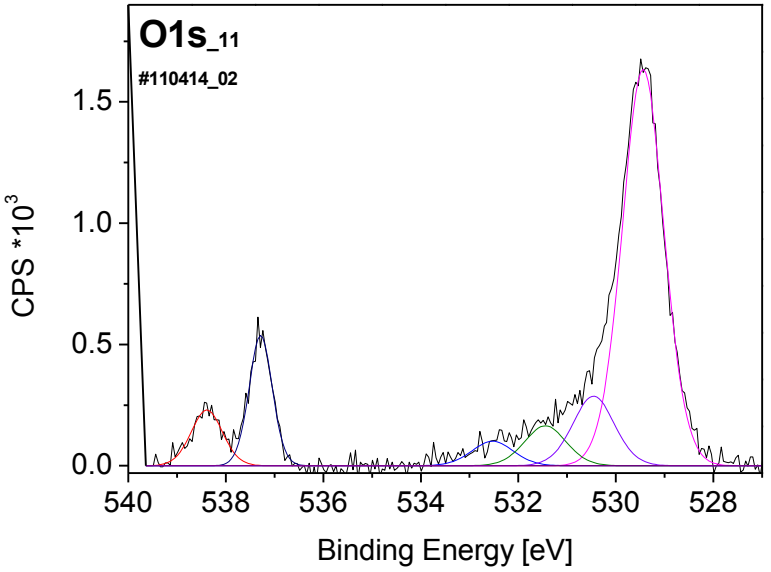


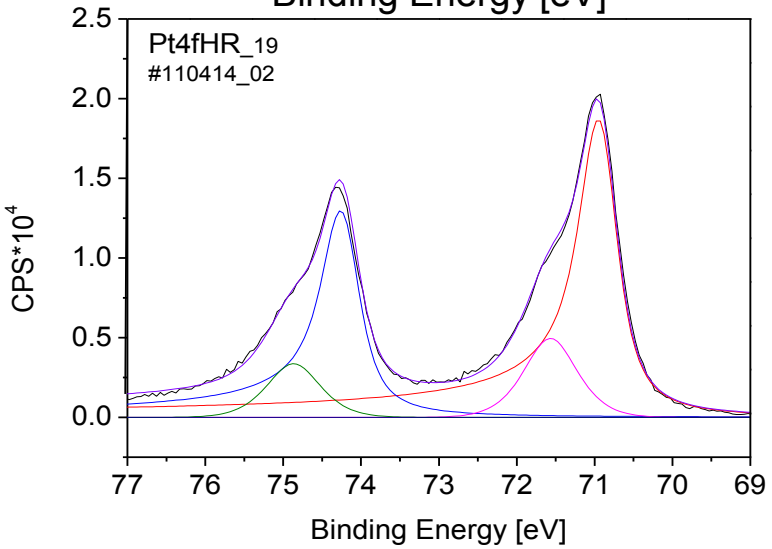
R1+C2/R2	1-Set	21-set
R1 (Ω.cm²)	1.68	1.69
C2 (µF/cm²)	51	48.9
R2 (Ω.cm²)	**2901**	5 151



Nature of the Pt “rust” film



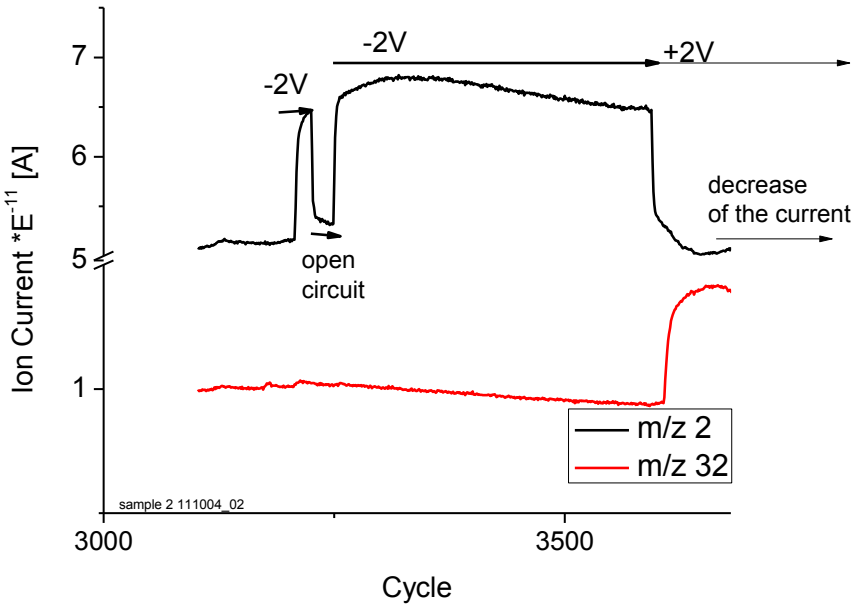




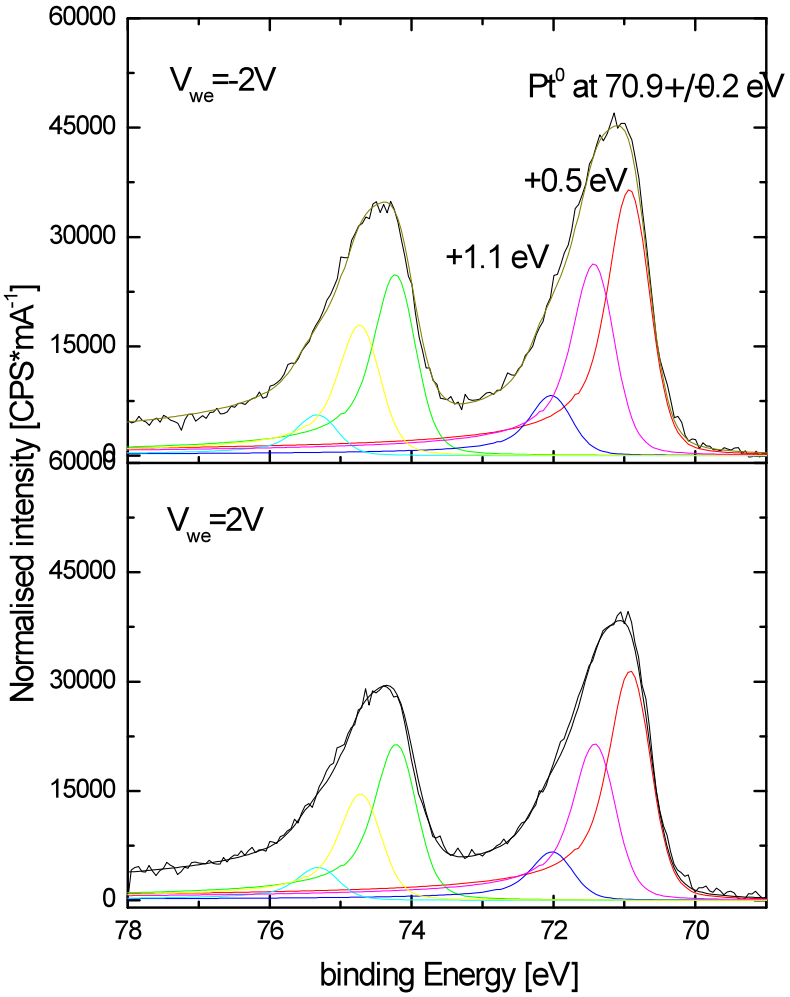
Ambient pressure XPS at very high resolution and extreme surface sensitivity:

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

In-situ observation



Pt forms a mixture of sub-surface oxygen species converting gradually into Pt O (OH)



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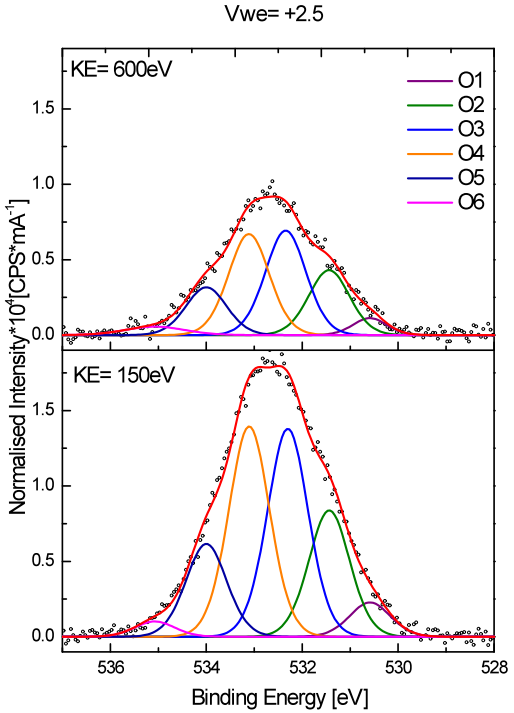

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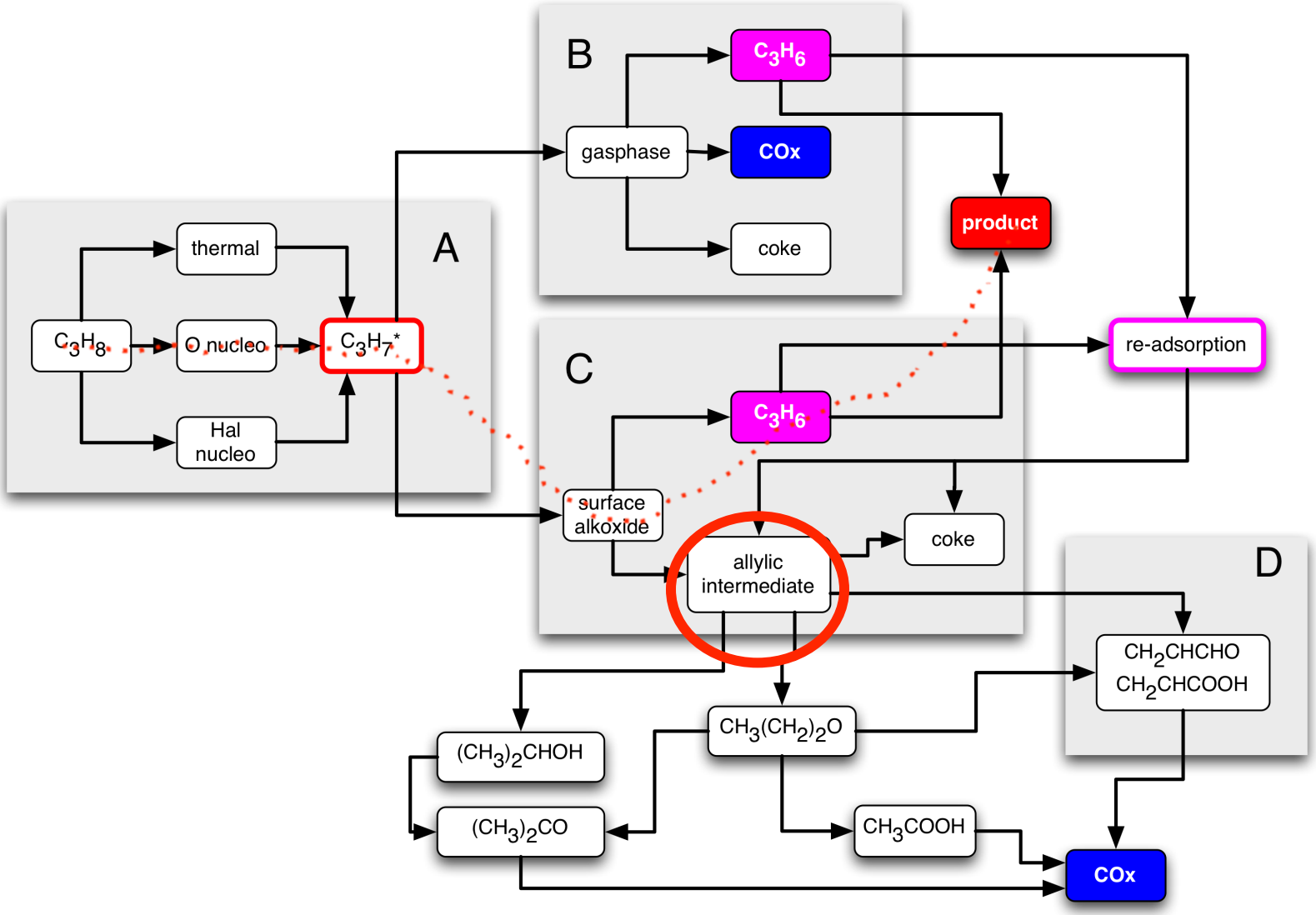
C3 oxidation: C_3H_8 to C_3H_6 a “simple” reaction network



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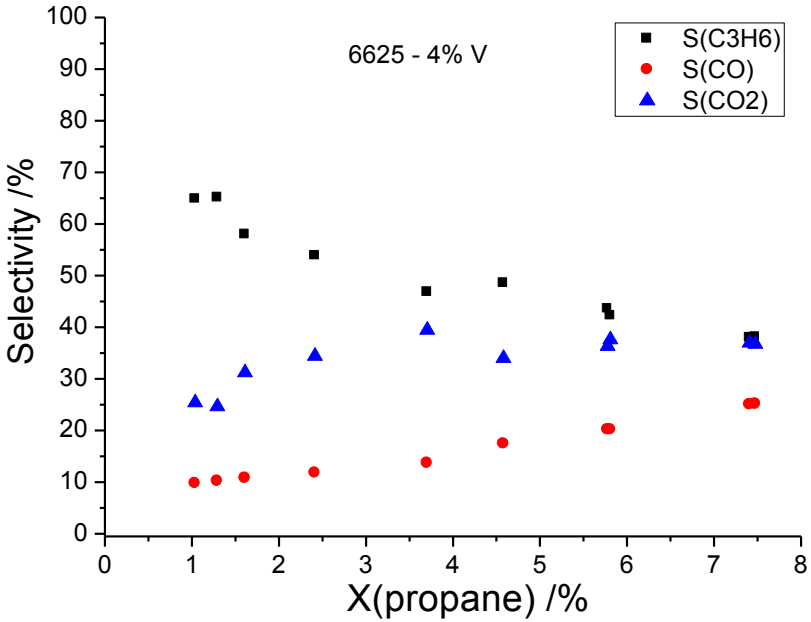
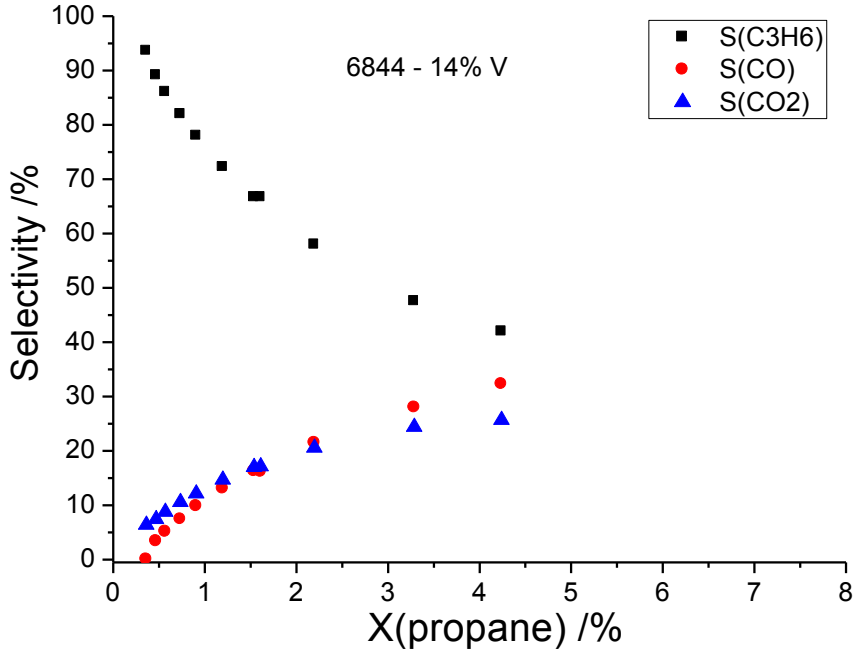
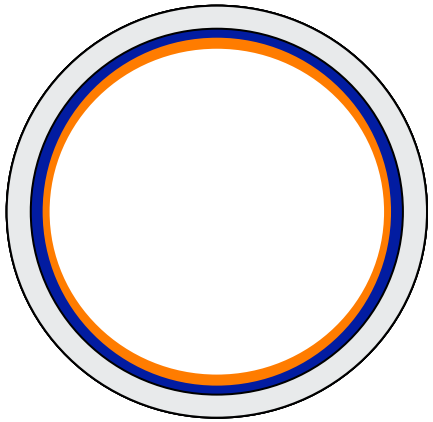




An oxide model system monolayers in a bottle



V-Ti/SiO_2

Why SBA-15?

- Regular pore structure allows the application of an extended number of physico-chemical methods
- High surface density of silanol groups available for anchorage of metal oxide species = high number of exposed V species
- V/SBA-15 is an efficient catalyst for oxidative dehydrogenation of propane (STY_{max} (FHI) = 1.5 g C_3H_6 /g_{cat} / h)

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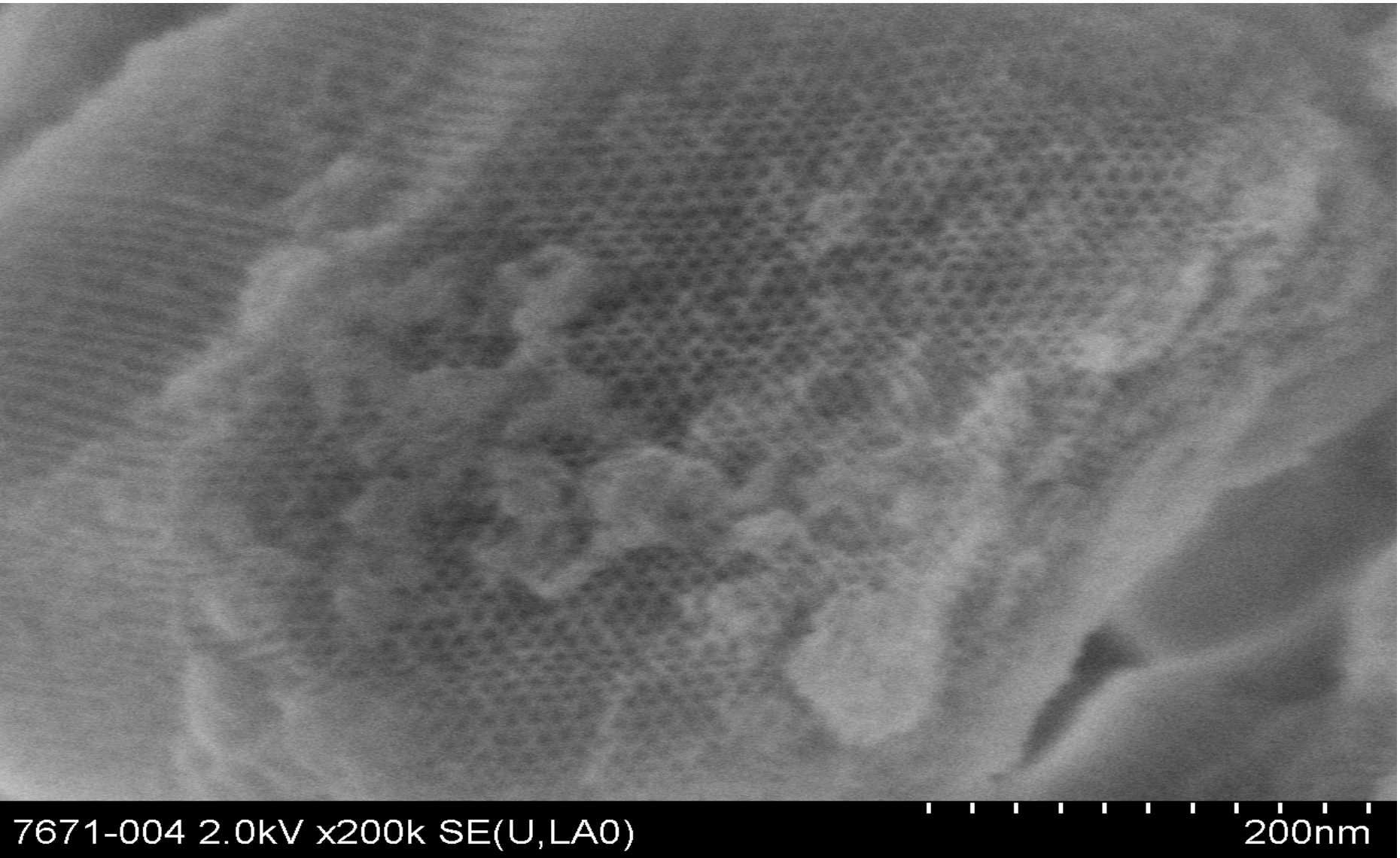

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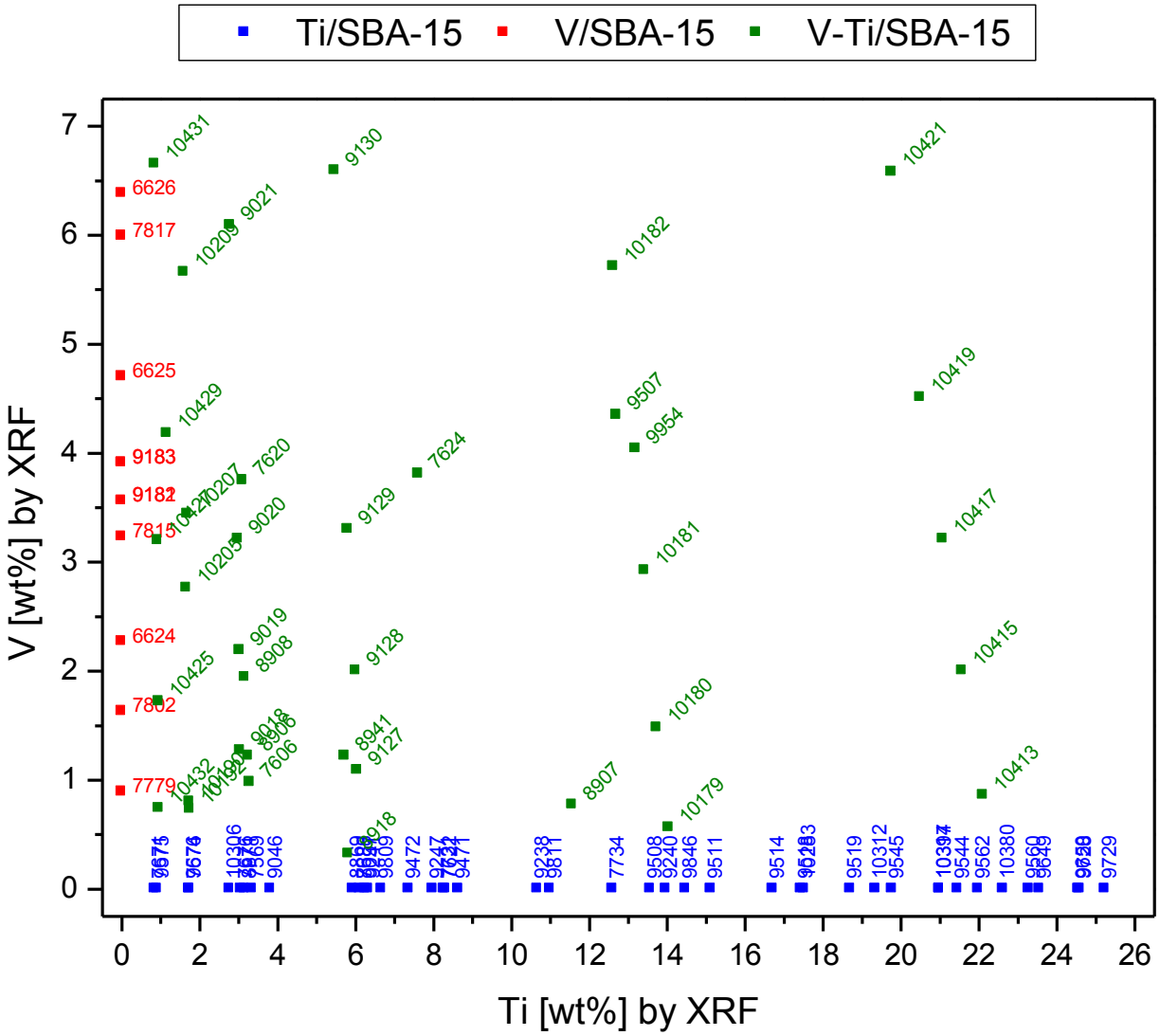
A catalyst library based on a common structure



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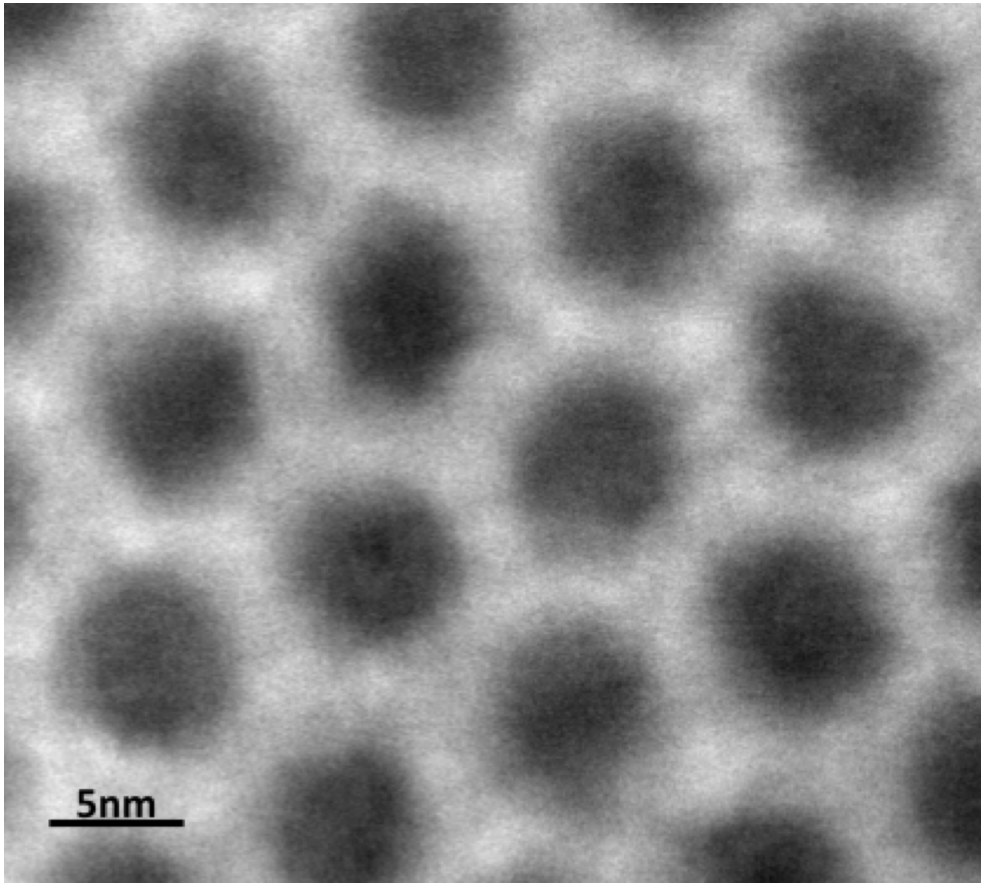

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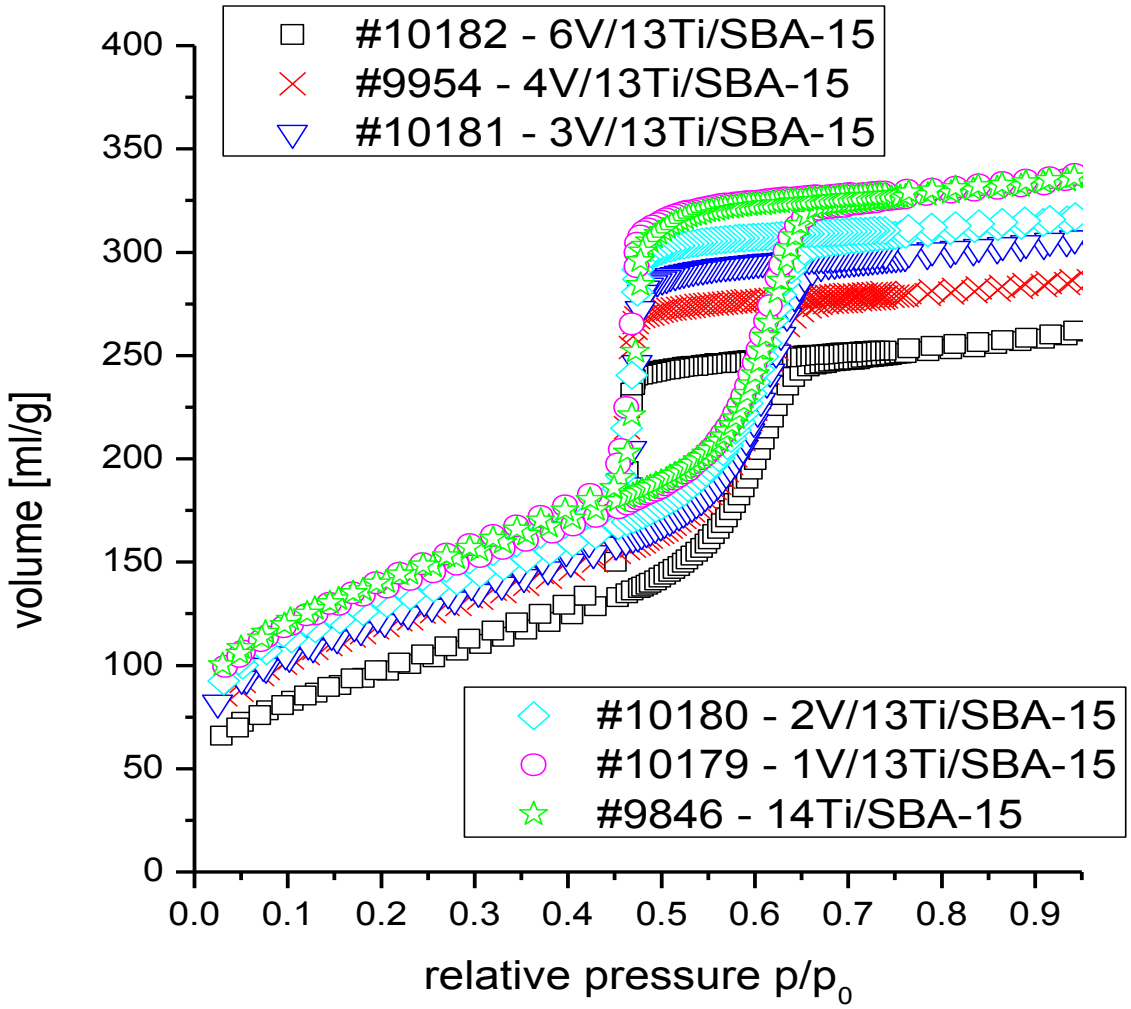

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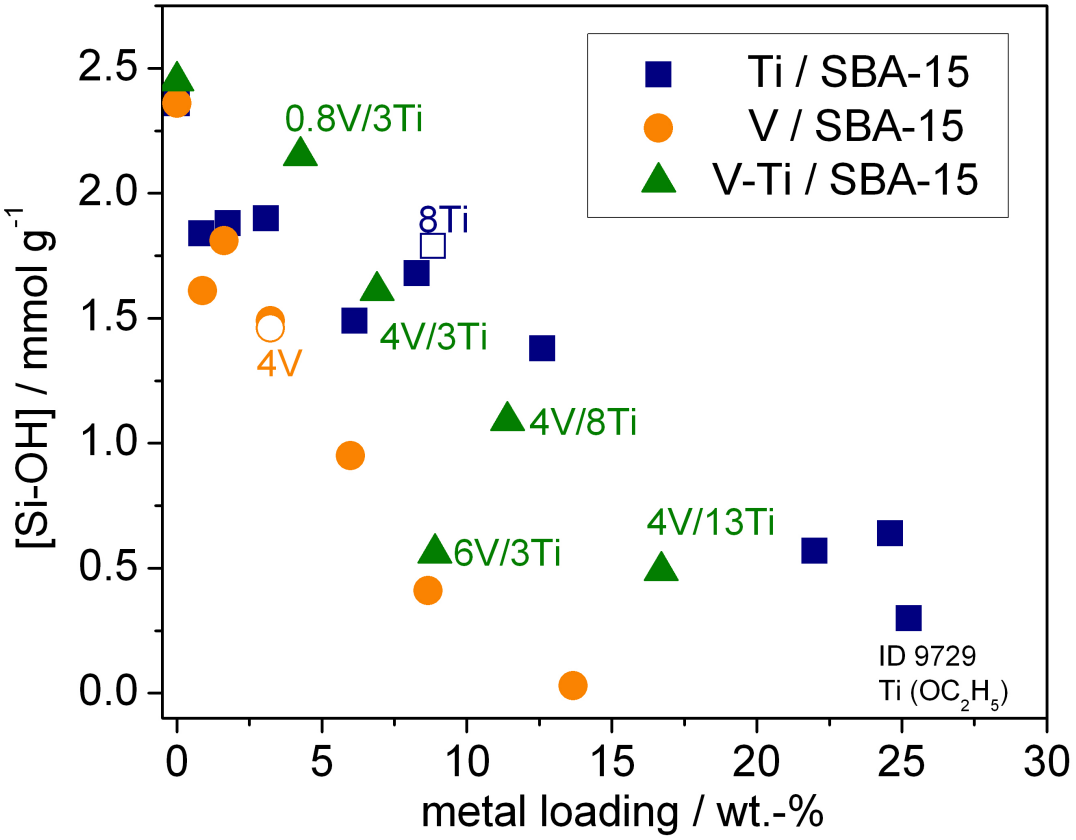
The design concept of a homogeneous library



V locates on mixed systems both in pores of SBA and on Ti:

V-Si dominated by V-V interactions (homodimer)

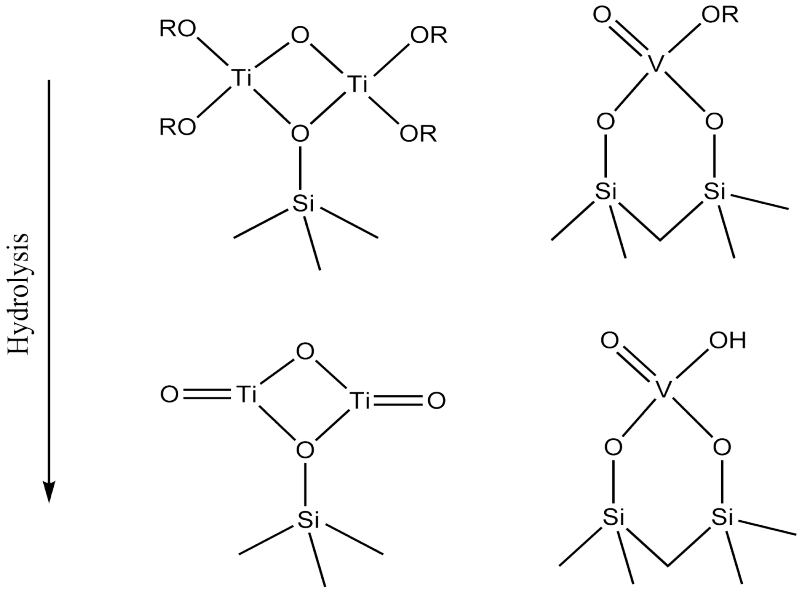
V-Ti dominated by V-Ti bonds (heterodimer)

V seems to require exactly twice as many silanol groups than Ti

Only V introduces Broensted OH into the system, Ti exhibits no free OH

As Ti liberates 2 alkoxide per molecule, dimer structure as long as sufficient space

The design concept of a homogeneous library



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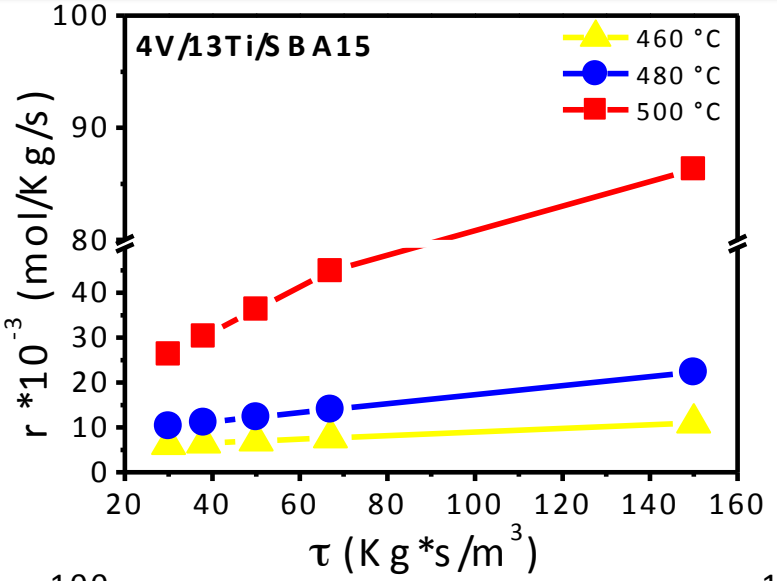
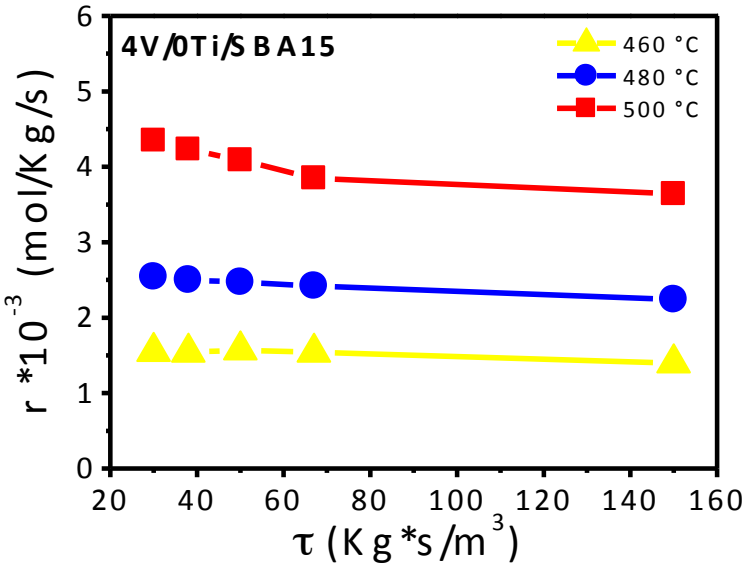
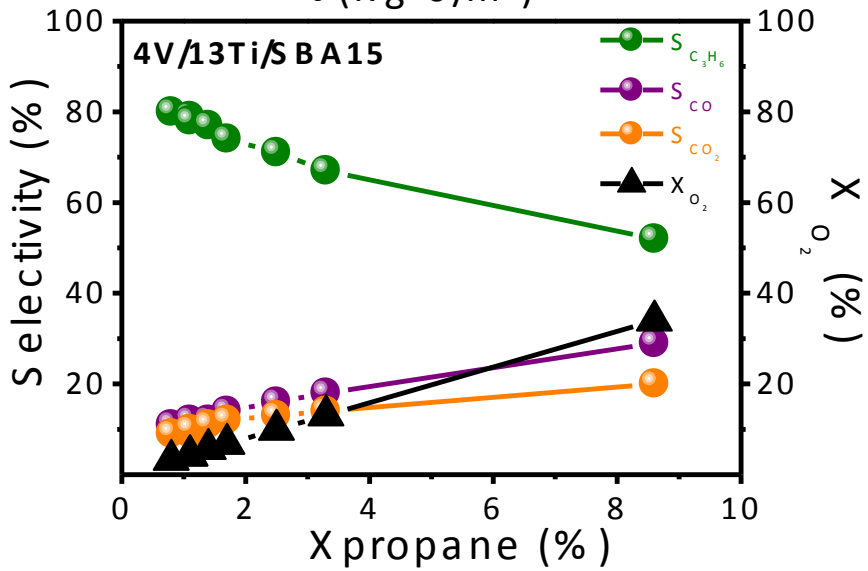
Is this good?







Catalysis:
Massive improvement of performance when V is deposited on Ti that is sufficiently covered to minimize O_2^-
Gold standard:
10^{-2} mol/kg/h

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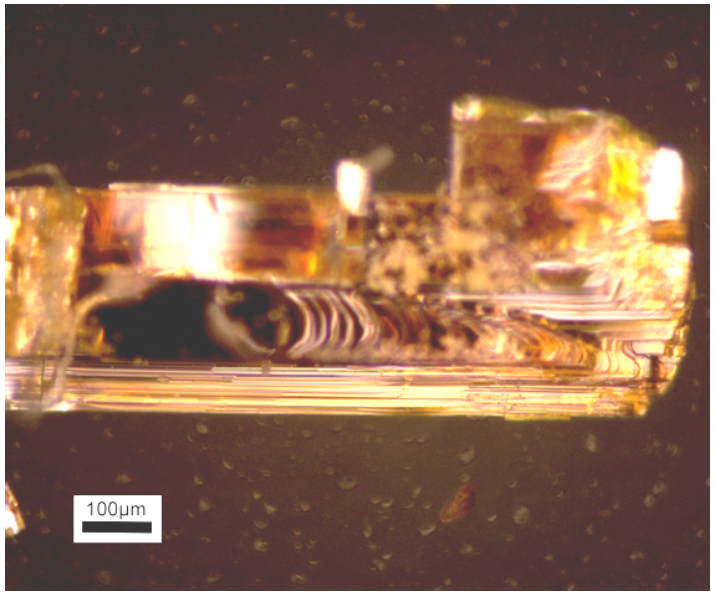
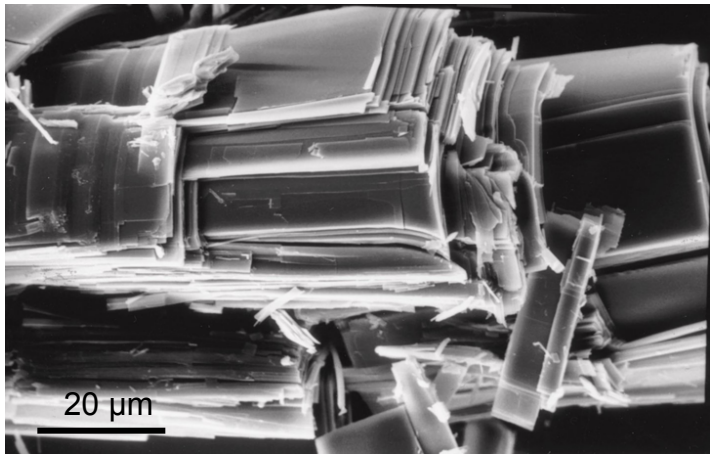
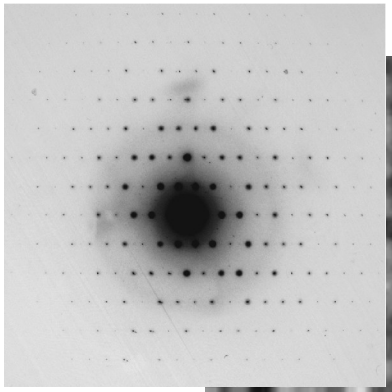
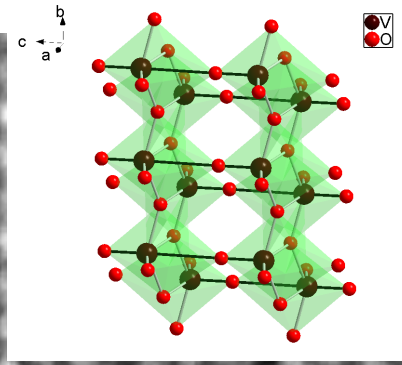
V_2O_5 the parent reference









Methodical development as basis for application in catalysis

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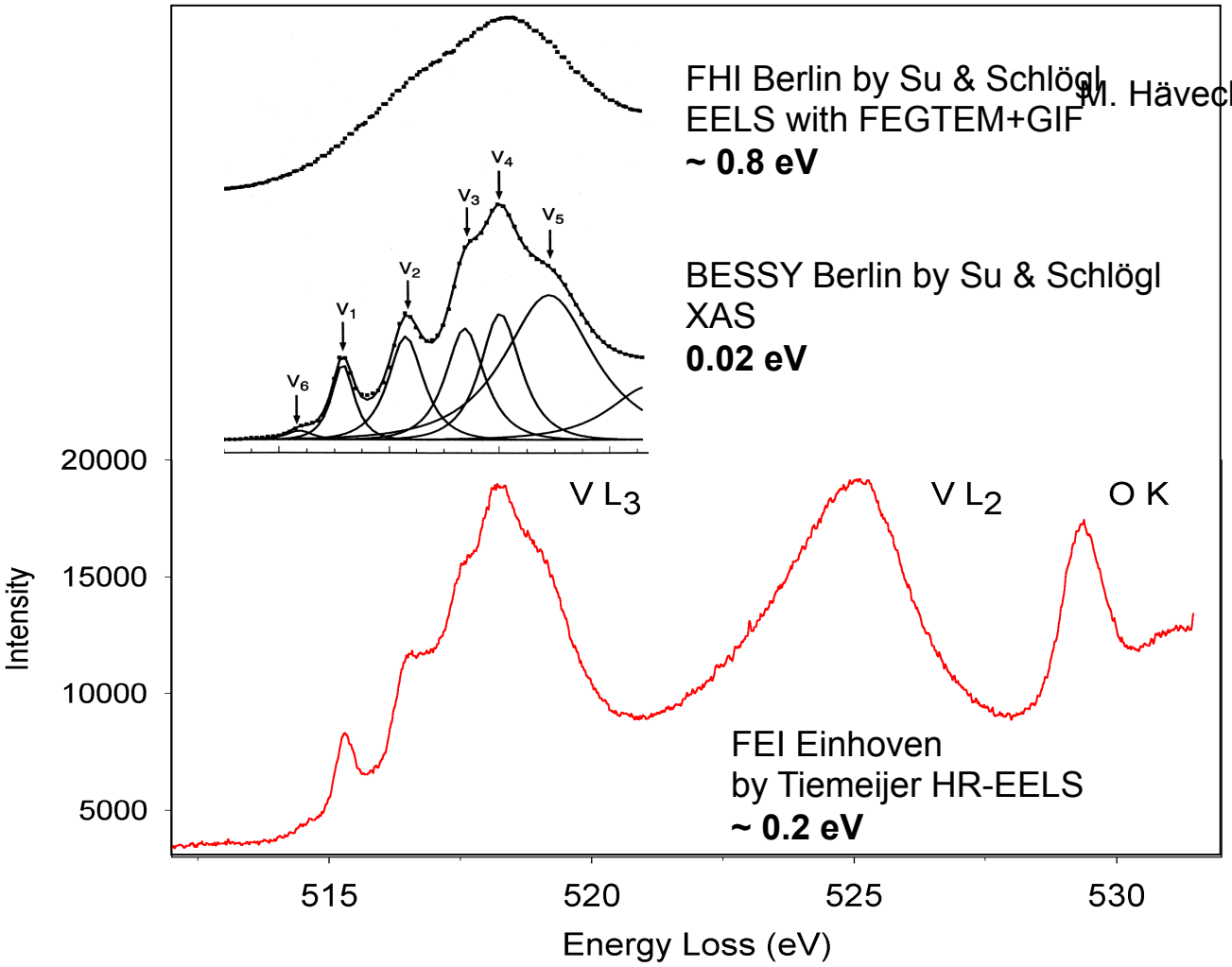

M. Hävecker, F. Neese et al 2012

Methodical development as basis for application in catalysis

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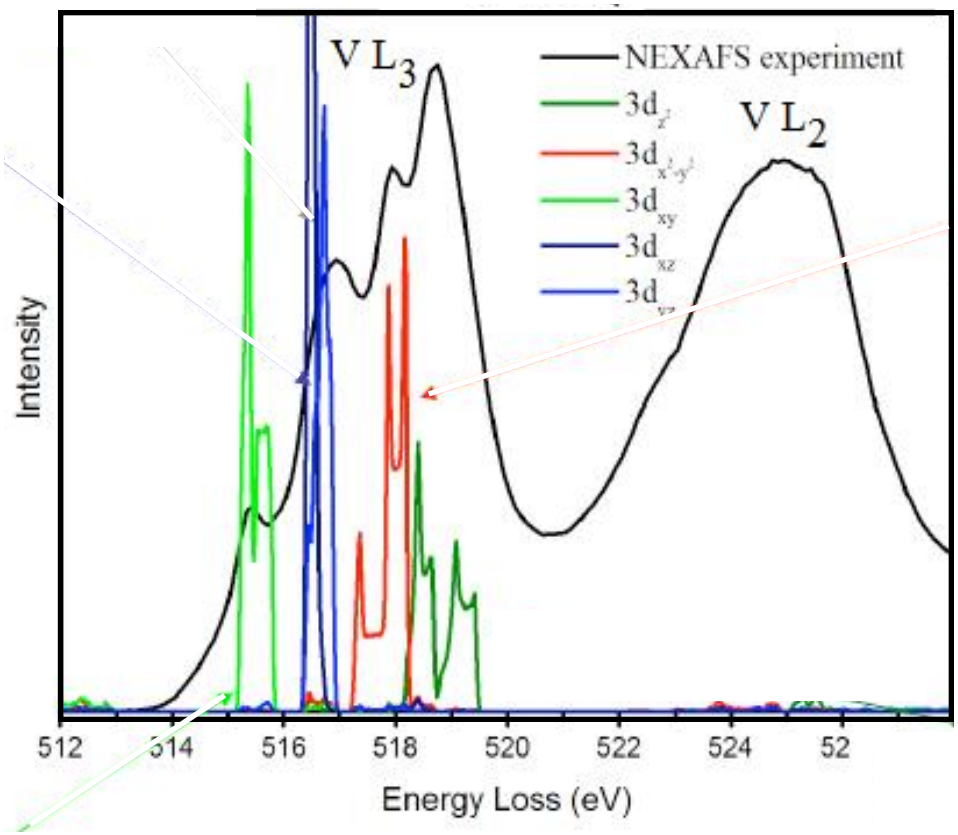
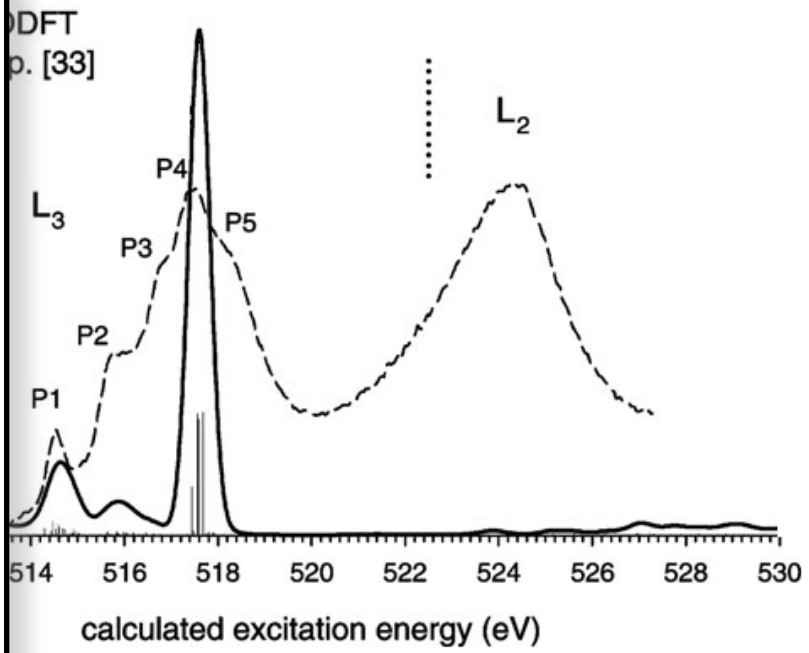
Ligand Field Multiplet



(M. Willinger et al, 2006.)

TD-DFT



p, R.; Stener, M.; Causa, M.; Toffoli, D.; Fronzoni, *Chemistry Chemical Physics* **2006, 8,** 4300**.**

Methodical development as basis for application in catalysis

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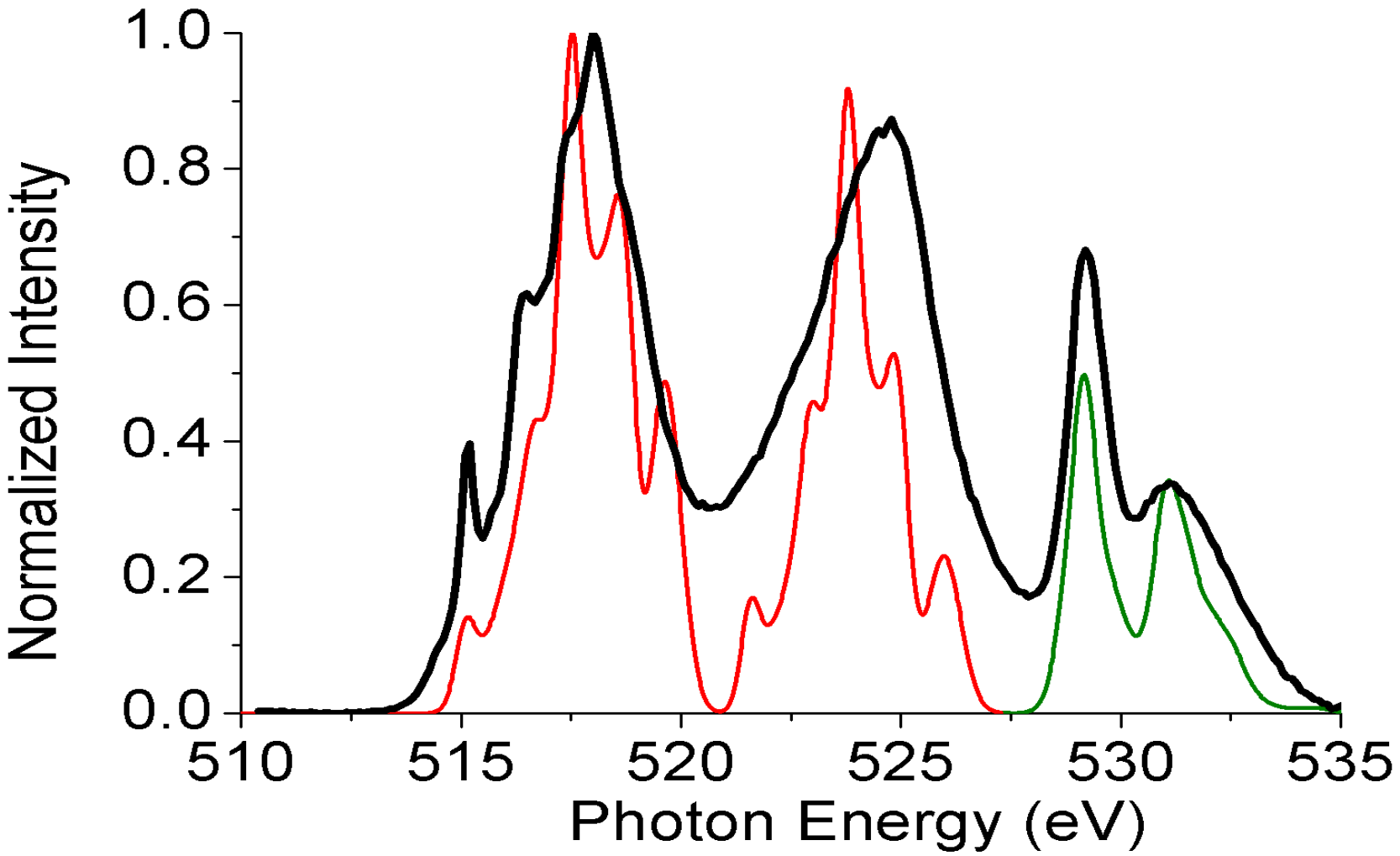

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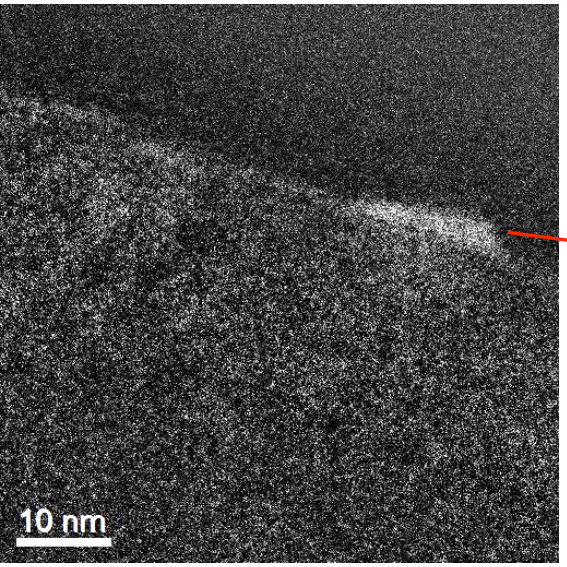
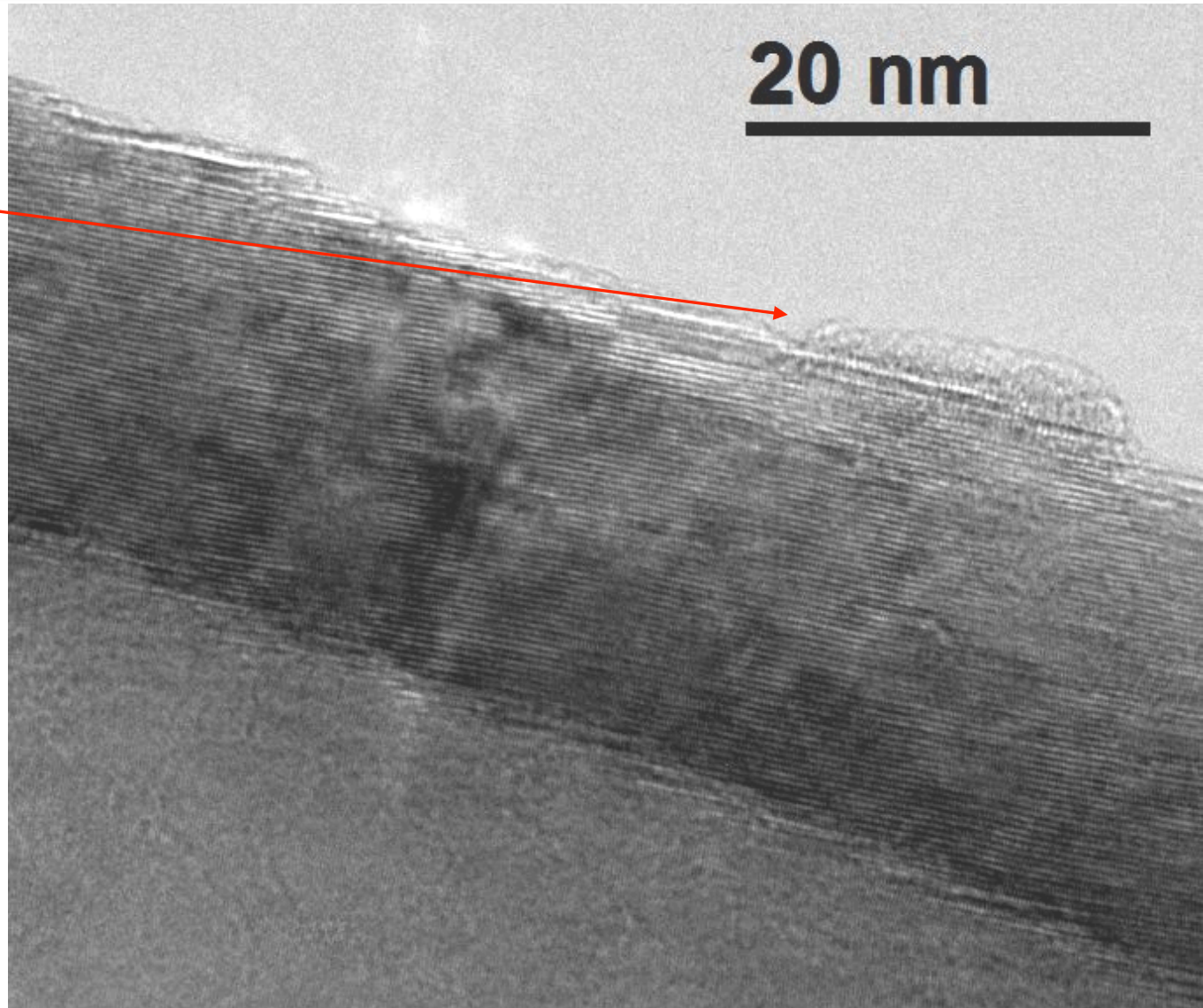
CNT supported VxOy reactivity vs. structural dynamics





Vanadium map

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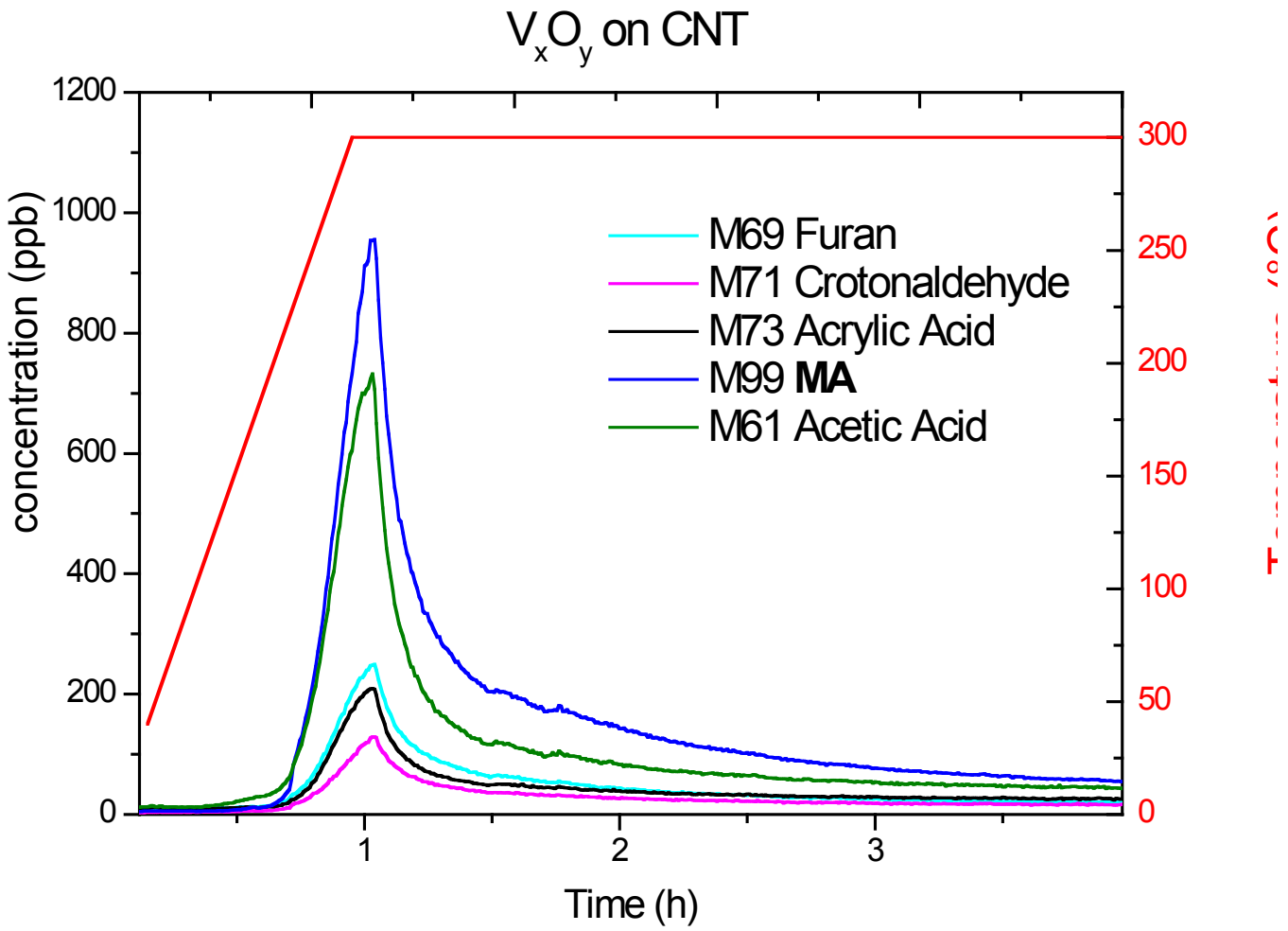

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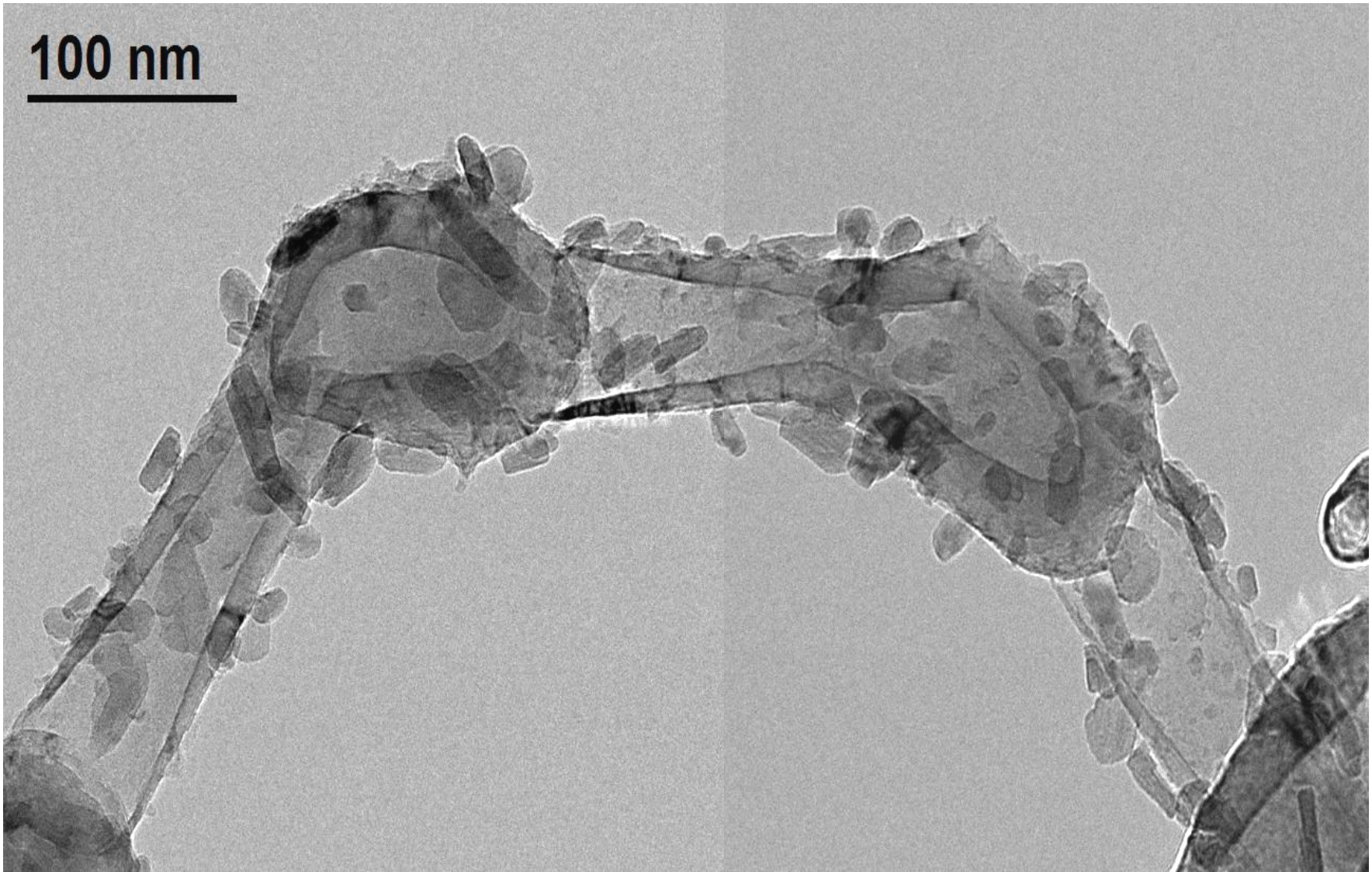
CNT supported VxOy
reactivity vs. structural dynamics



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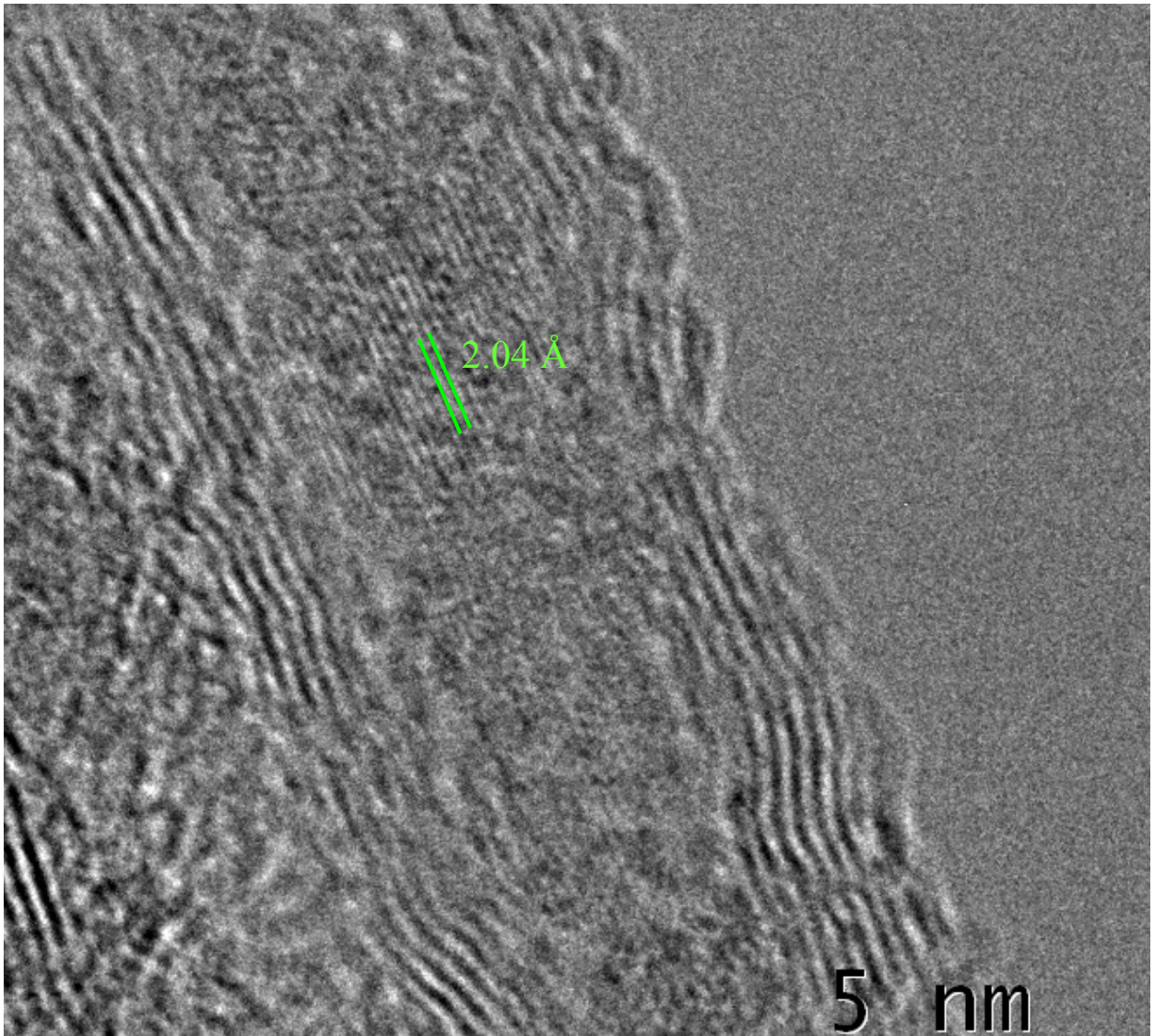

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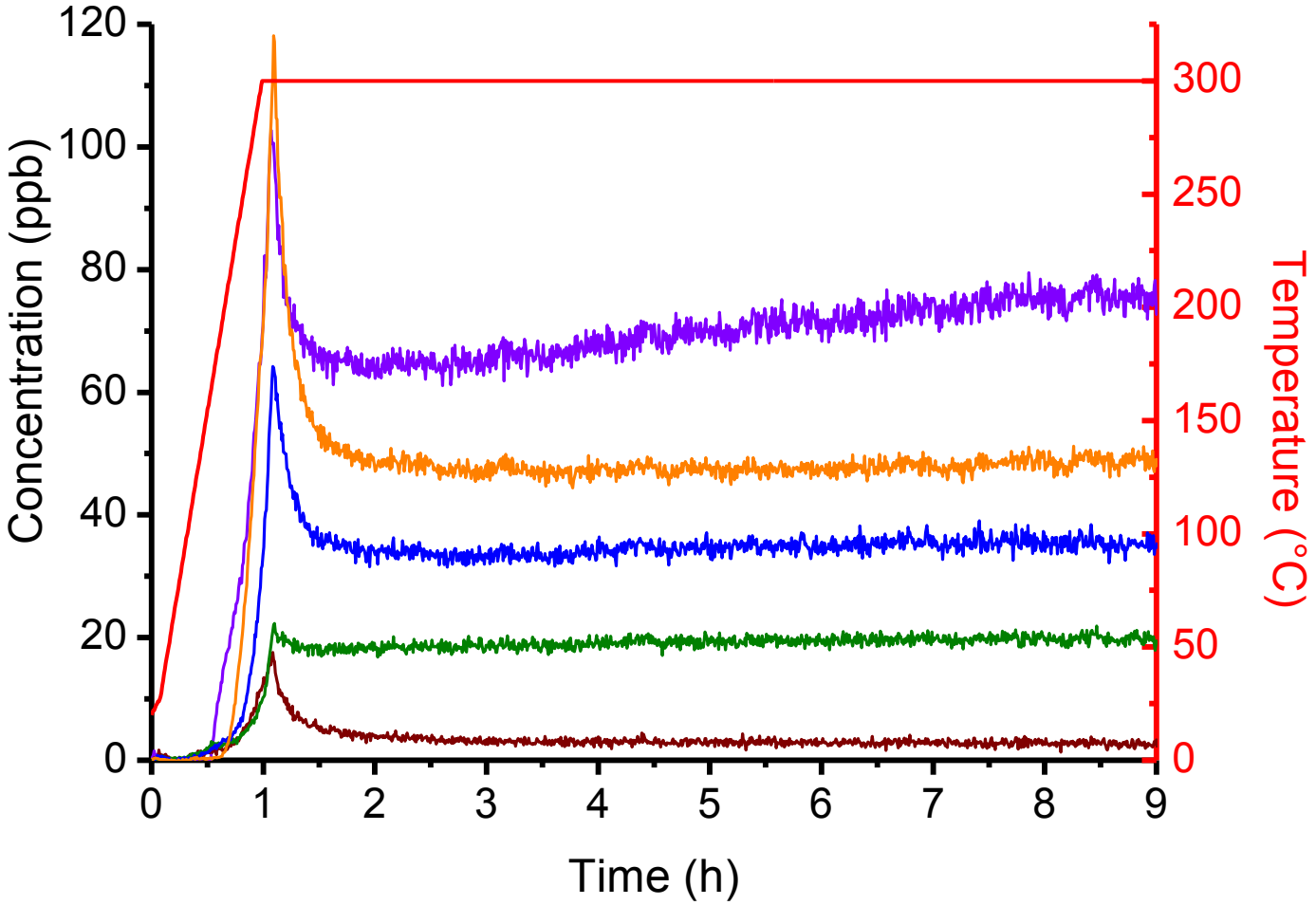

C3 oxidation II

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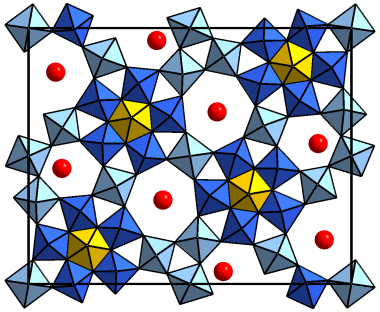
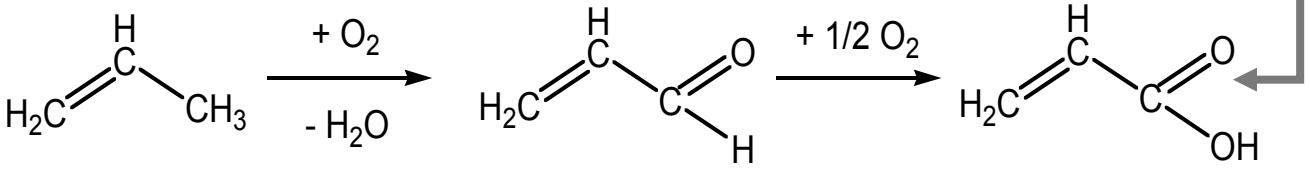
- MoVTeNb oxide
- polycrystalline
- M1/M2 phases

M1



- Y < 55 %
- stability is an issue

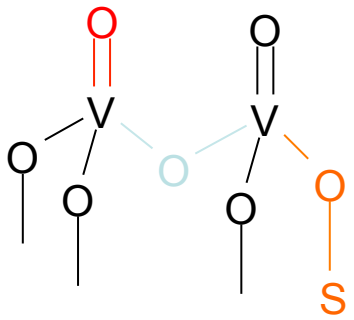
MoVTeNb



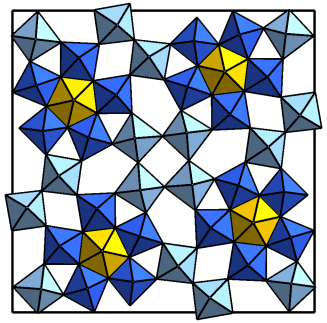
V

MoBi

MoVW



$(Mo,Nb,V)_5O_{14}$



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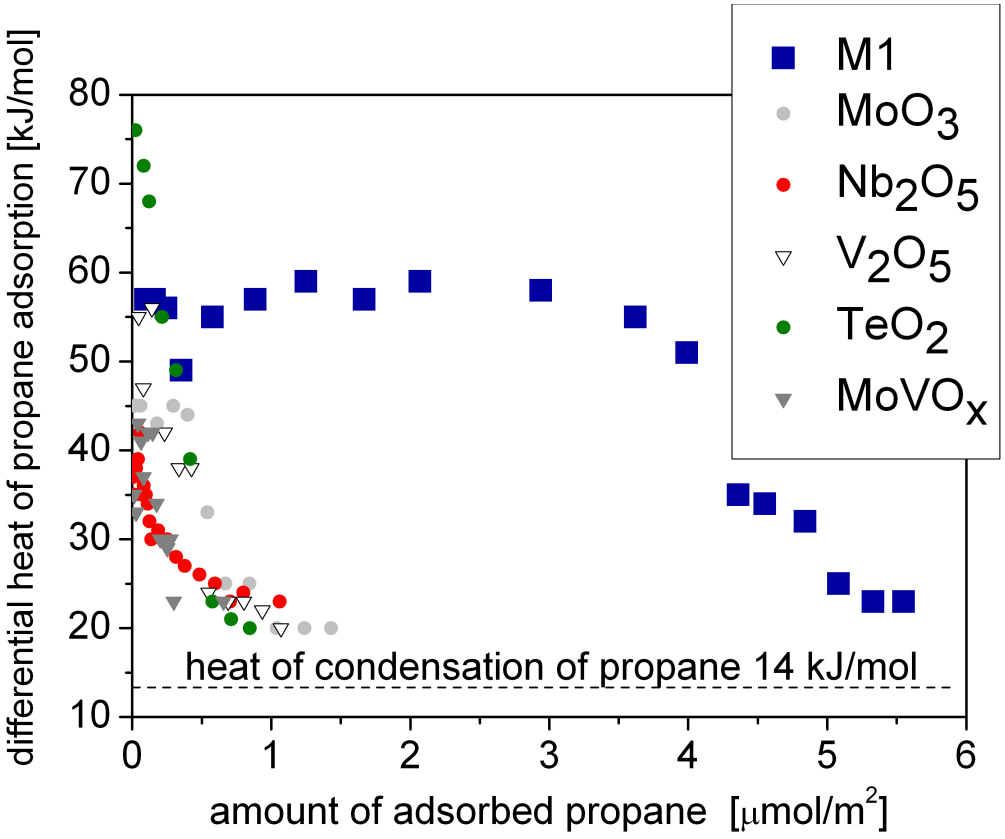
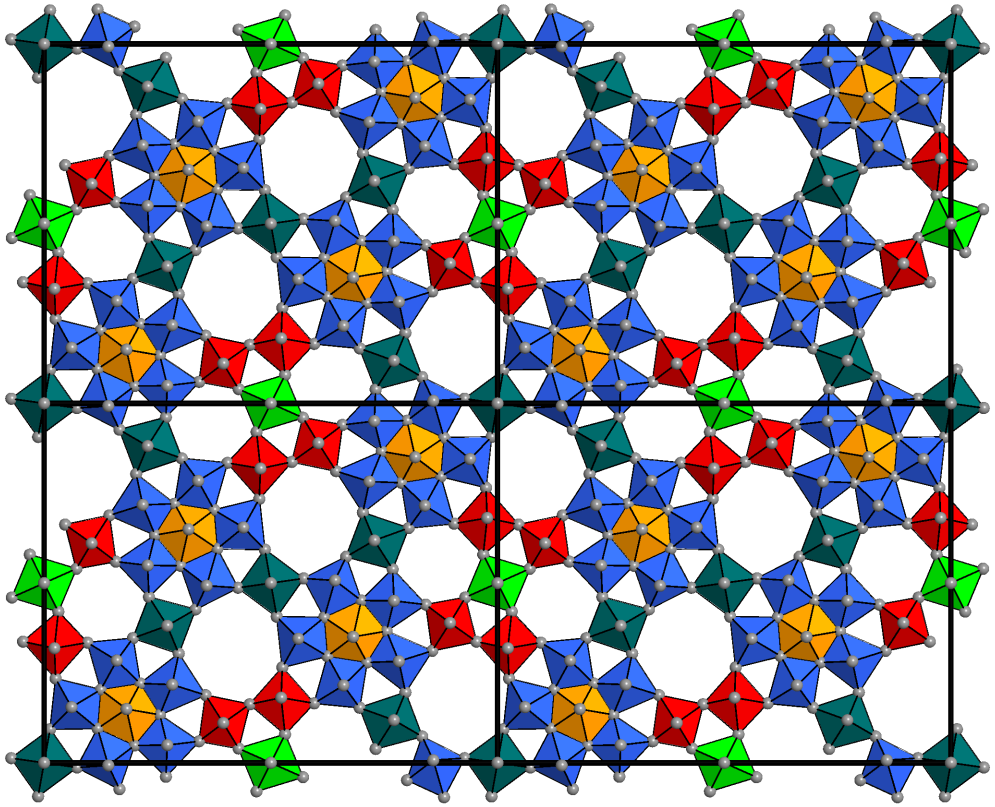
Synergy: adsorption as probe

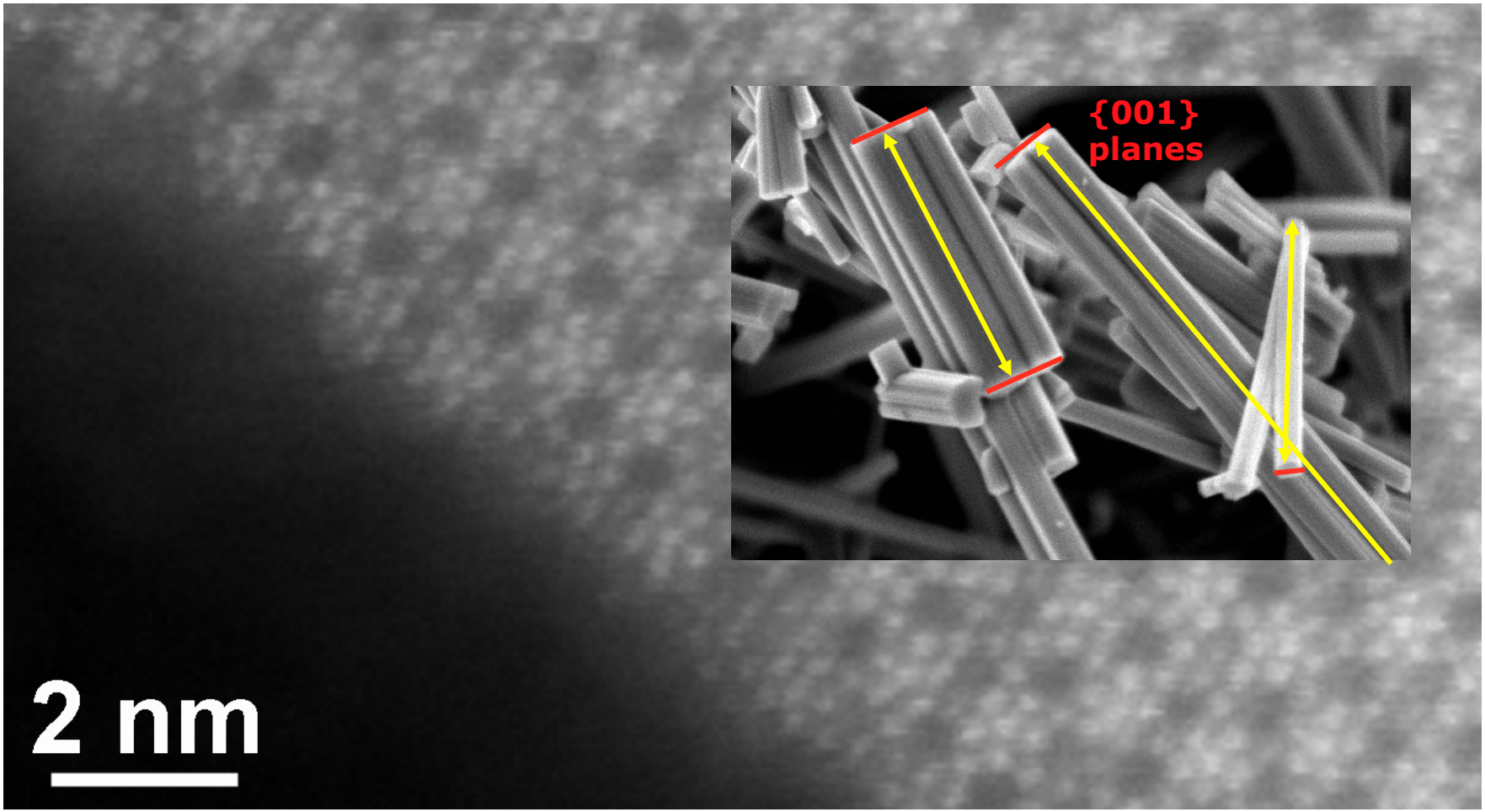


- Propane is strongly adsorbed on tellurium oxide
- High density of energetically homogeneous adsorption sites on M1

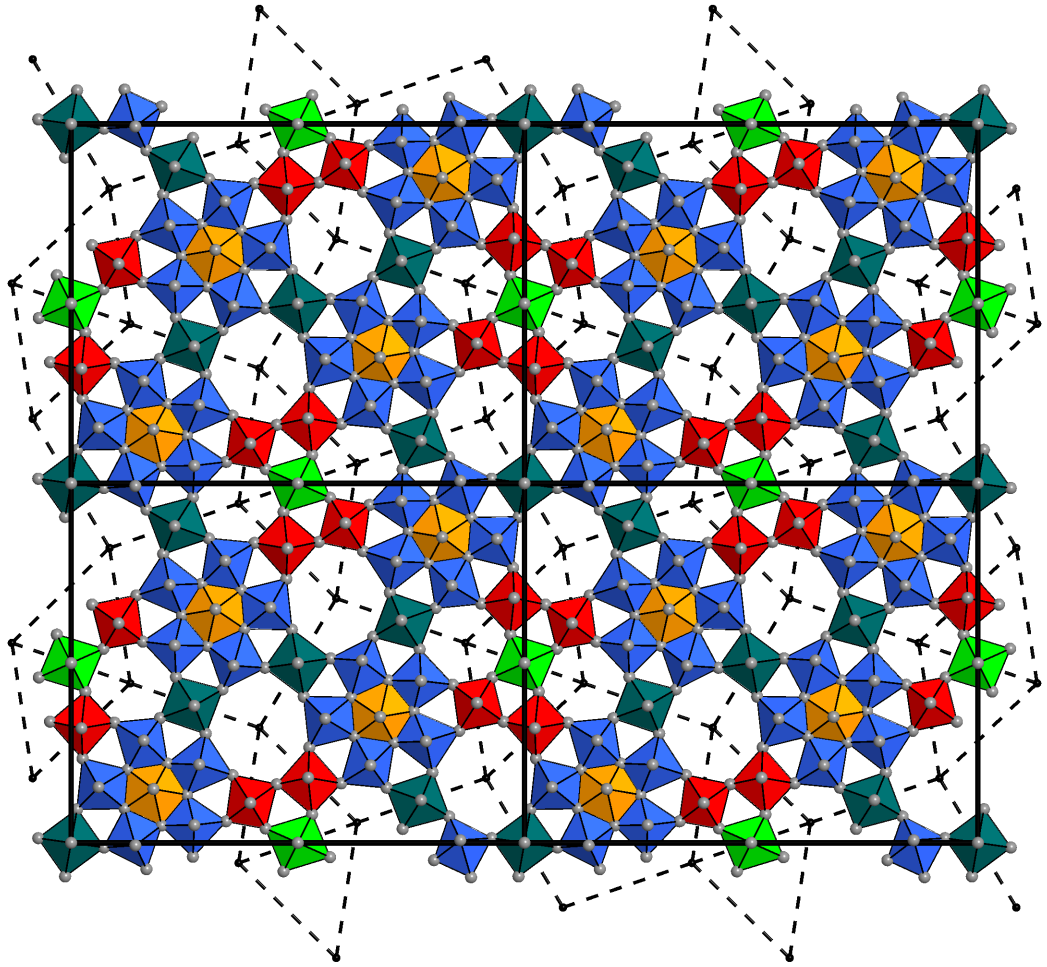
Termination of the prismatic faces



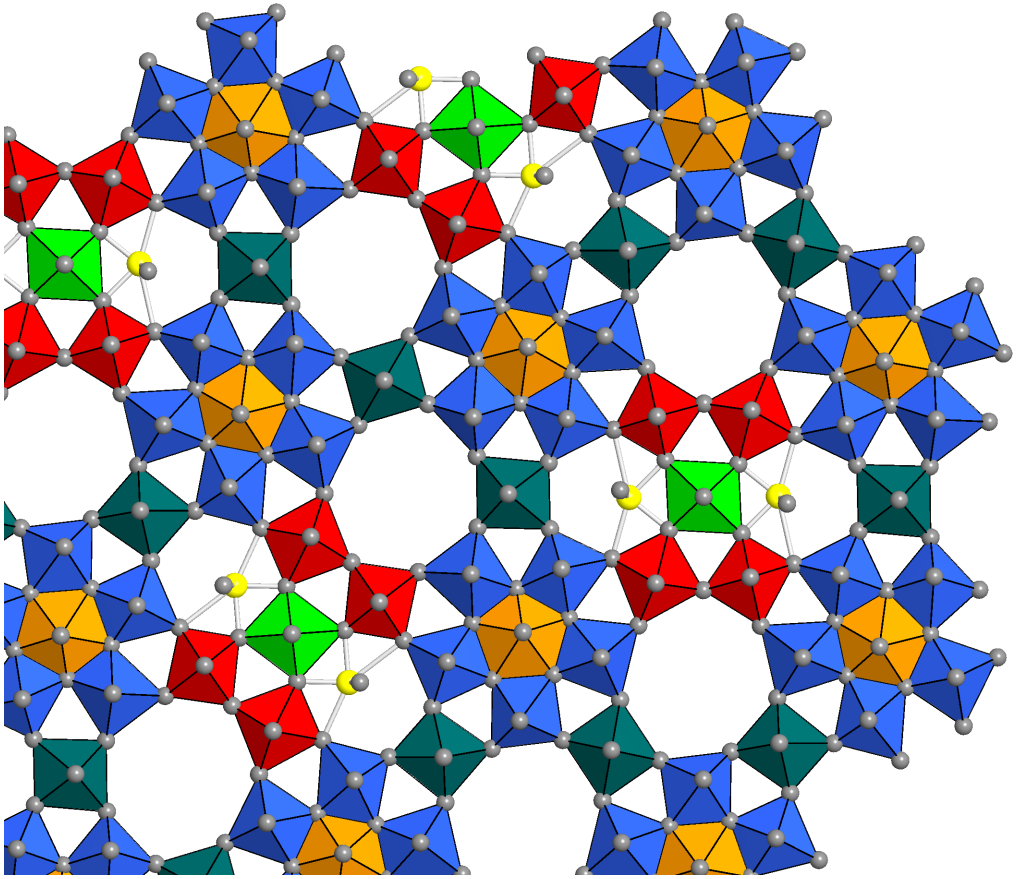
Termination of the prismatic faces



The active site feature
Kinetics of synthesis decides over activity



The active site feature
Kinetics of synthesis decides over activity



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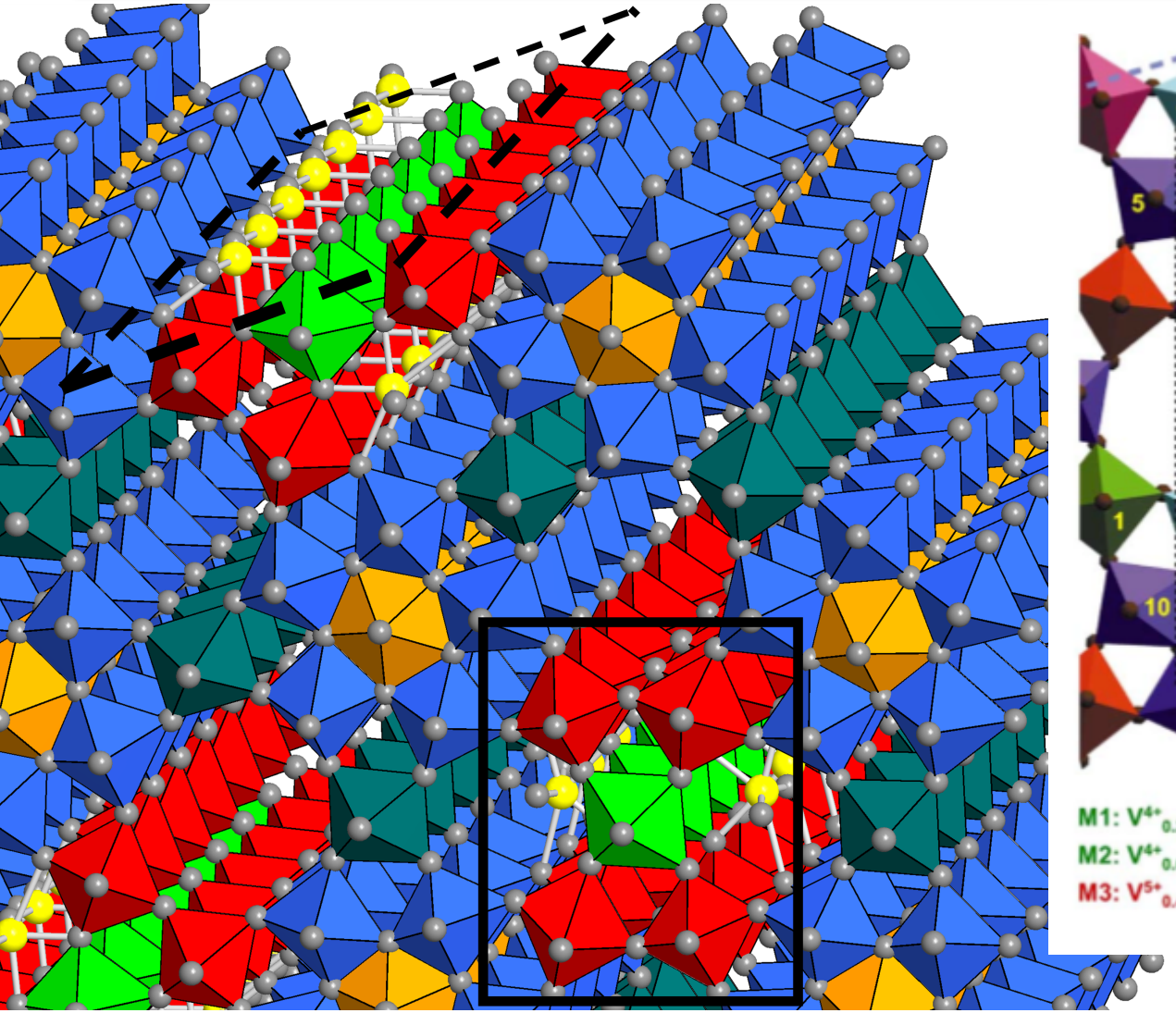
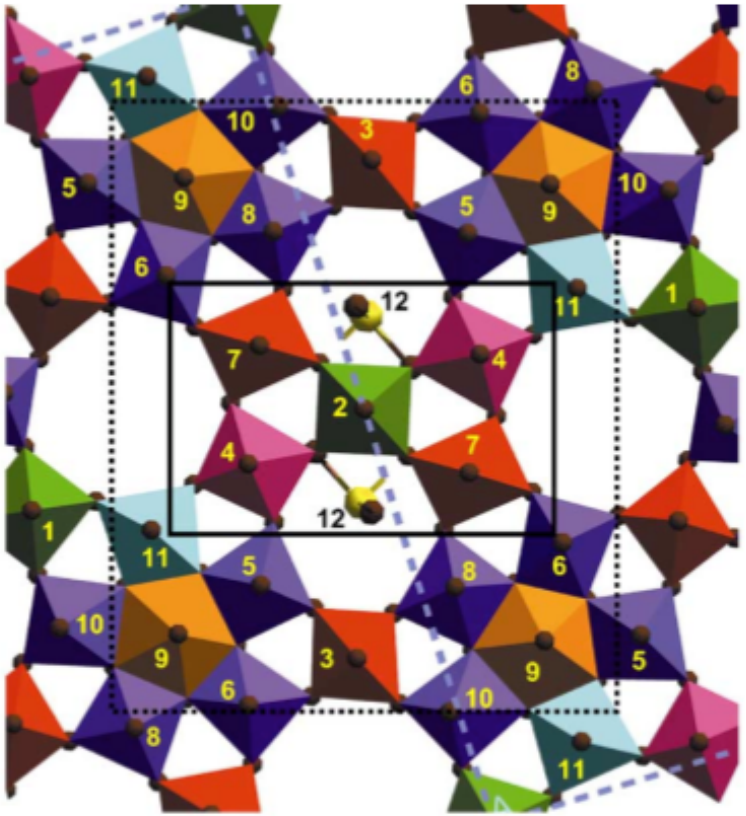
The active site feature
Kinetics of synthesis decides over activity



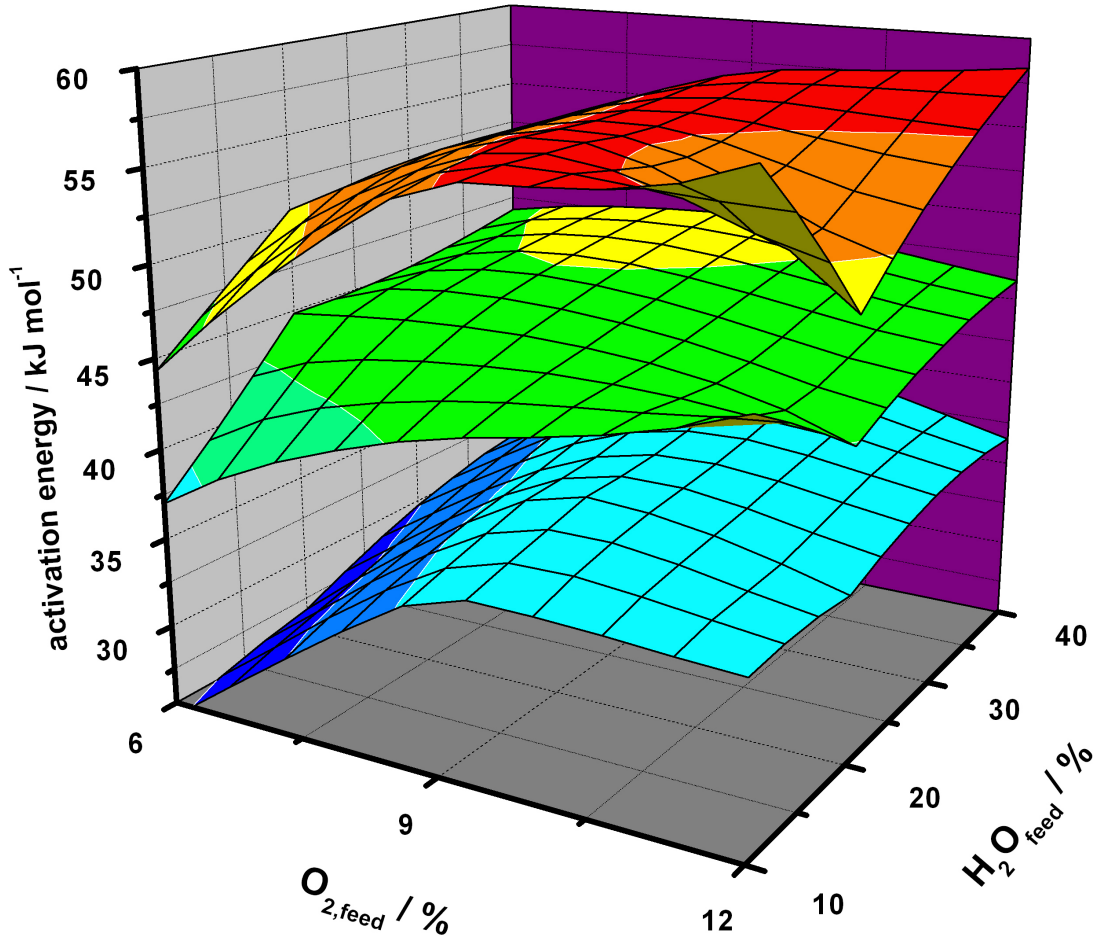


Surface Dynamics

- Catalysts terminate different from their bulk.
- Termination controlled by (chemical) nanostructure.
- A low-dimensional active structure with fast kinetics of structural transformation: dynamics
- Allowing facile reaction with reactants: “activation”.
- Suitable for adaptive active sites.
- Difficult to detect at low performance condition of typical analysis.
- Stable systems are not dynamical and thus not active in suitable times: activity and stability are counteracting!

Dynamics vs stability

Activation energy for propane consumption



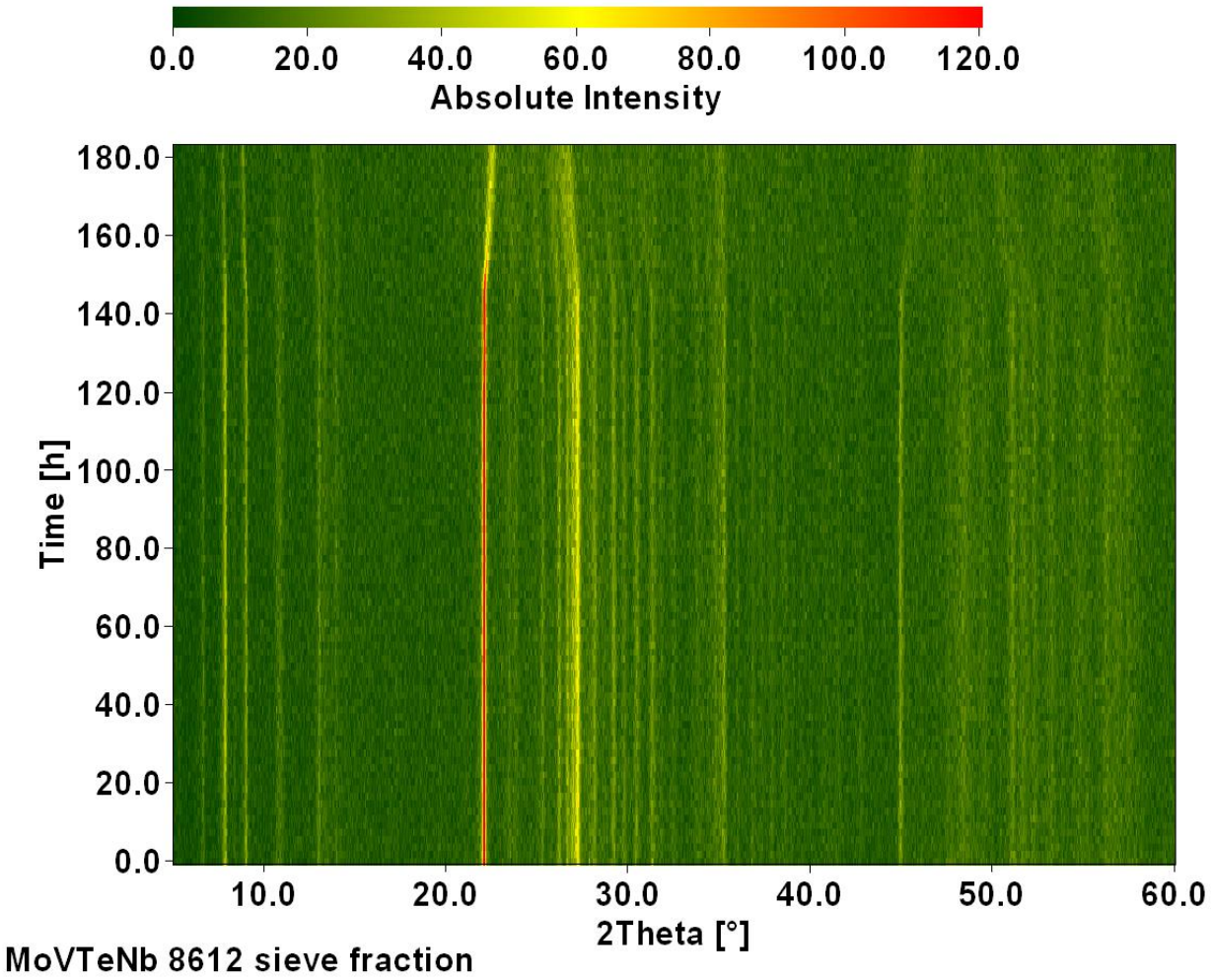
15000 ml g-1 h-1

30000 ml g-1 h-1

60000 ml g-1 h-1

SN6902
$C_3H_{8,feed}$: 3 %
T: 350 - 390°C

Dynamics vs stability



MoVTeNb 8612 sieve fraction

H_2O / O_2 / propane

0 / 0 / 3

5 / 0 / 3

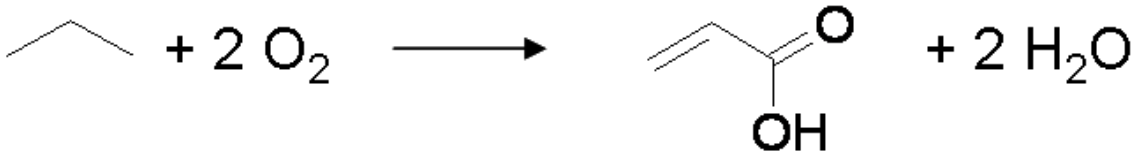
5 / 12 / 3

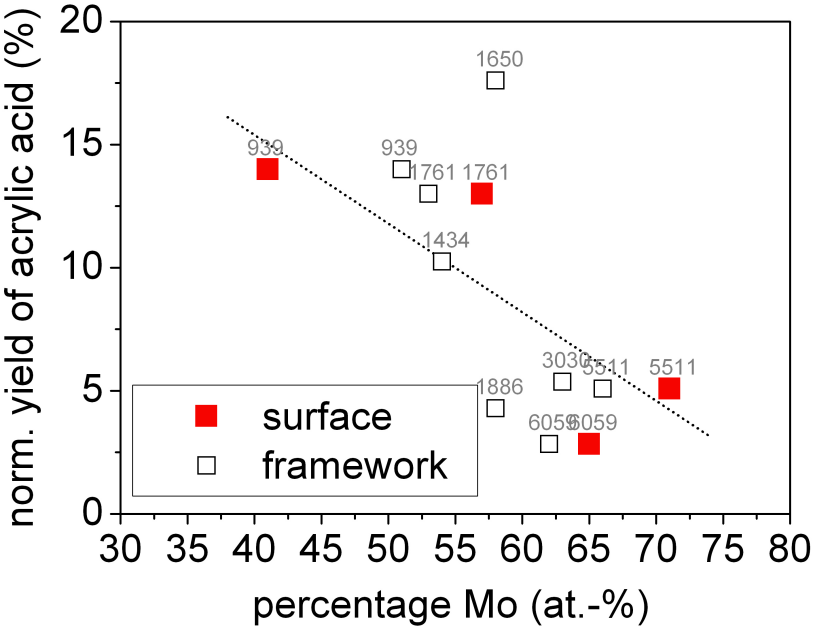
0 / 12 / 3

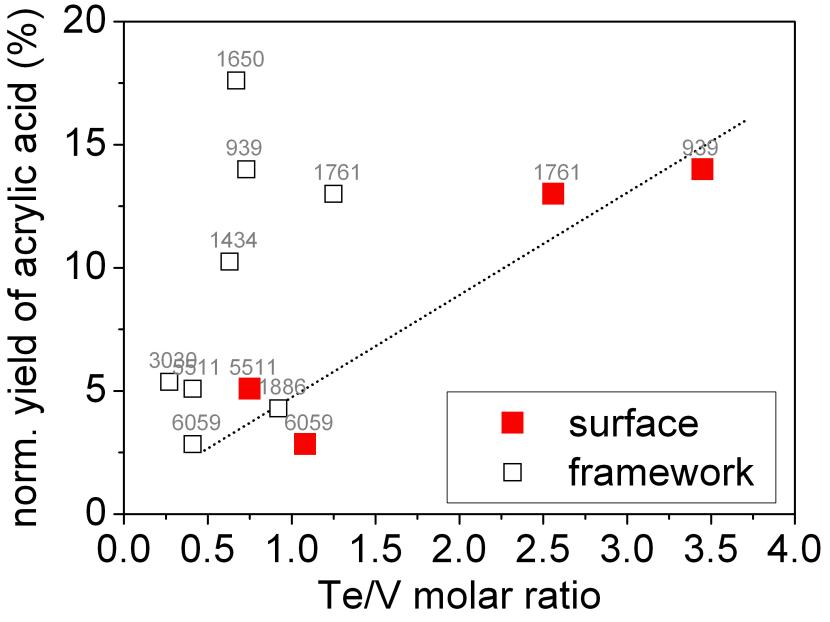
GHSV=5000h^{-1}
T=673K

A dynamical oxide

$Mo_1V_{0.3}Te_{0.23}Nb_{0.125}O_x$







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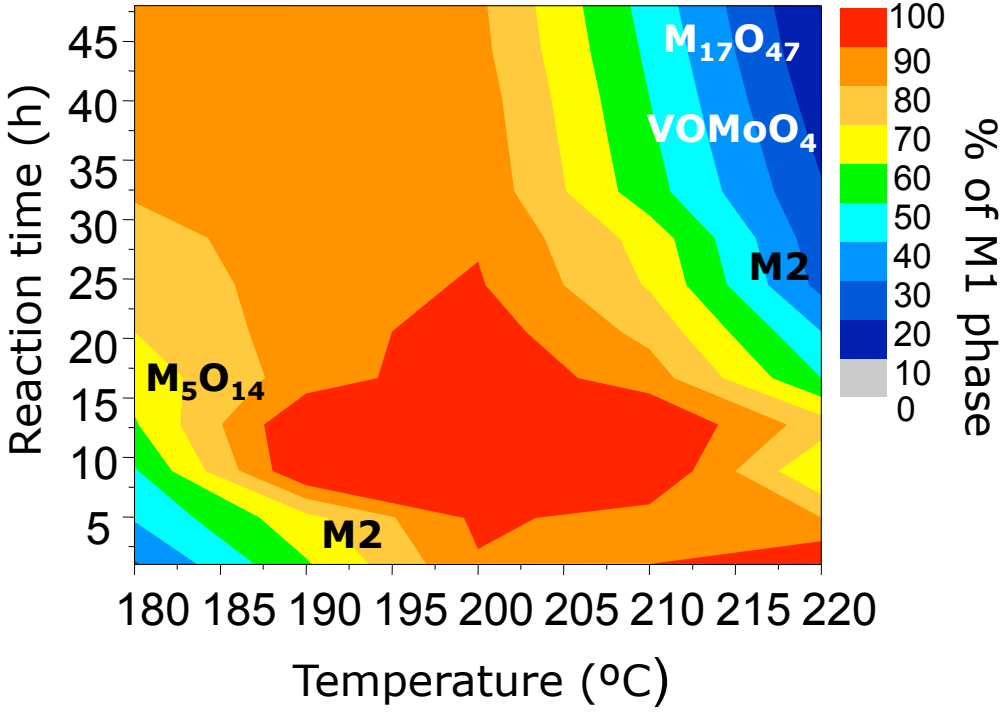
Synthesis of a complex catalyst catalysis by itself?

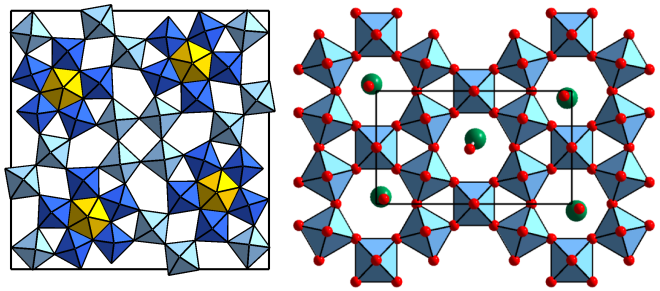
Nominal stochiometry: $MoV_{0,25}Te_{0,23}Nb_{0,124}$



Secondary phases

Intermediates

M_5O_{14} M2



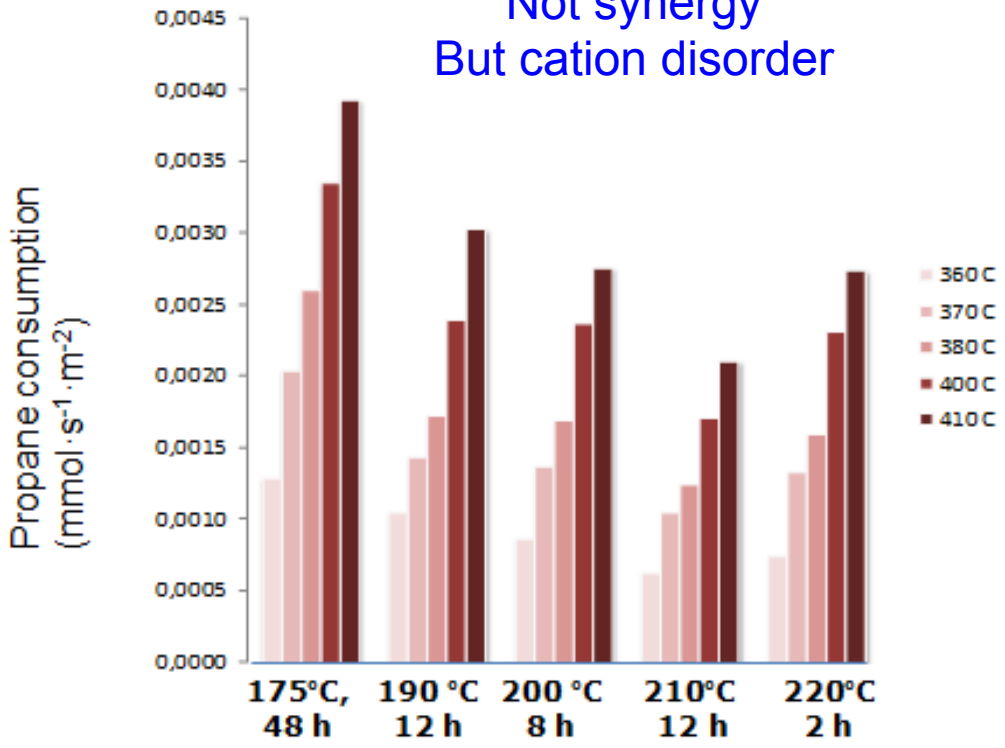
decomposition products

$M_{17}O_{47}$, $VOMoO_4$, M2

- At higher T and longer reaction times, thermodynamically favoured products are formed
- Optimum conditions: 190-200°C, 6-12 h
- At lower T and much longer times still better catalysts.

Synthesis of a complex catalyst catalysis by itself?

Not synergy
But cation disorder



Processes during mixing reactants in-situ RAMAN with species analytics

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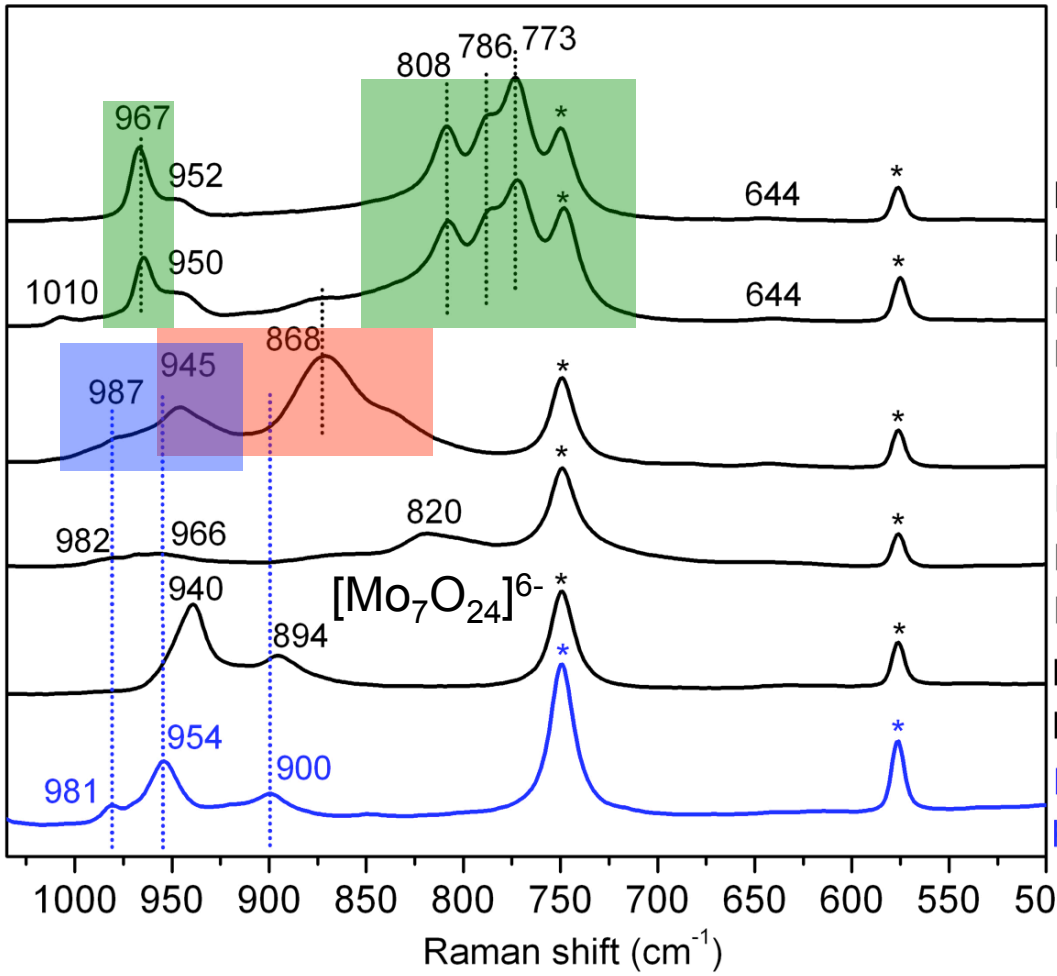
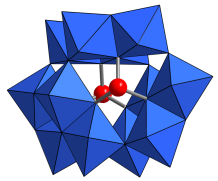
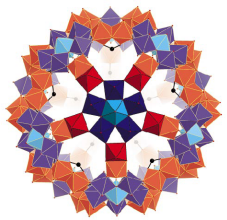
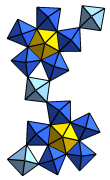


$[(TeO_3)_2Mo_{12}O_{36}]^{4-}$



$\{Mo_{72}V_{30}\}$



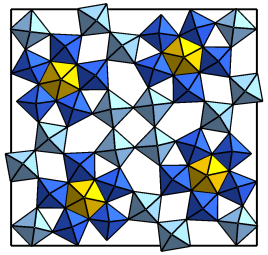


$[Mo_{36}O_{112}]^{8-}$

- Initially formed (M)M5 building blocks are decomposed by reaction with tellurium

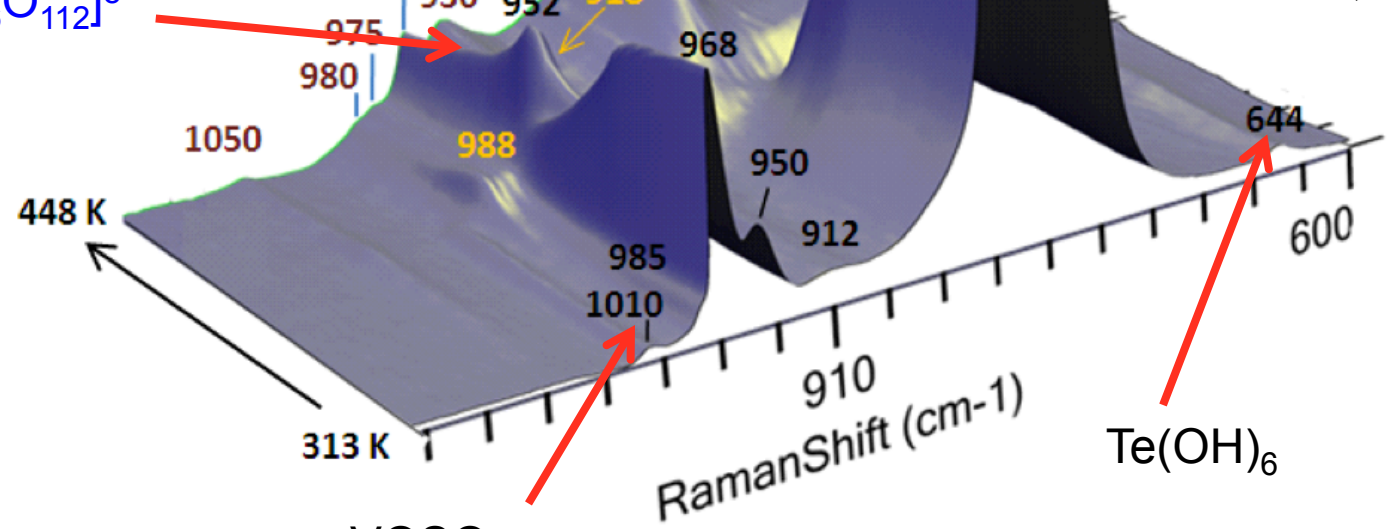
Destruction-reconstruction during heating: where is the active phase?

M_5O_{14} intermediate

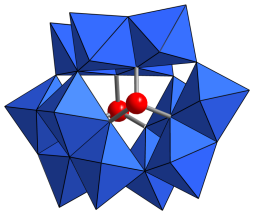


T>120°C

$[Mo_{36}O_{112}]^{8-}$



$[(TeO_3)_2Mo_{12}O_{36}]^{4-}$



$VOSO_4$

$Te(OH)_6$

The active sites grow during ageing: cation distribution

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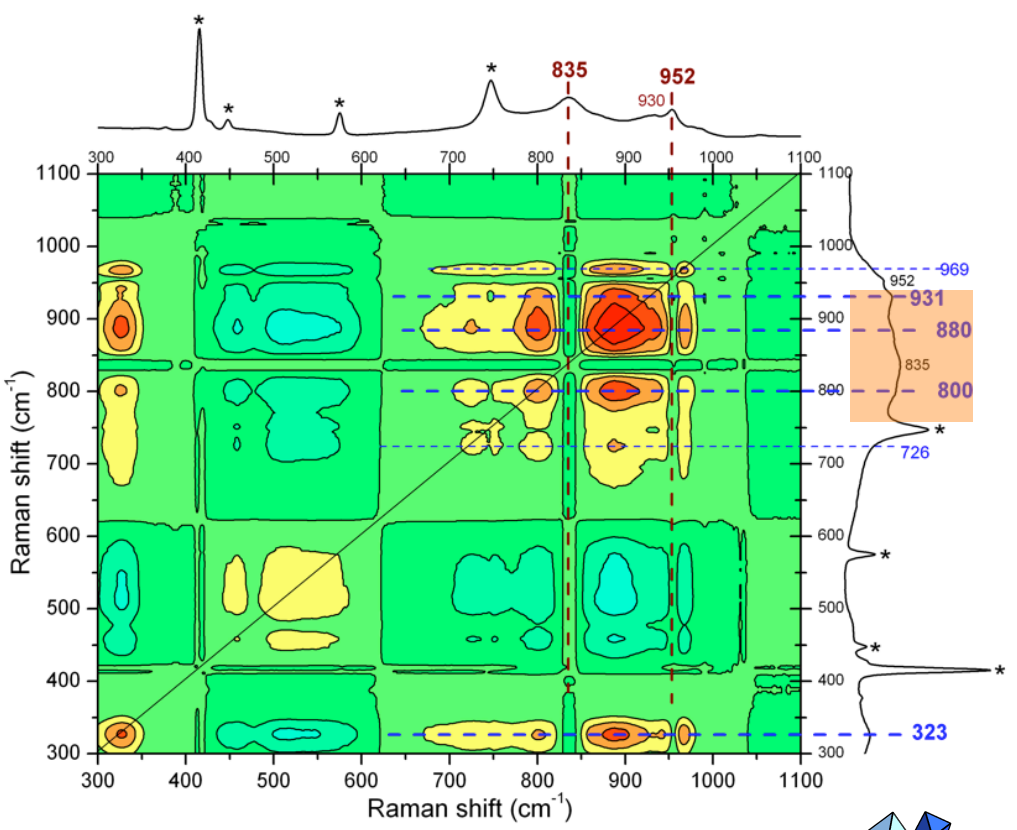

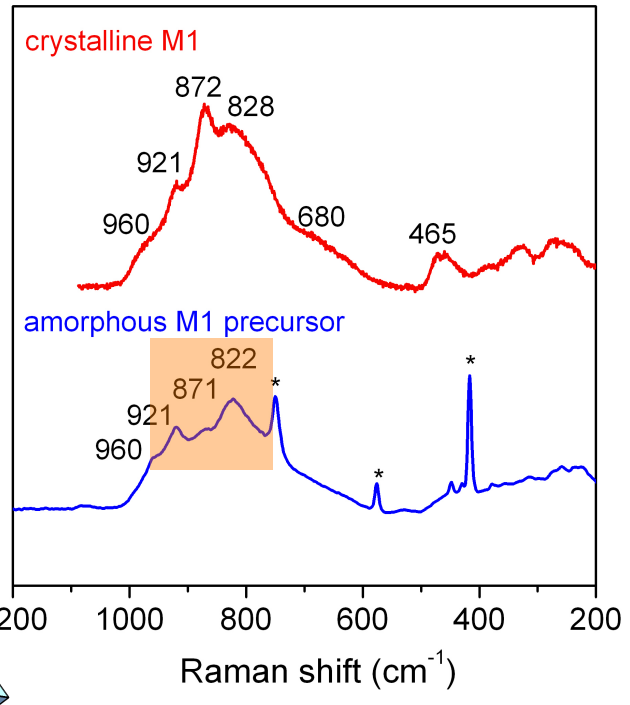

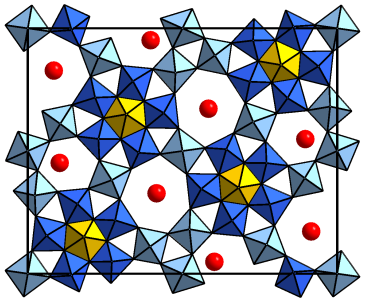

The practical use of the synthesis knowledge rational design

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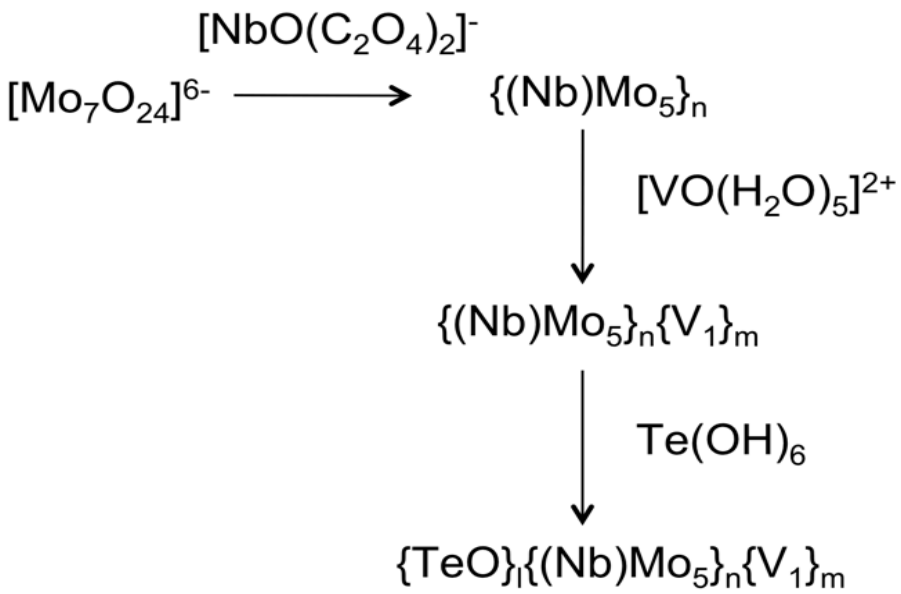

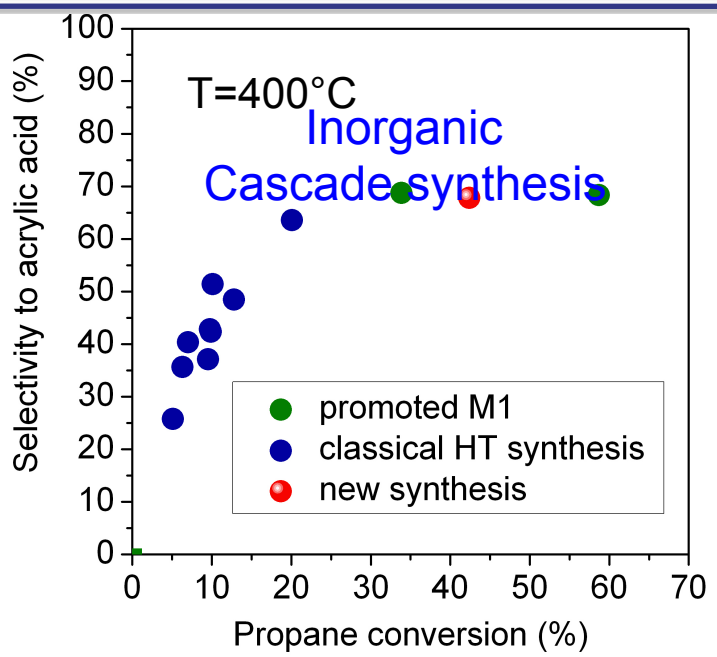

	Classical M1 synthesis (catalyst ID 11811) T=190°C t = 12 h	Novel, step-wise M1 synthesis (catalyst ID 12639) T=175°C t = 2 h
Formulation normalized to Mo (XRF)	$MoV_{0.228}Te_{0.267}Nb_{0.318}$	$MoV_{0.207}Te_{0.180}Nb_{0.207}$
S_{BET} [m^2/g]	1.5	4.7
Ea [kJ/mol]	72	55
Space time yield [$mg_{aa}/g_{cat}h$] at 673 K	9.3	48.8

The practical use of the synthesis knowledge rational design

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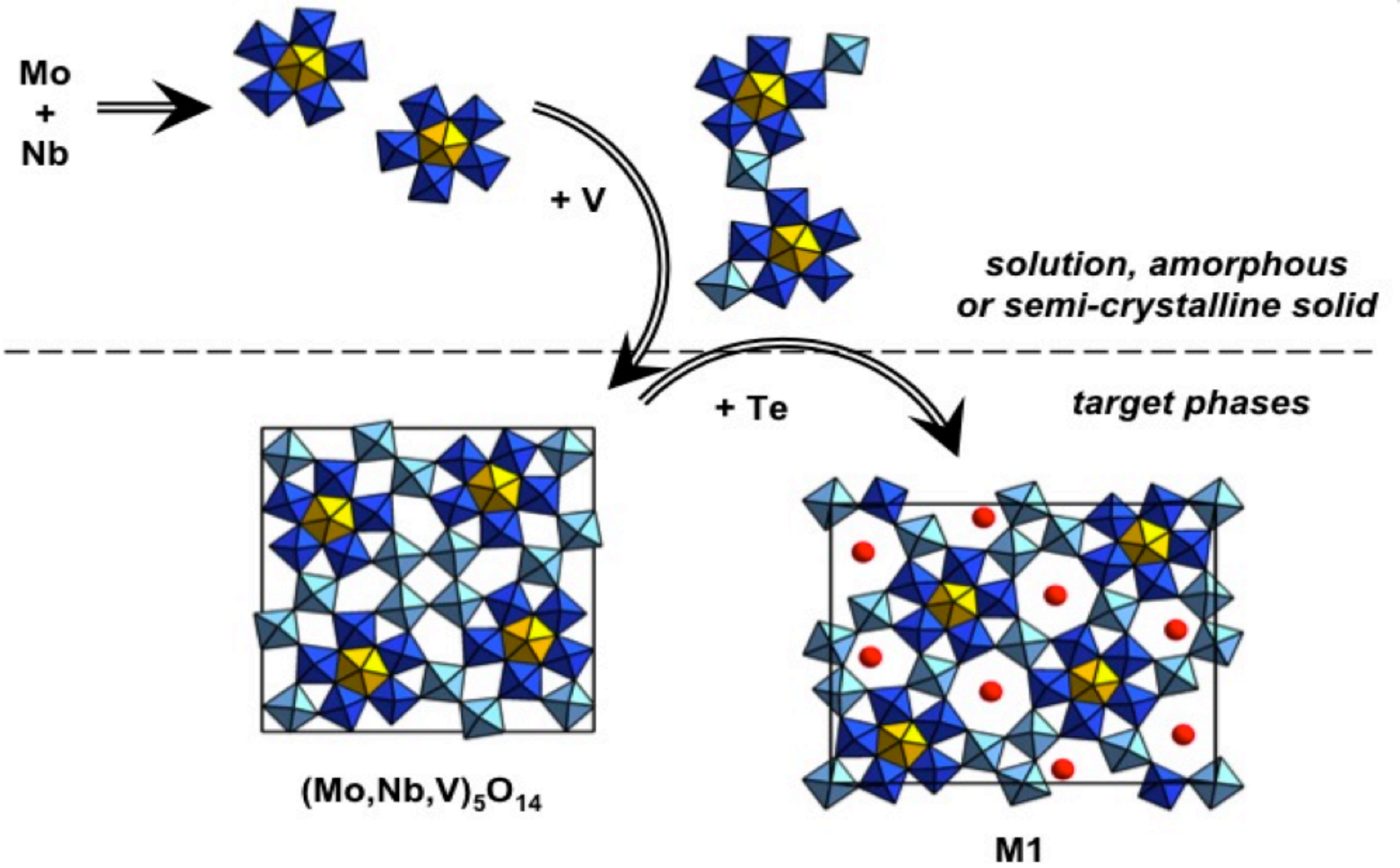

Summary

- Oxides are highly versatile catalysts for a variety of reaction families.
- They exhibit complex terminations, “simple” oxides terminate often passivated.
- High performing systems exhibit a “monolayer” active phase stabilized by a bulk withstanding the chemical potential of the reaction environment.
- Semiconducting properties relevant.
- This causes complex crystal structures to be functional, also as storage phase for the active component.

Dem Anwenden muss das Erkennen vorausgehen

Max Planck

Thank You

VPP in MA synthesis: well-known here active species across pressure gap

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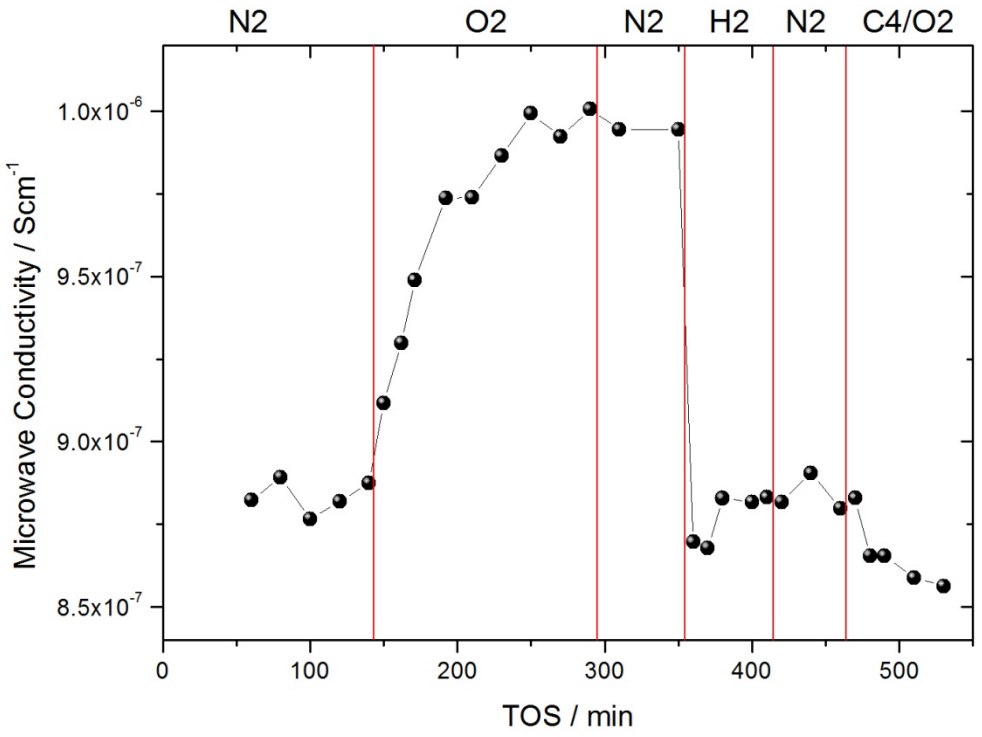
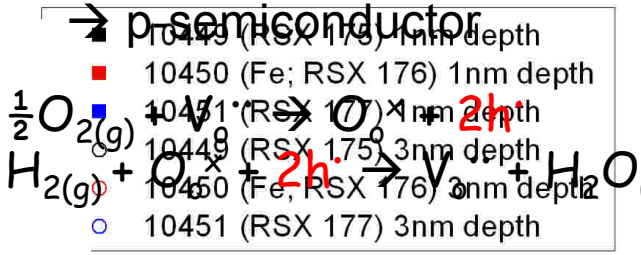
GHSV: 3540 h^{-1}; N2: 100% N_2; O2: 20% O_2; H2: 14% H_2; C4/O2: 2% n-butane, 20% O_2, residual gas always N_2; 0.5-1 mm split

12829 (RSX 600)



Contactless microwave frequency perturbation

→ p-semiconductor



$$\frac{1}{2}O_{2(g)} + V_x^0 \rightarrow O_x^0 + 2h^{\cdot}$$

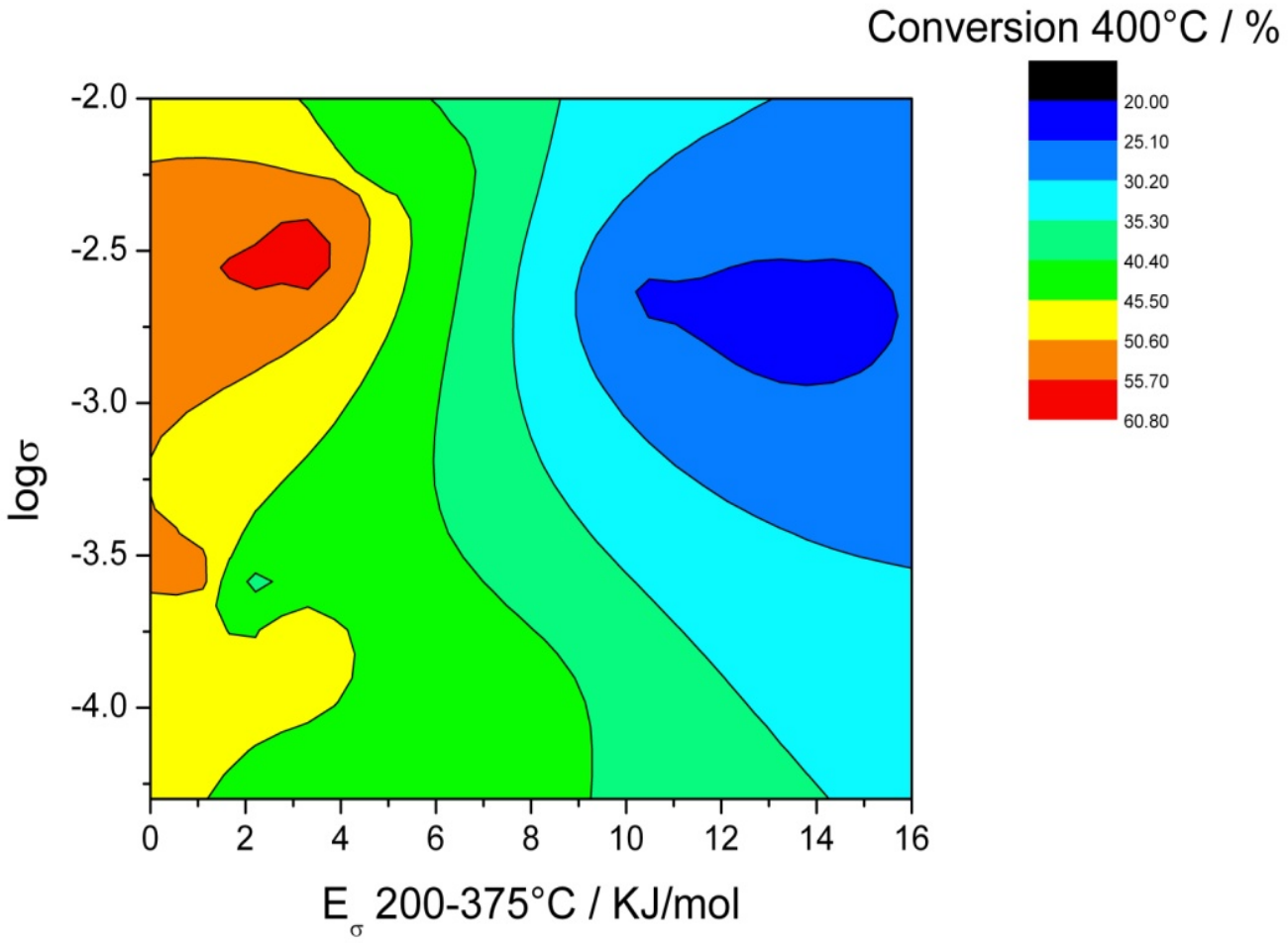
$$H_{2(g)} + O_x^0 + 2h^{\cdot} \rightarrow V_x^0 + H_2O_{(g)}$$

AP-PES
Strong variation of the "oxidation state" (surface structure) with chemical potential.

But only in the top few nm

How at atmospheric pressure with surface sensitivity?

Physics of site isolation correlation to performance



Propene metathesis: a side reaction in ODP?

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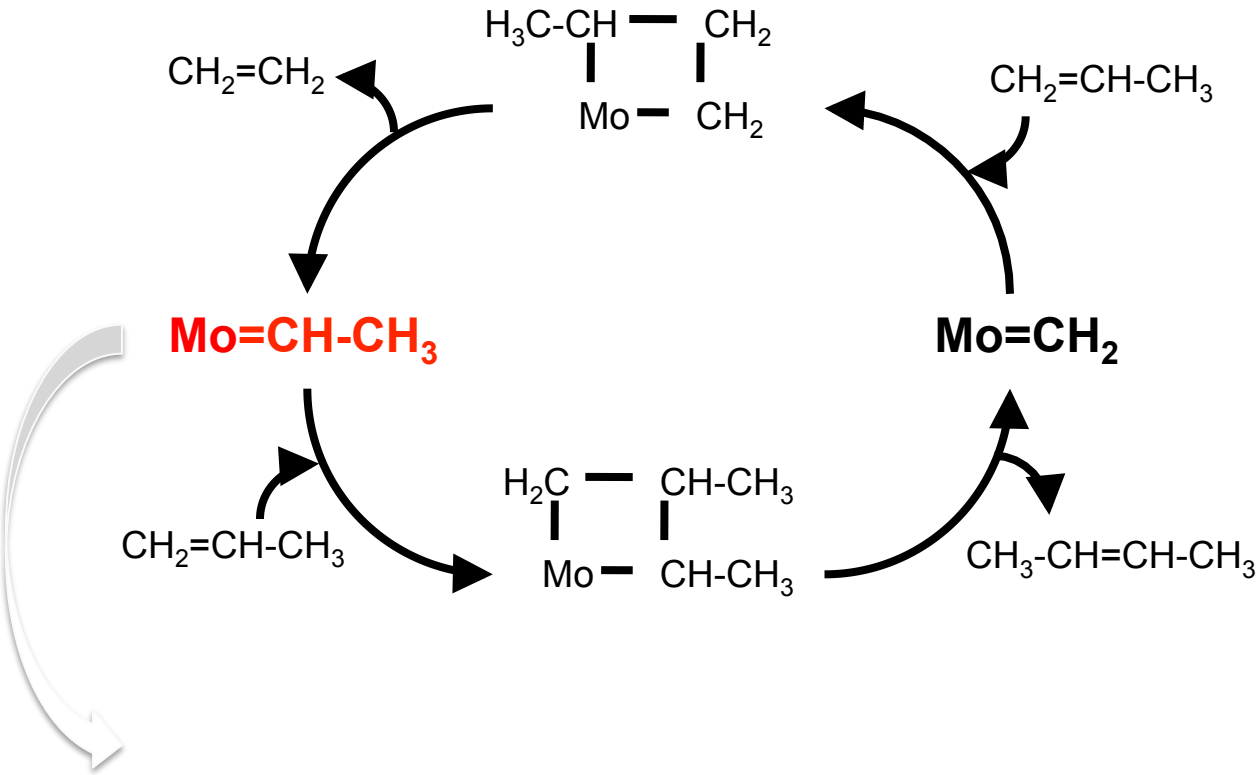

Post-reaction **CD_2=CD_2 metathesis** titrates Mo=CH-CH_2 sites, allowing quantification of the active carbene sites.

$$\mathbf{Mo{=}CH{-}CH_3} + CD_2{=}CD_2 \rightarrow Mo{=}CD_2 + \mathbf{CD_2{=}CH_2{-}CH_3}$$

A modified version of the method described by Handzlik in *Catal. Lett. 88(2003)119*

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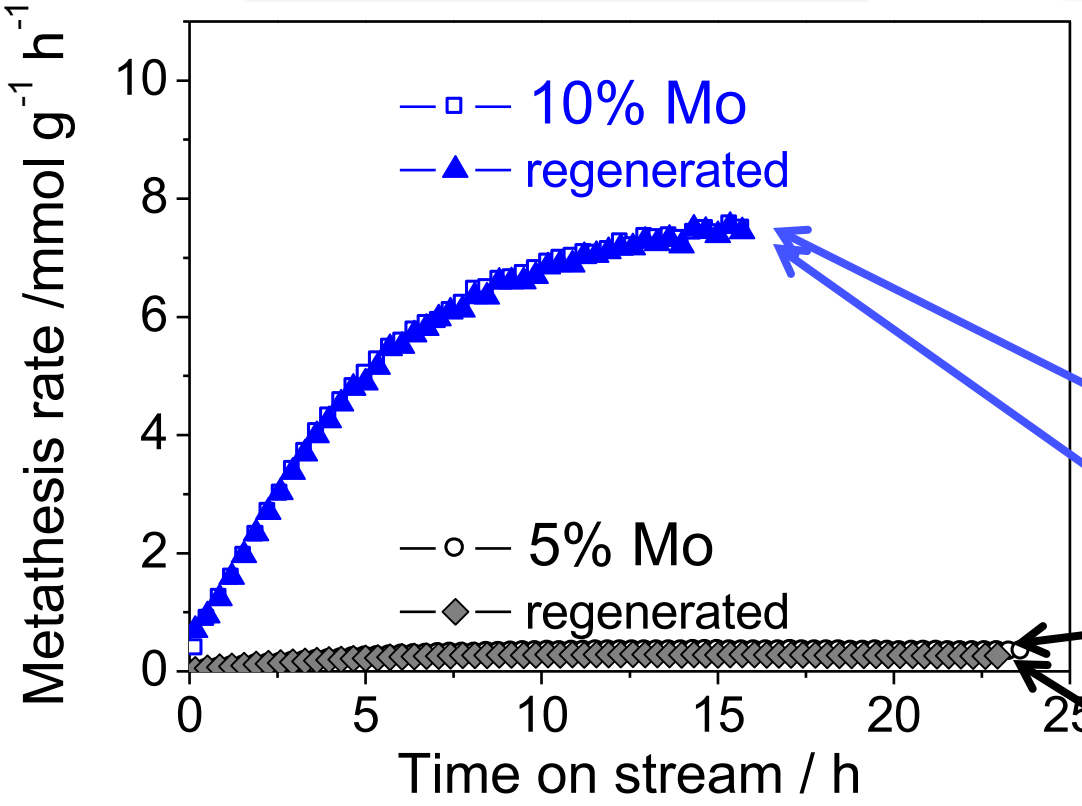
Few sites are highly active

Activity of MoO_x/SBA-15



post-reaction carbene titration

Active site density (µmol g^{-1})	Active site fraction (atom-%)	Intrinsic activity (h^{-1})
15	1.5	500
14	1.4	530
3.7	0.7	90
2.2	0.4	120

Activity not proportional to loading: structural variations

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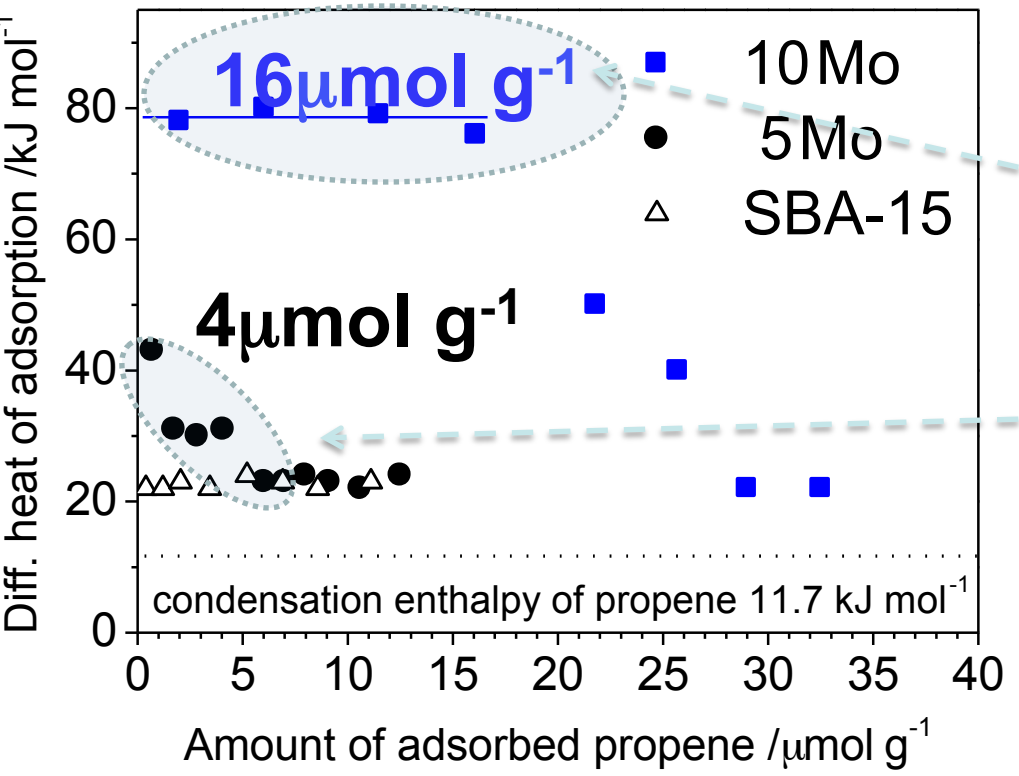
Chemisorption identifies active sites

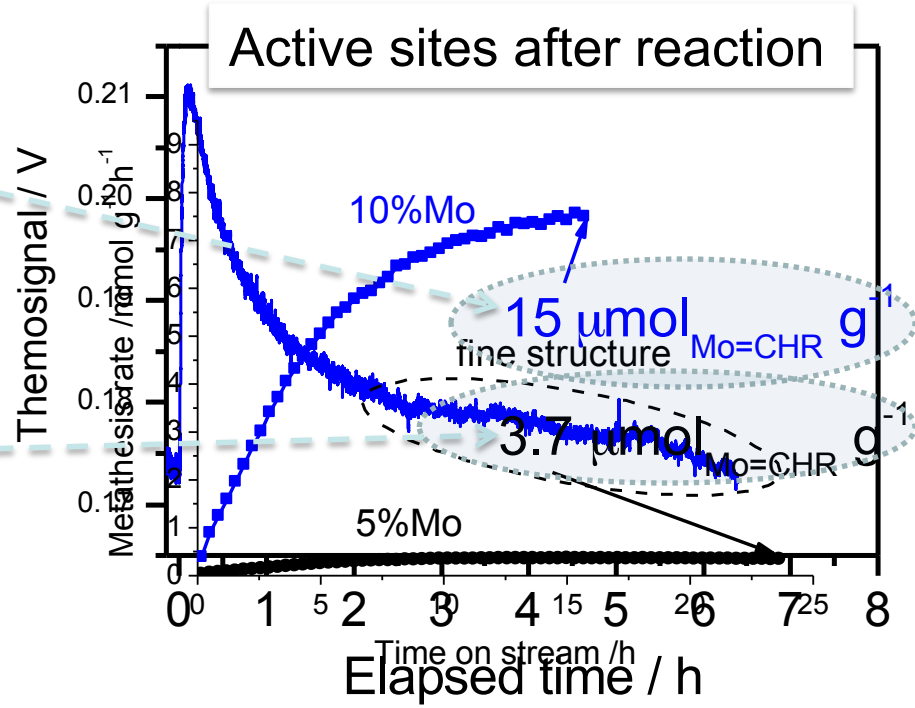
HZB Helmholtz Zentrum Berlin

unicat Unifying Concepts in Catalysis

C_3H_6 Calorimetry



Active sites after reaction



The site densities of strong and irreversible adsorption coincide with the carbene site densities measured by the post-reaction titration.

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In-situ formation of active species: selective oxidation