Solid state chemistry and catalysis: Structure-function relations?

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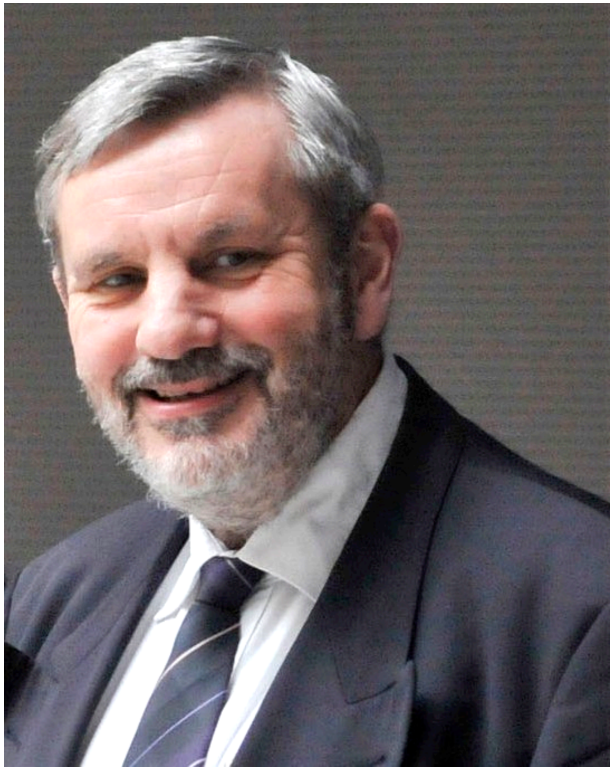
Helmut Schubert
Not always mainstream

„Schubert is known for materials processing technology. The major focus is to create materials and processes with respect to application simultaneously. Hence, materials characterization and description of properties are his research subjects.“



Is there a relation to catalysis other than being able to synthesize oxides?

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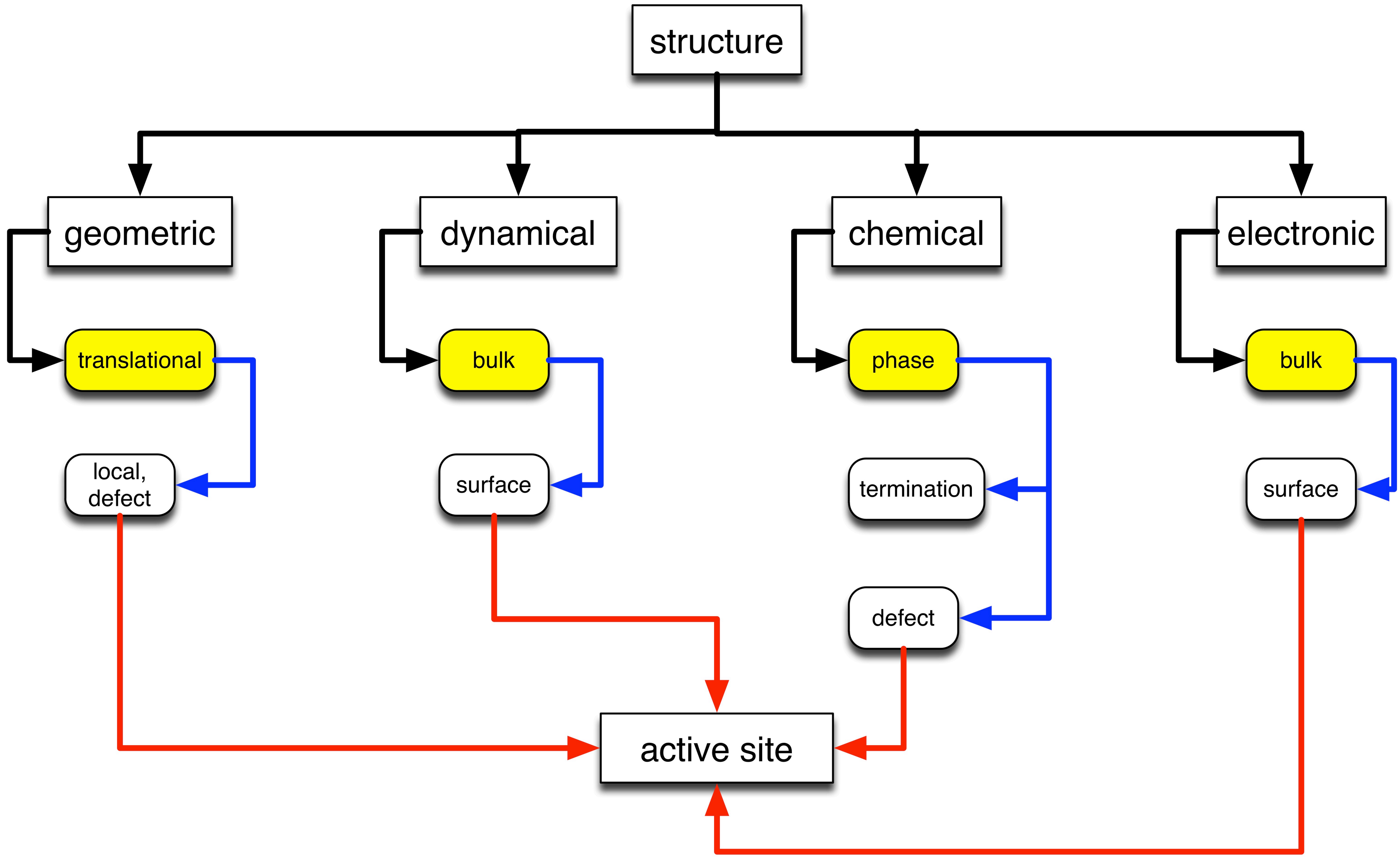
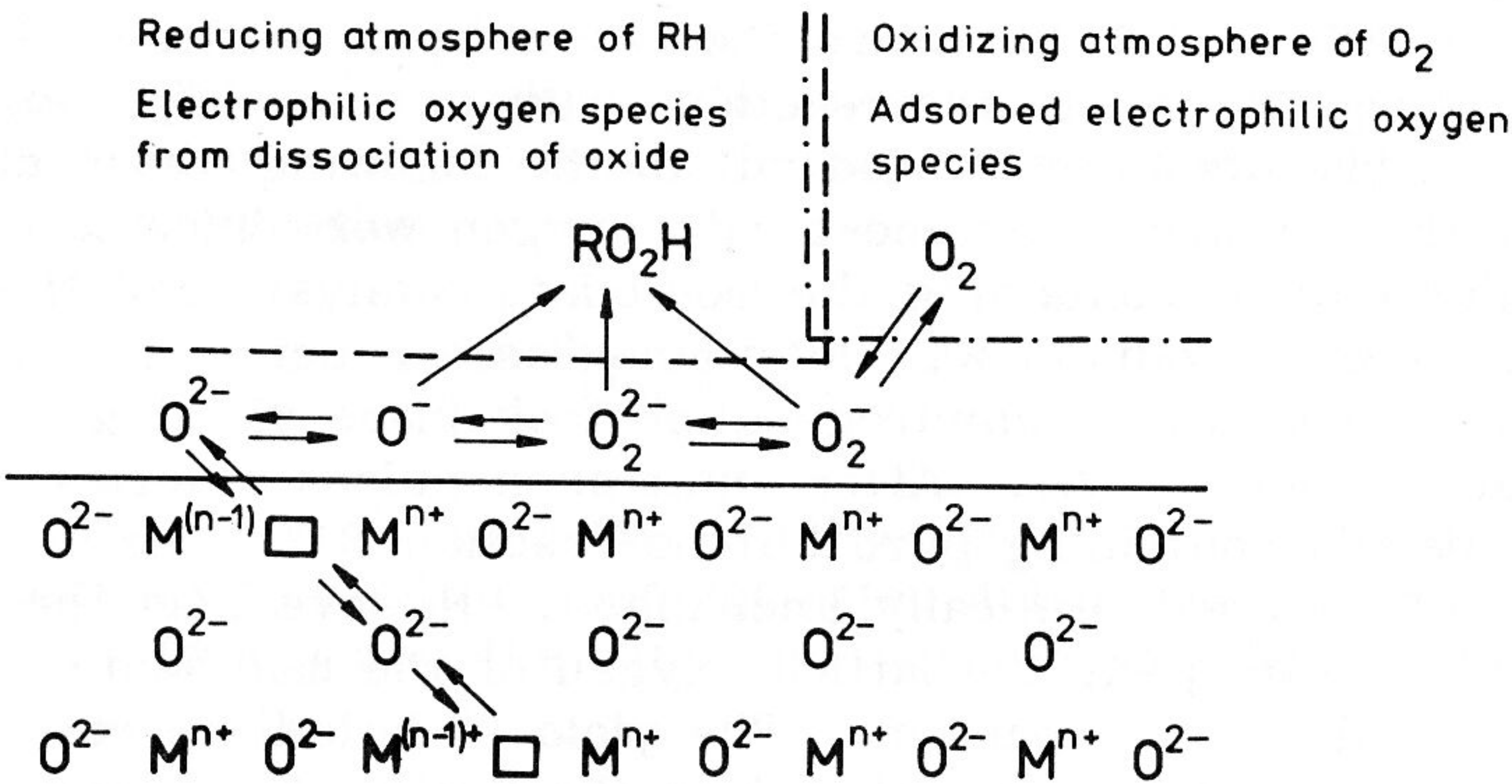
Catalyst structure: A variable target describing only part of its performance



Bulk lattice oxygen vs surface lattice oxygen



high activity

J. Haber, 1991

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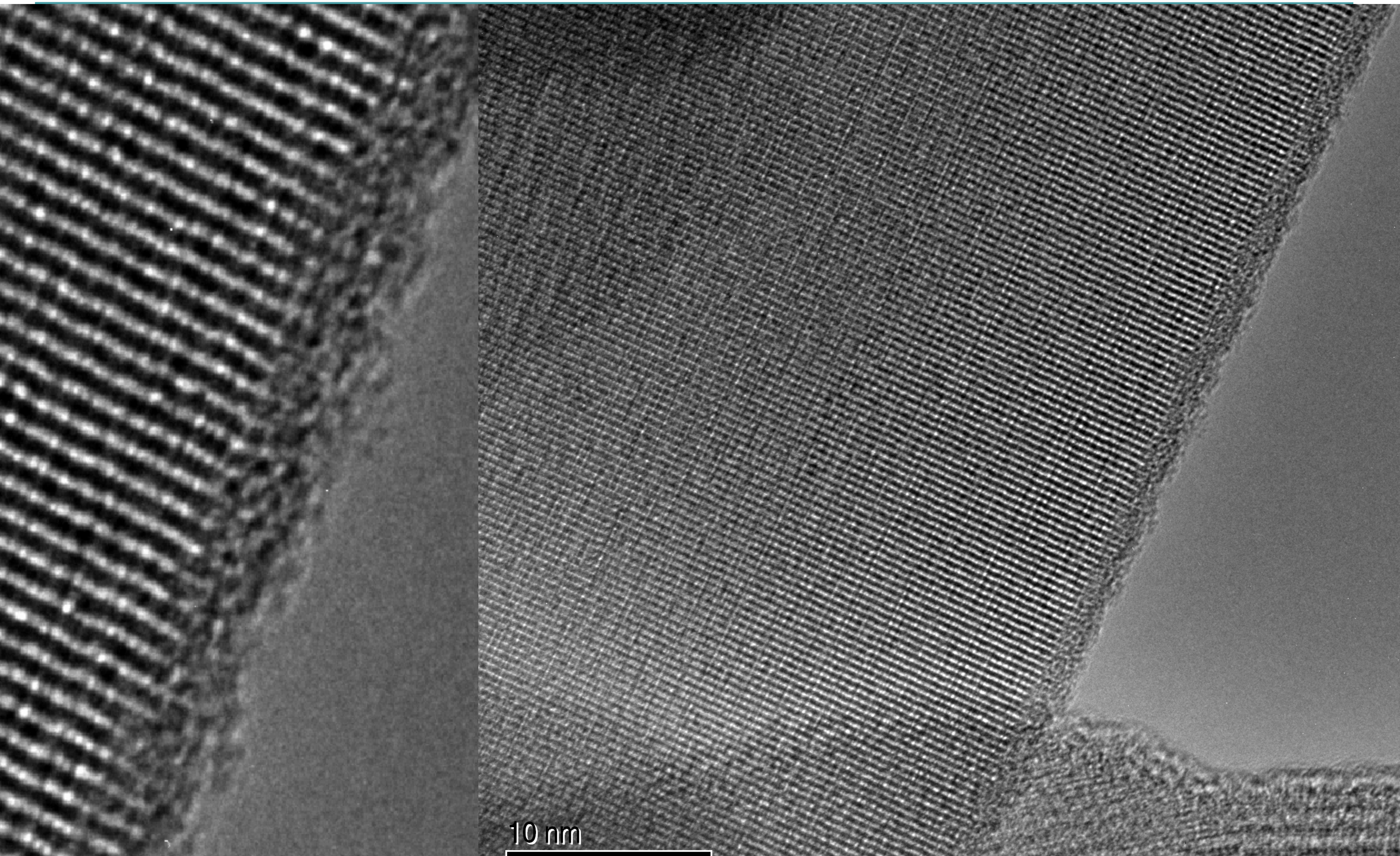
Bulk lattice oxygen vs surface lattice oxygen



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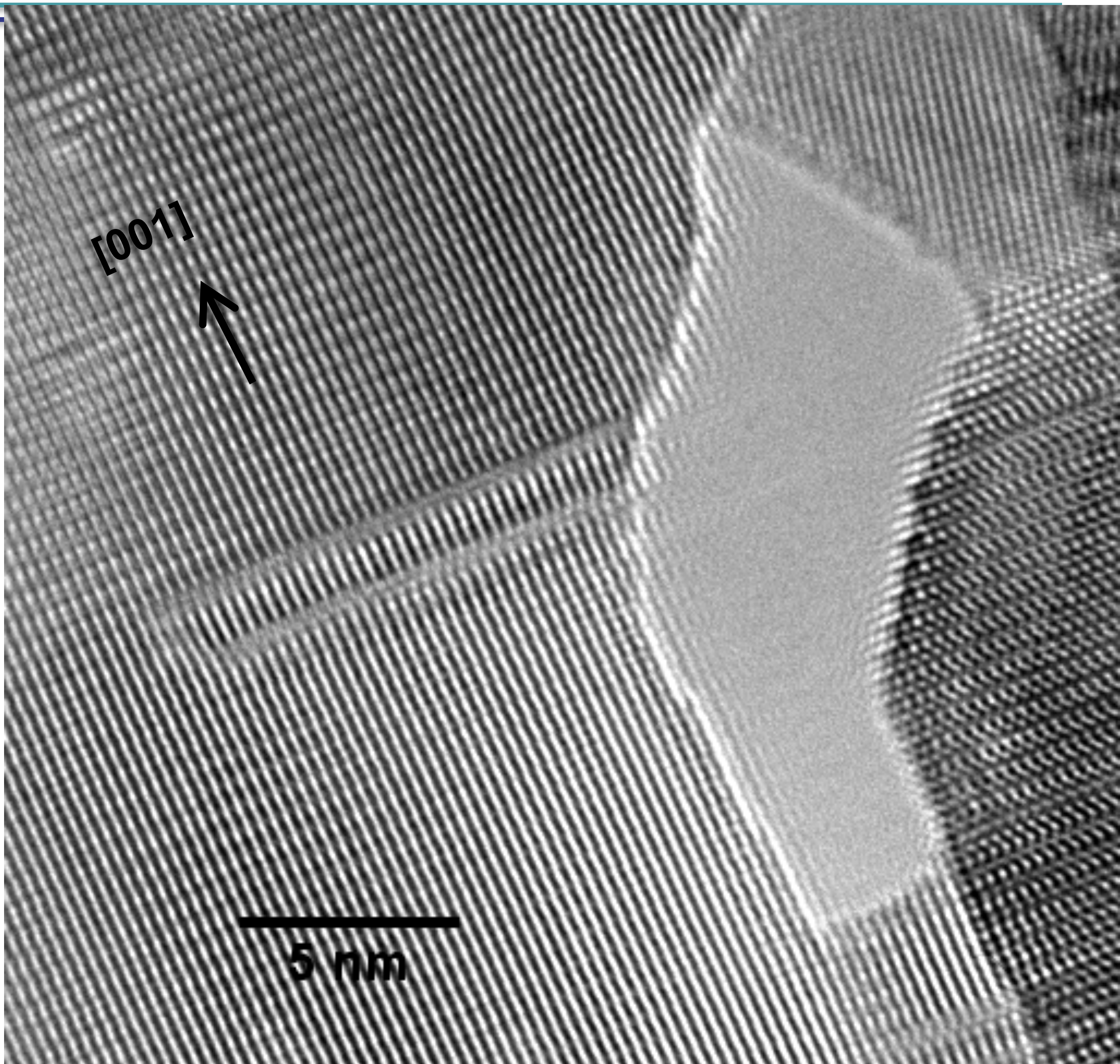
Bulk lattice oxygen vs surface lattice oxygen



C3 oxidation: C_3H_8 to C_3H_6 a "simple" reaction network

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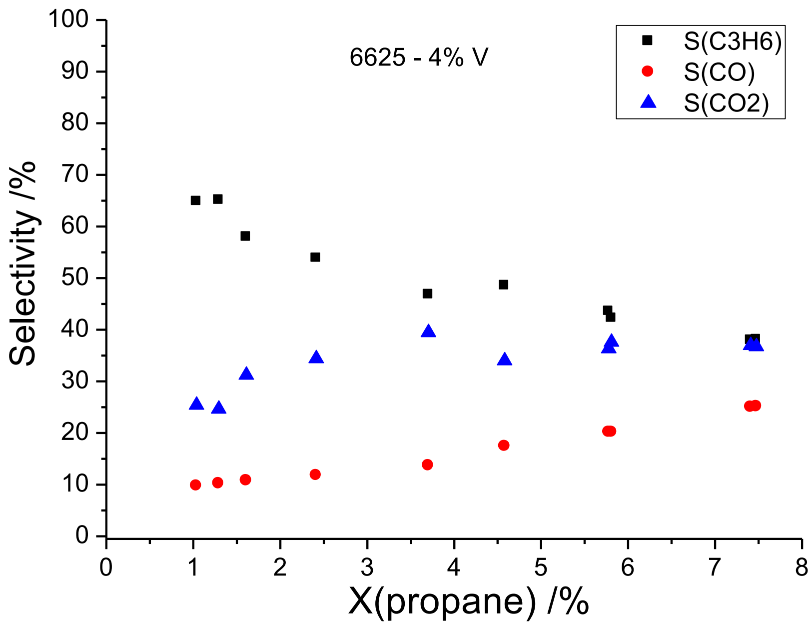

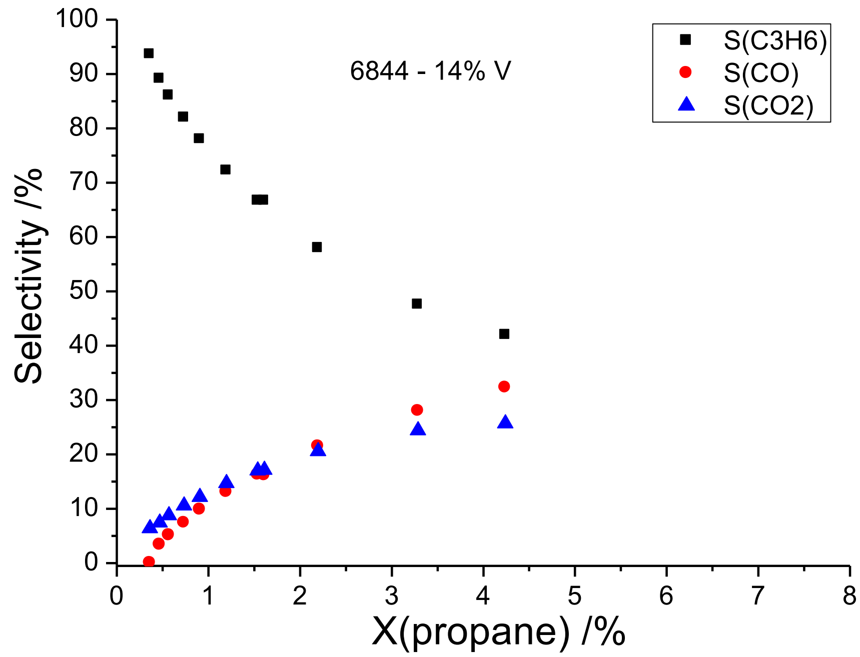

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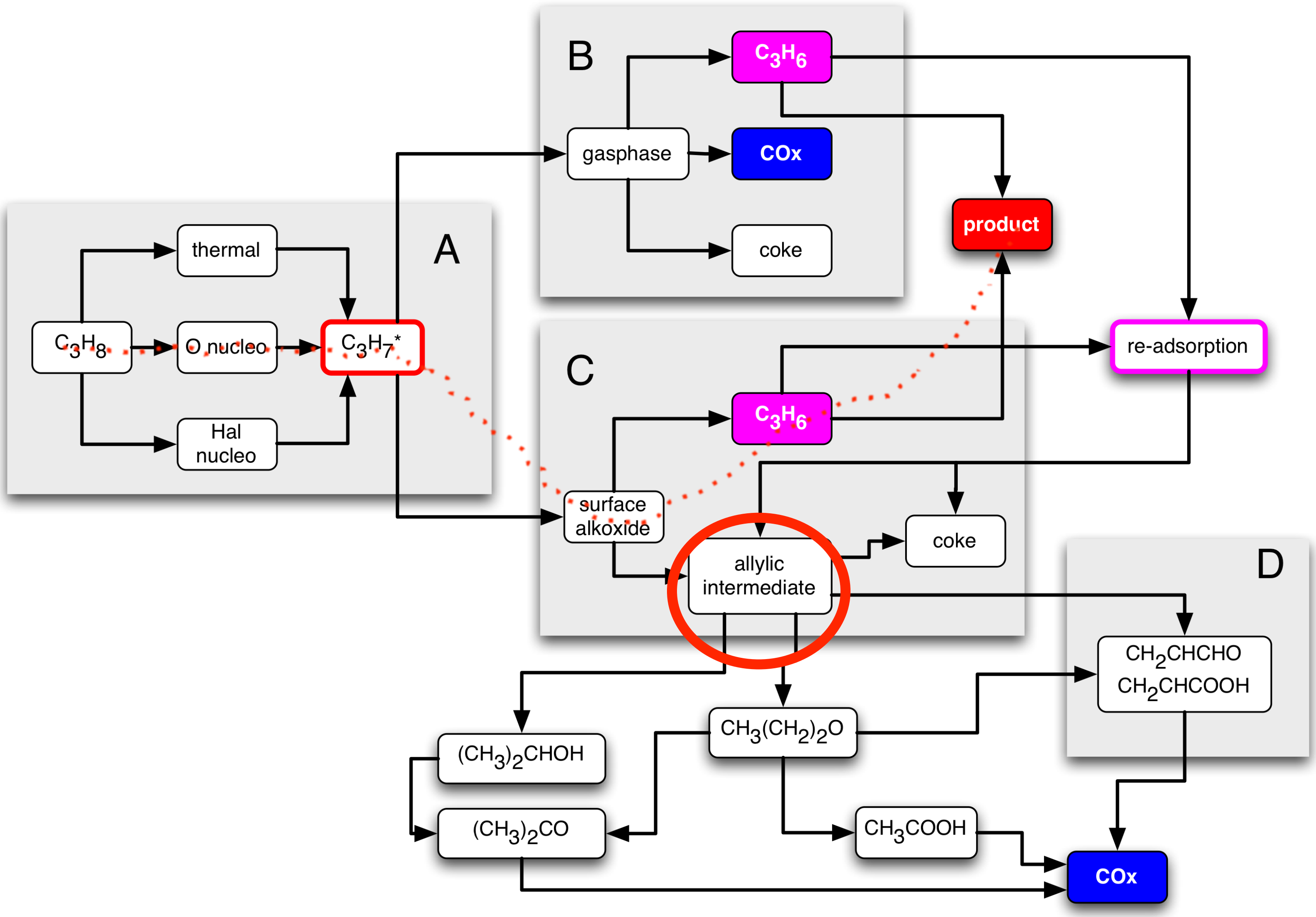
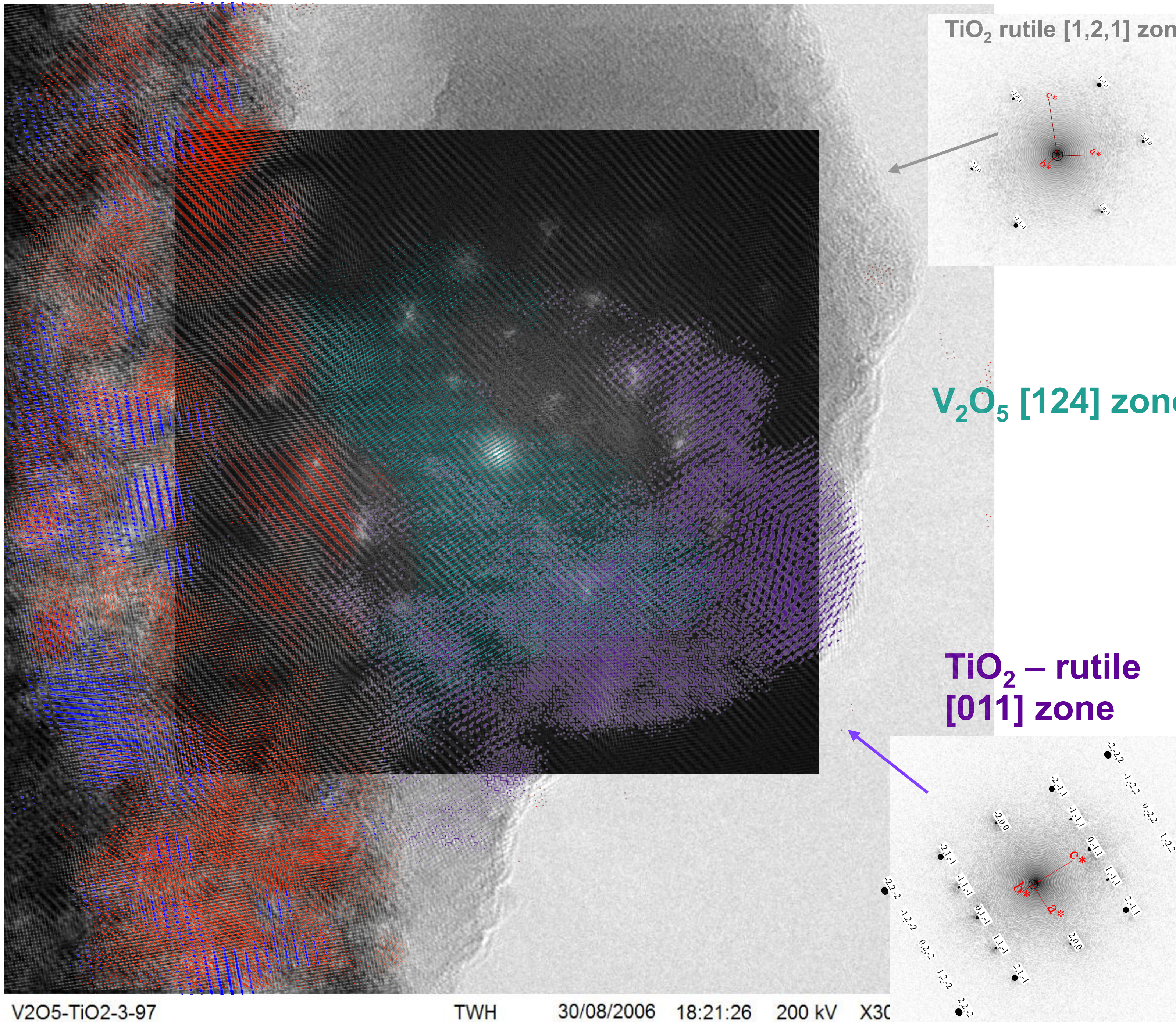
C3 oxidation: C_3H_8 to C_3H_6 a “simple” reaction network



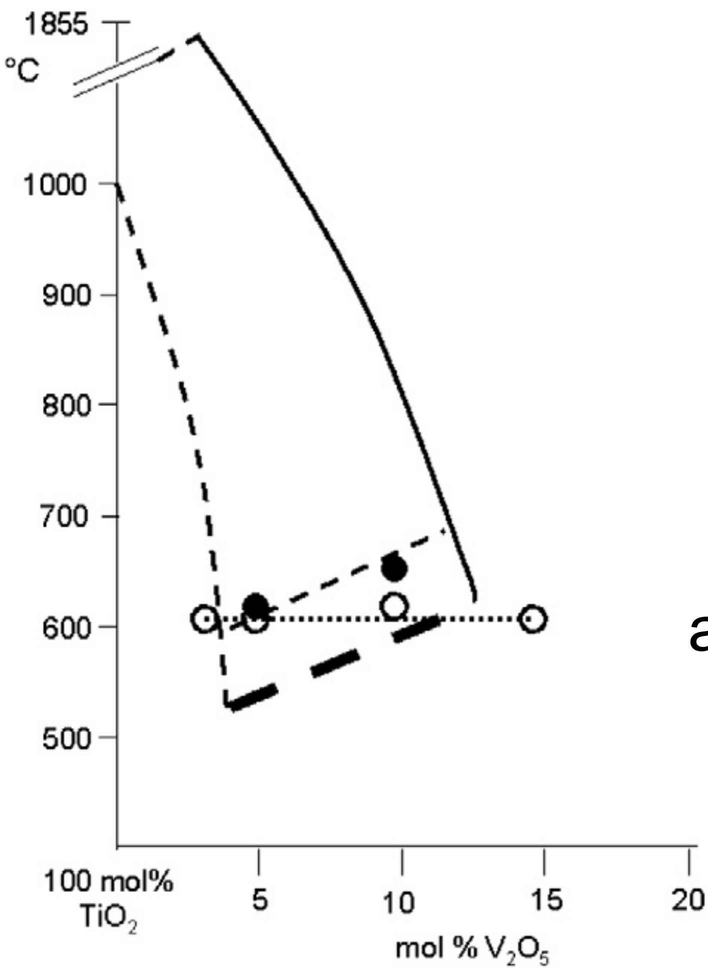
V_2O_5
[001] zone

TiO_2 -
anatase
[011] zone

TiO_2 rutile
in [001]



H. Schubert: Role of the solid state chemical potential



R. Mitdank et al. 2011

Exactly at the conditions of loading and preparation there is a ceramic phase transition of the binary TiO_2 / V_2O_5 support system into a single solid solution phase.

Detection through quantitative analysis of Rutherford backscattering intensity profile simulation.

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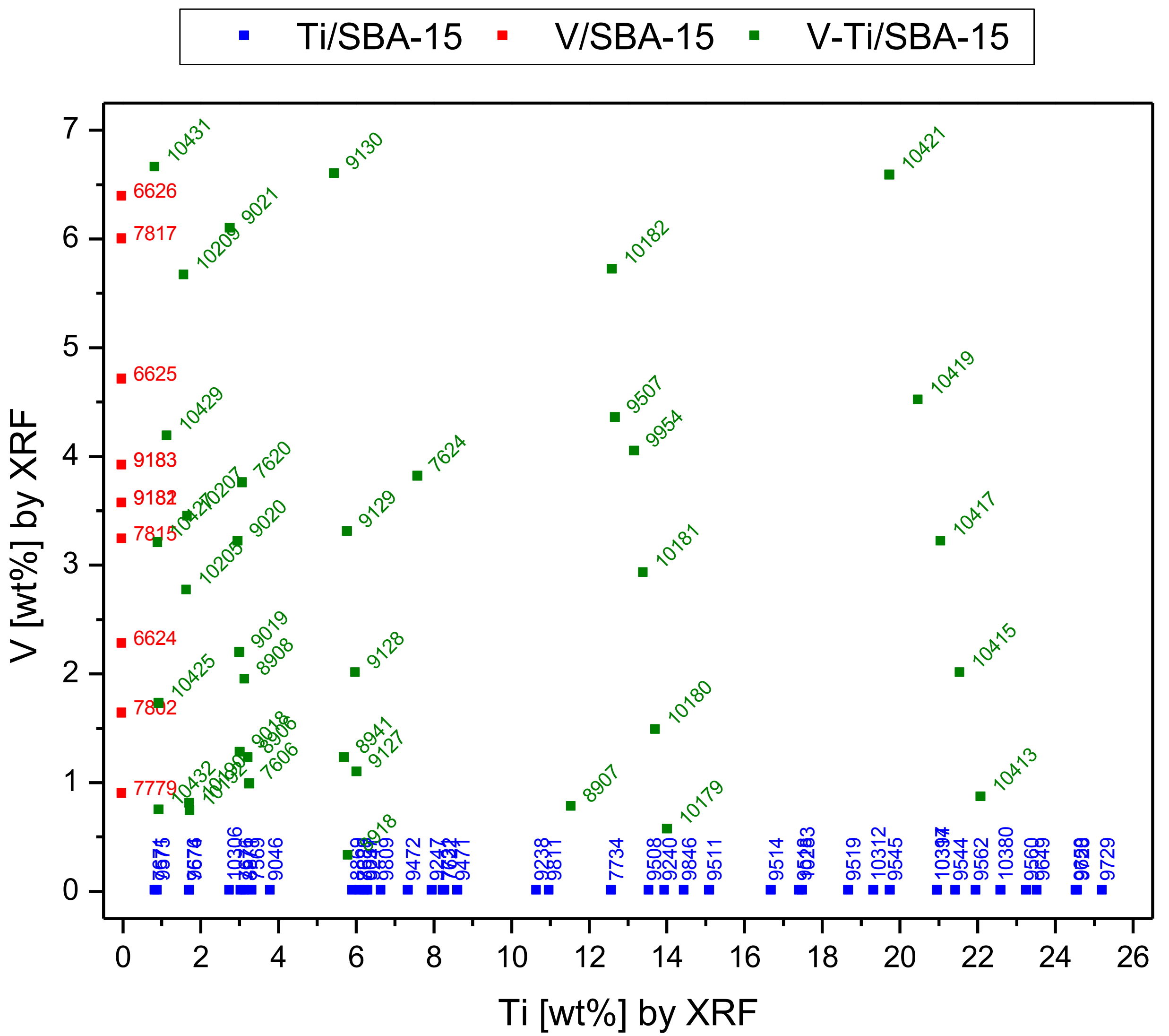
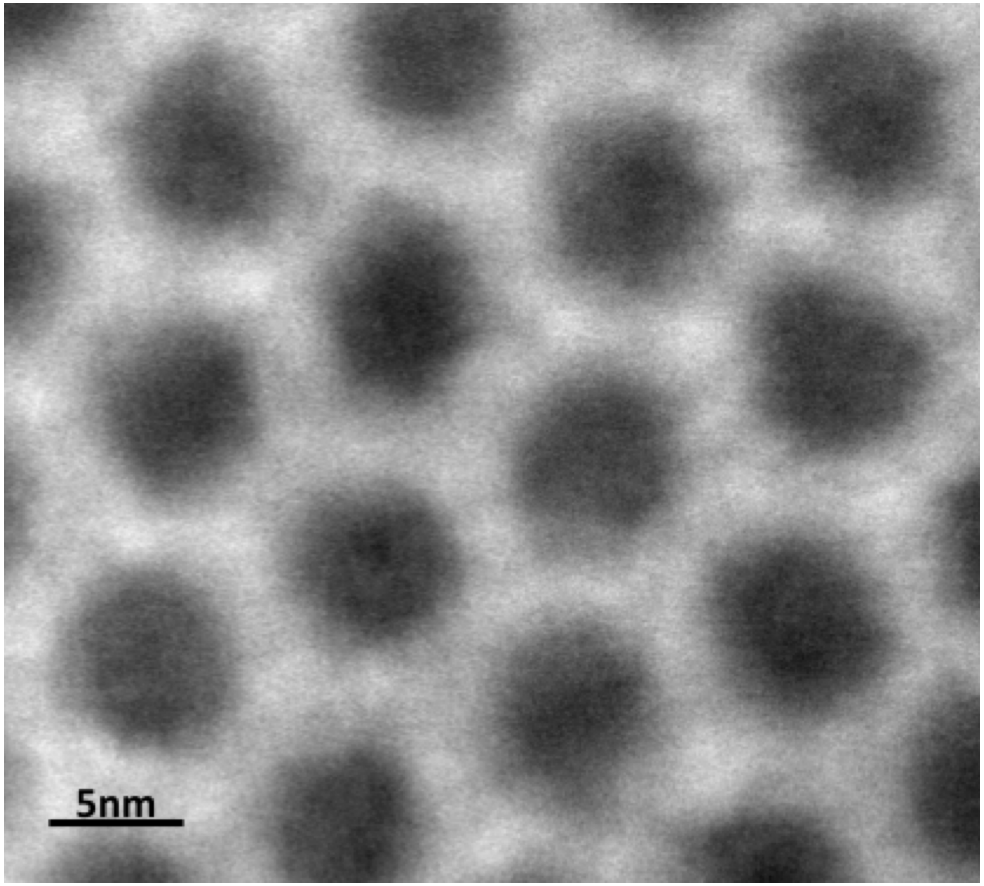
A catalyst library based upon a monolayer active phase



A catalyst library based upon a monolayer active phase



A catalyst library based upon a monolayer active phase

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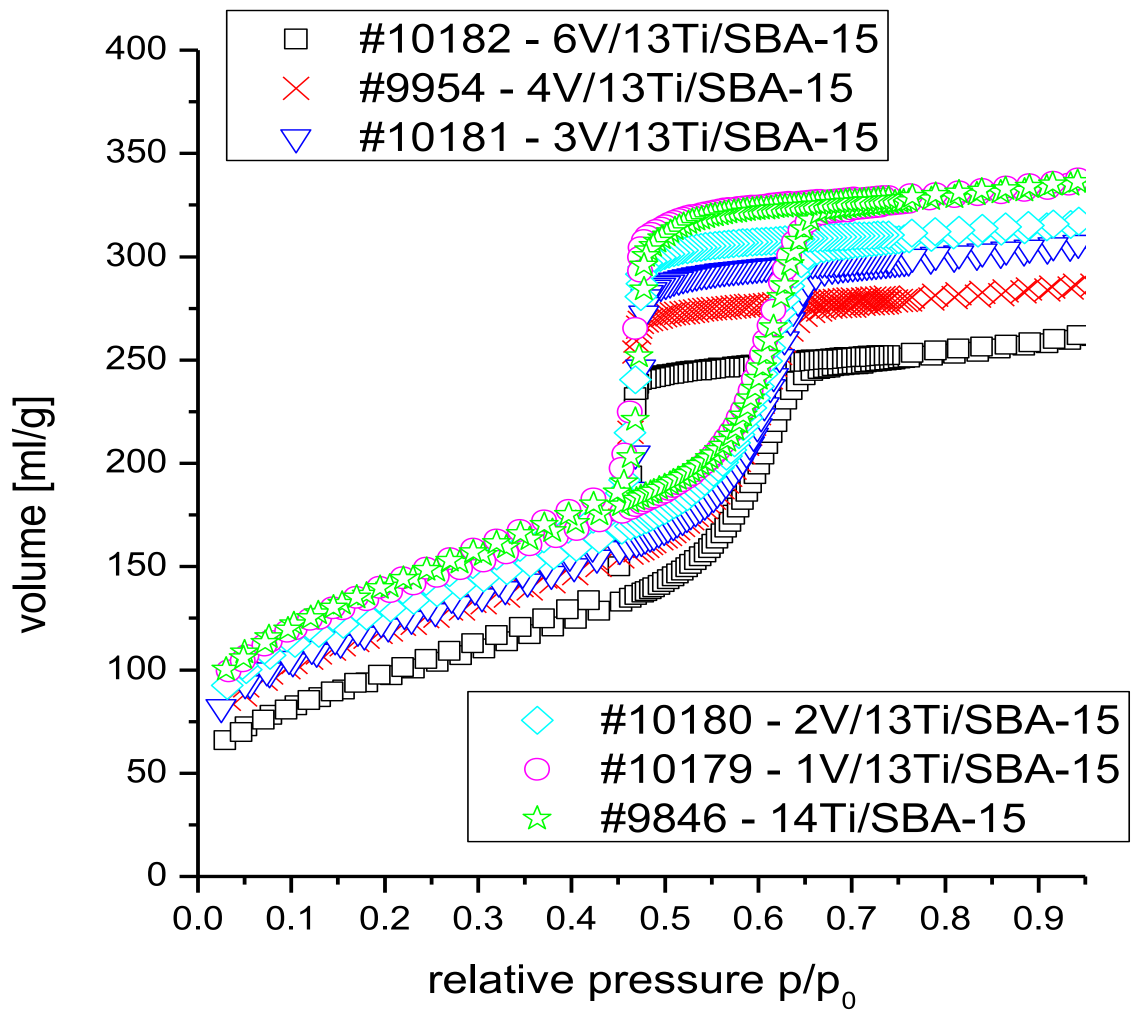

The activated state

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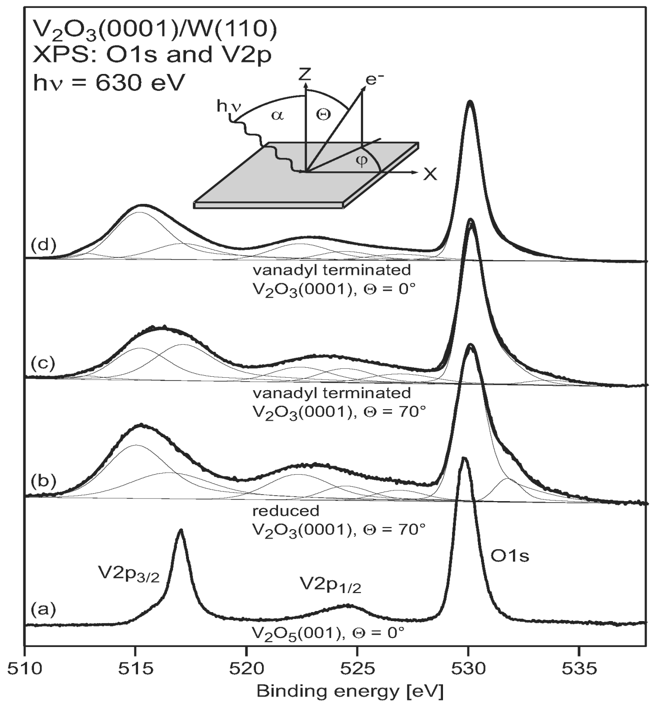
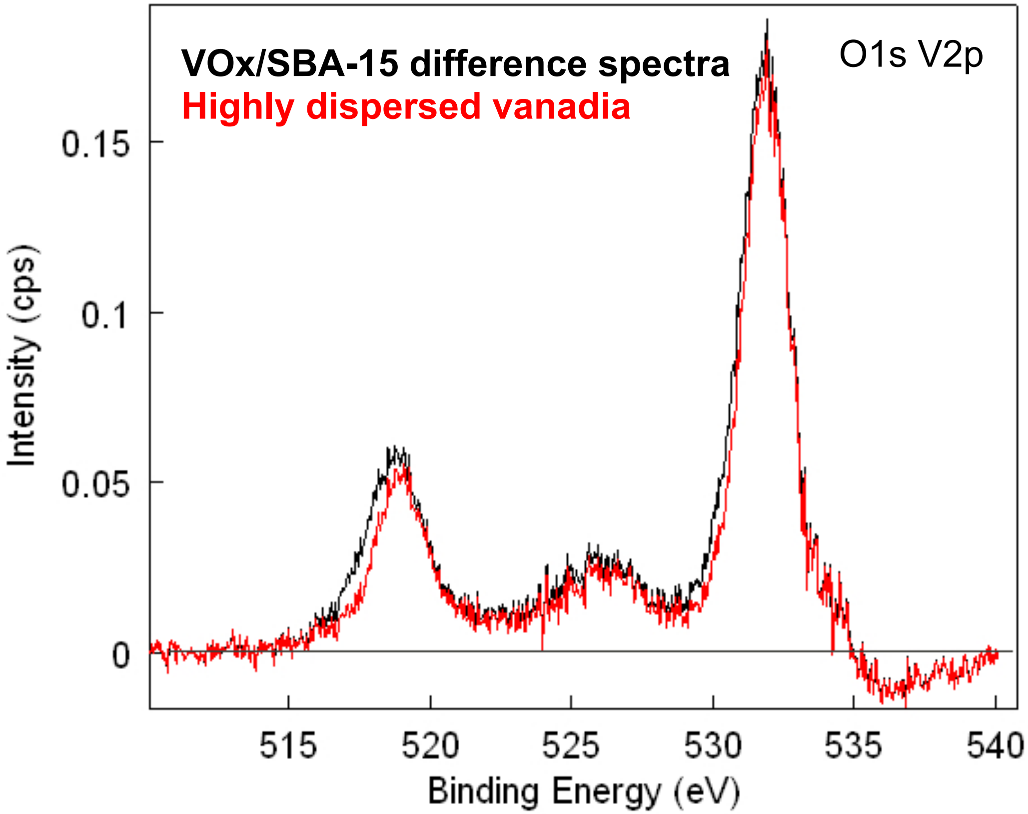


Freund et al., Surf. Sci. 2003



XPS as a tool to identify the nature of vanadia species on well-defined model systems as being very similar to high performing polycrystalline systems: Caveat: without models the calibration of surface analysis would be impossible.

Is this good?

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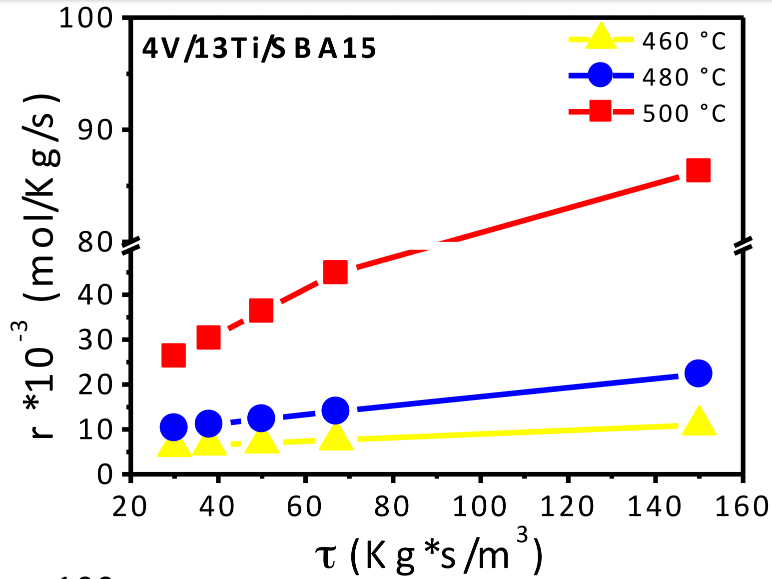

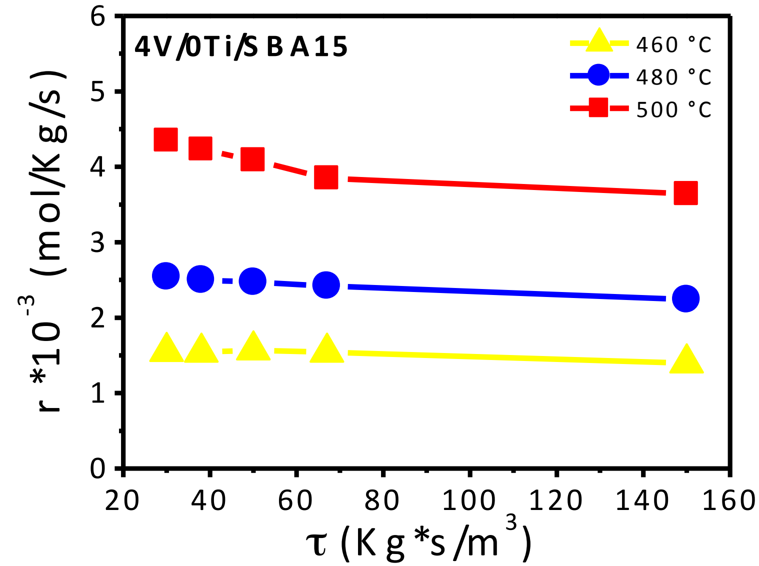

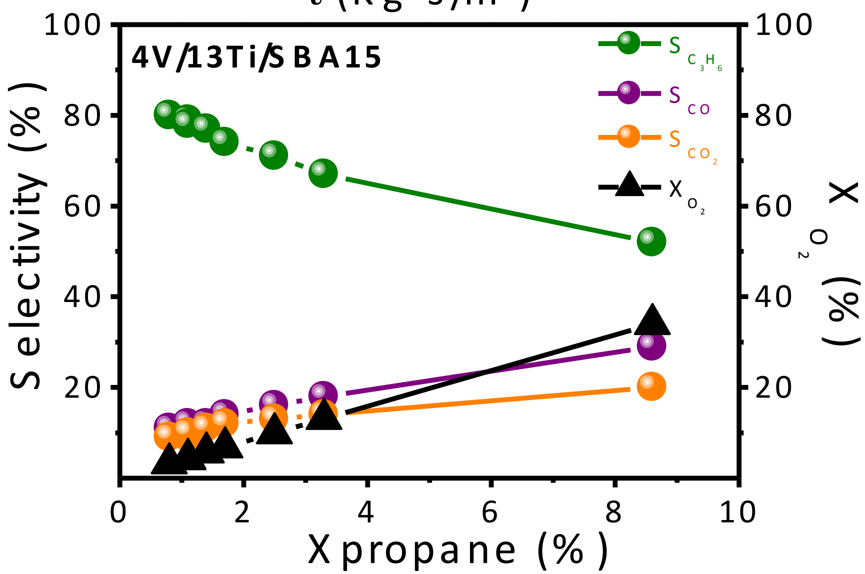

Catalysis:
Massive improvement of performance when V is deposited on Ti that is sufficiently covered to minimize O_2^-
Gold standard:
10^{-2} mol/kg/s

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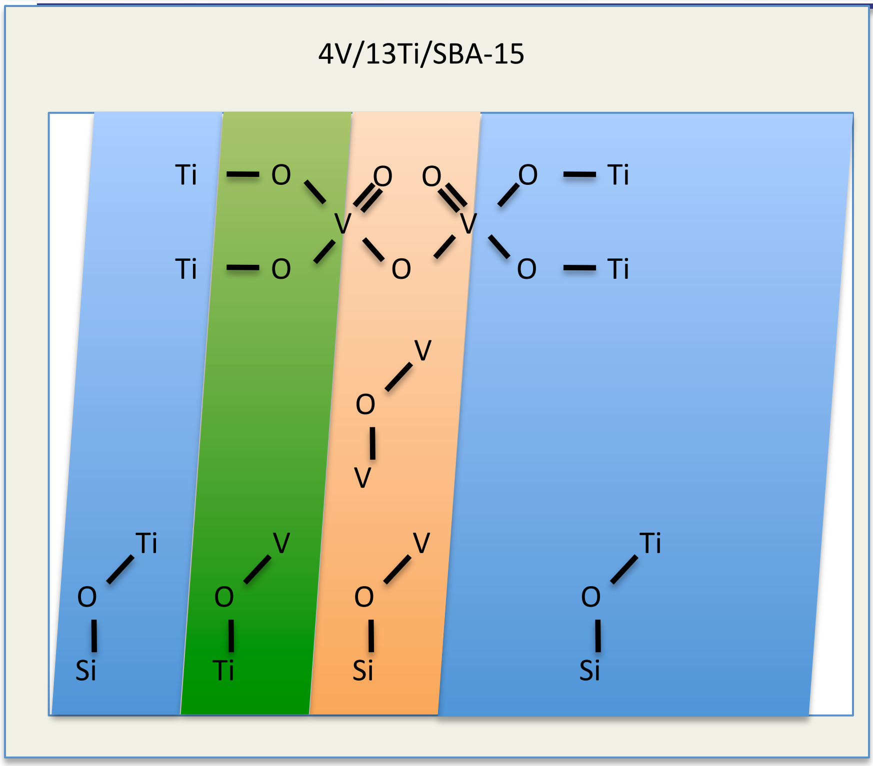
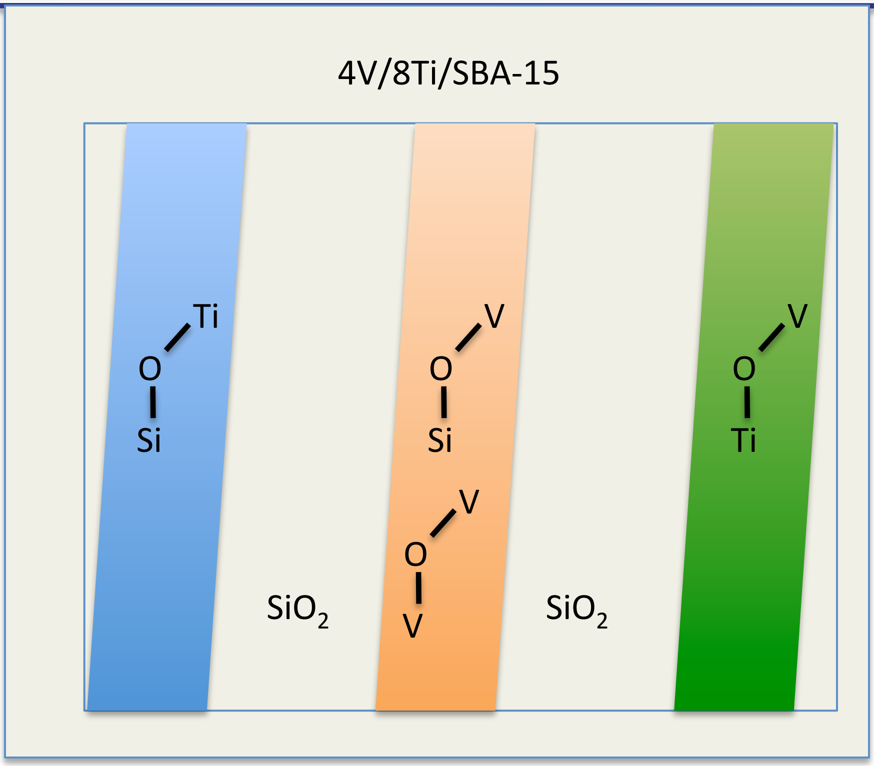
Is this good?





Butane oxidation: the challenge

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

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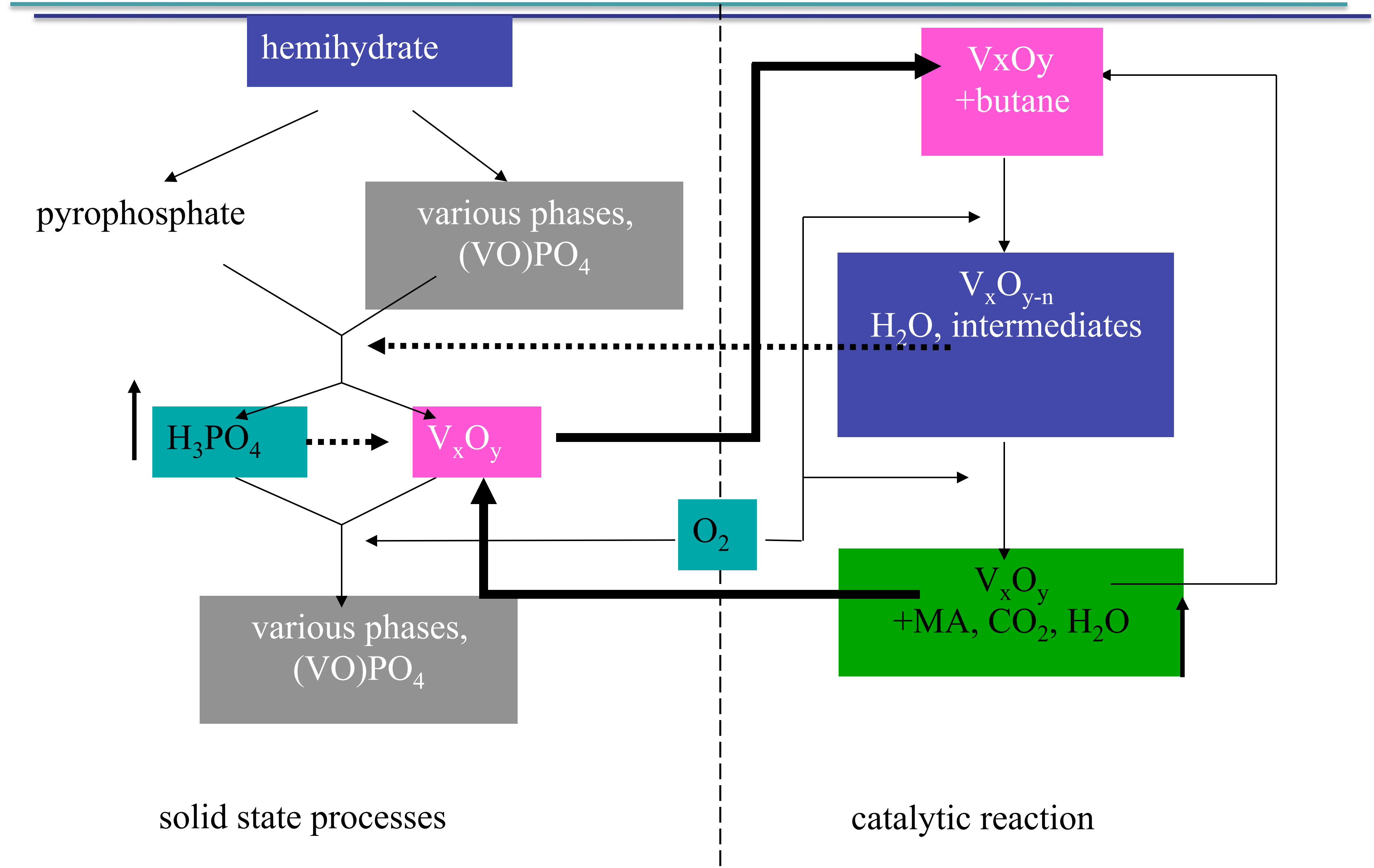

VPP in MA synthesis: active species across pressure gap

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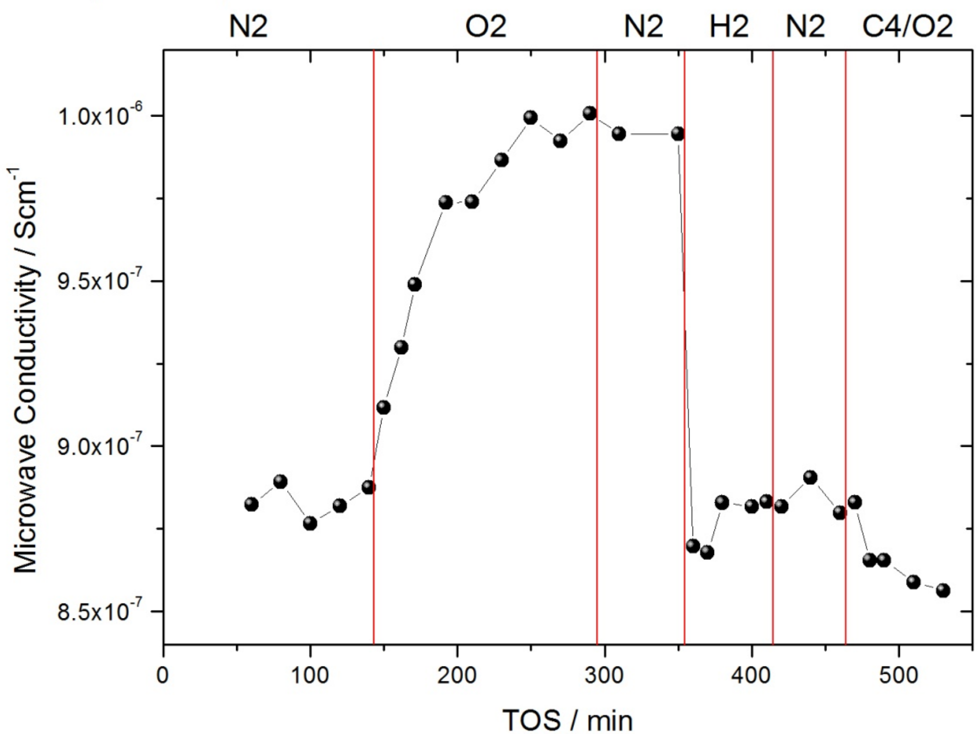
GHSV: 3540 h^{-1}; N2: 100% N_2; O2: 20% O_2; H2: 14% H_2; C4/O2: 2% n-butane, 20% O_2; residual gas always N_2; 0.5-1 mm split

175-300°C-400°C

12829 (RSX 600)



→ p-semiconductor

$$\tfrac{1}{2}O_{2(g)} + V_O^{\cdot\cdot} \rightarrow O_O^{\times} + 2h^{\cdot}$$

$$H_{2(g)} + O_O^{\times} + 2h^{\cdot} \rightarrow V_O^{\cdot\cdot} + H_2O_{(g)}$$

10449 (RSX 175) 1nm depth
10450 (Fe; RSX 176) 1nm depth
10451 (RSX 177) 1nm depth
10449 (RSX 175) 3nm depth
10450 (Fe; RSX 176) 3nm depth
10451 (RSX 177) 3nm depth

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?

Contactless microwave frequency perturbation

Physics of site isolation correlation to performance

A p-type semiconductor self-limits its redox-activity through a structurally different termination layer.

This allows for redox-dynamics (facile regeneration of reduced sites to V^{5+} sites).

The non-contact method detects local conductivity that is quantitatively related to catalytic performance.

VPP in MA synthesis: active species across pressure gap

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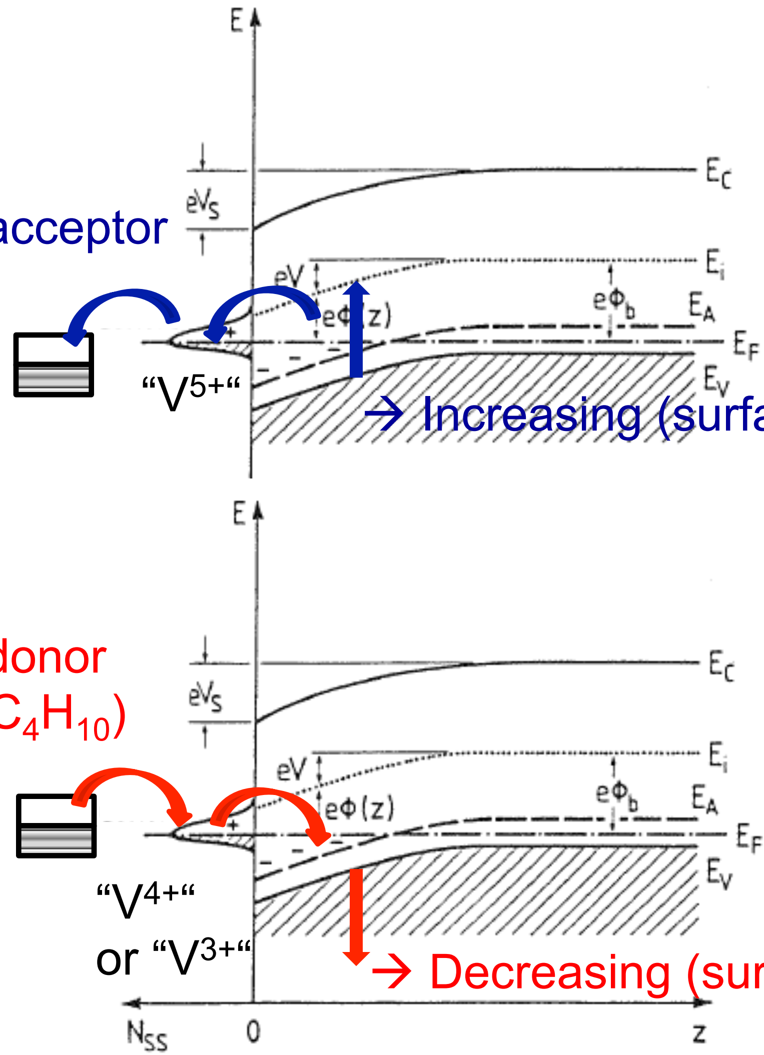
Adsorption of acceptor molecule (O_2)



→ Increasing (surface) conductivity

Adsorption of donor molecule (H_2, C_4H_{10})

→ Decreasing (surface) conductivity

VPP in MA synthesis: active species across pressure gap

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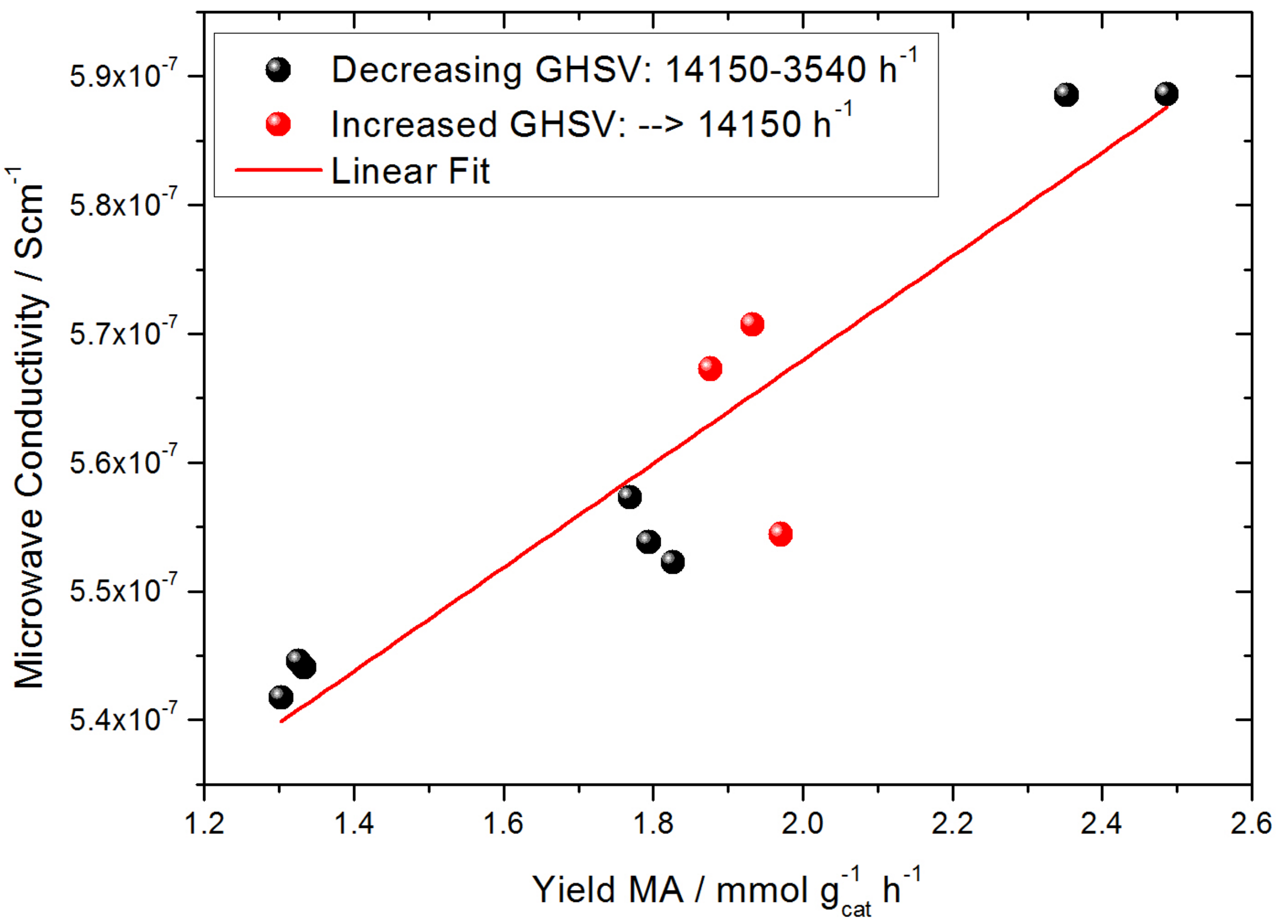
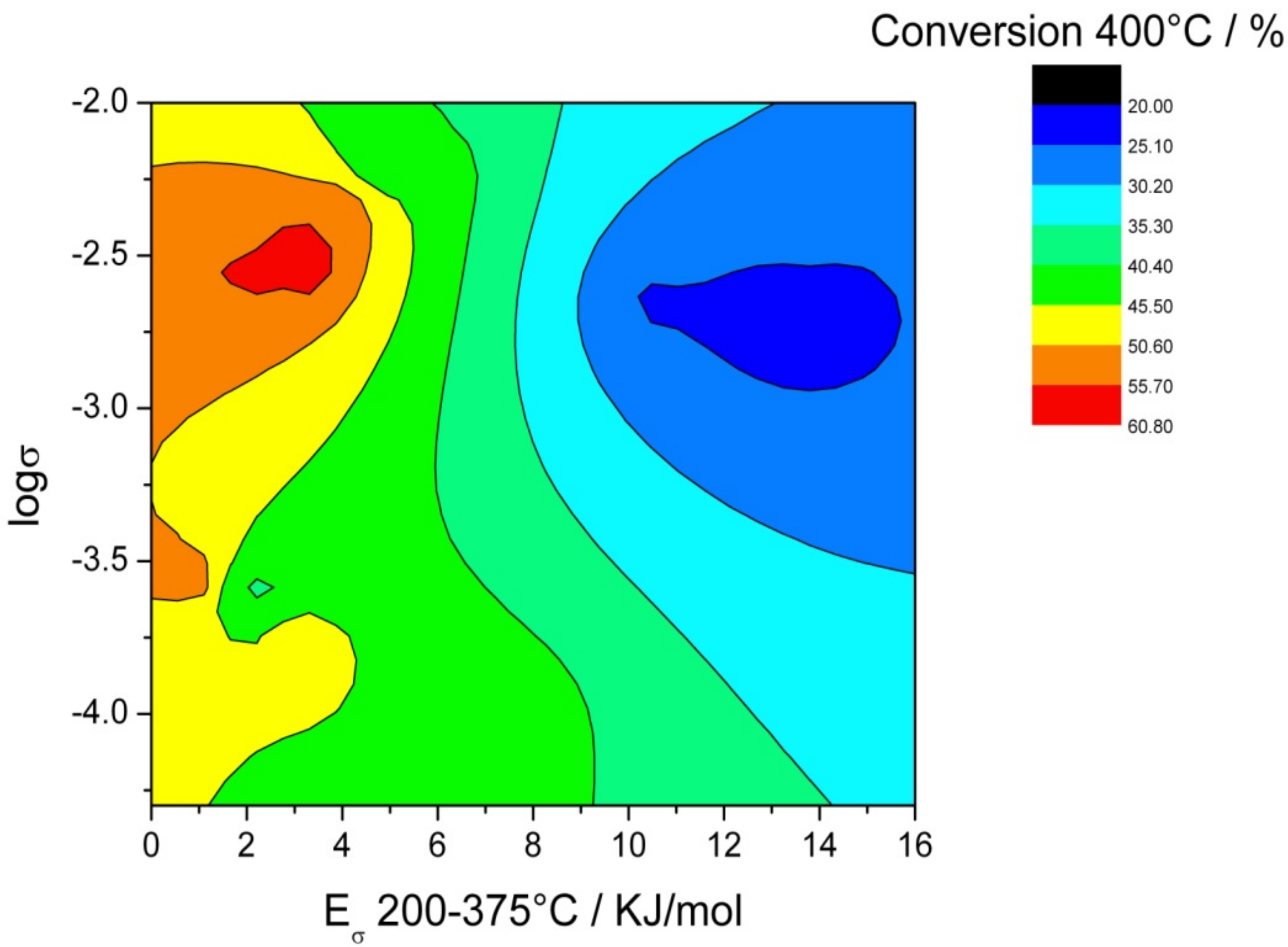


VPP in MA synthesis: active species across pressure gap



OCM; a core activity of unicat
H. Schubert played a very active role

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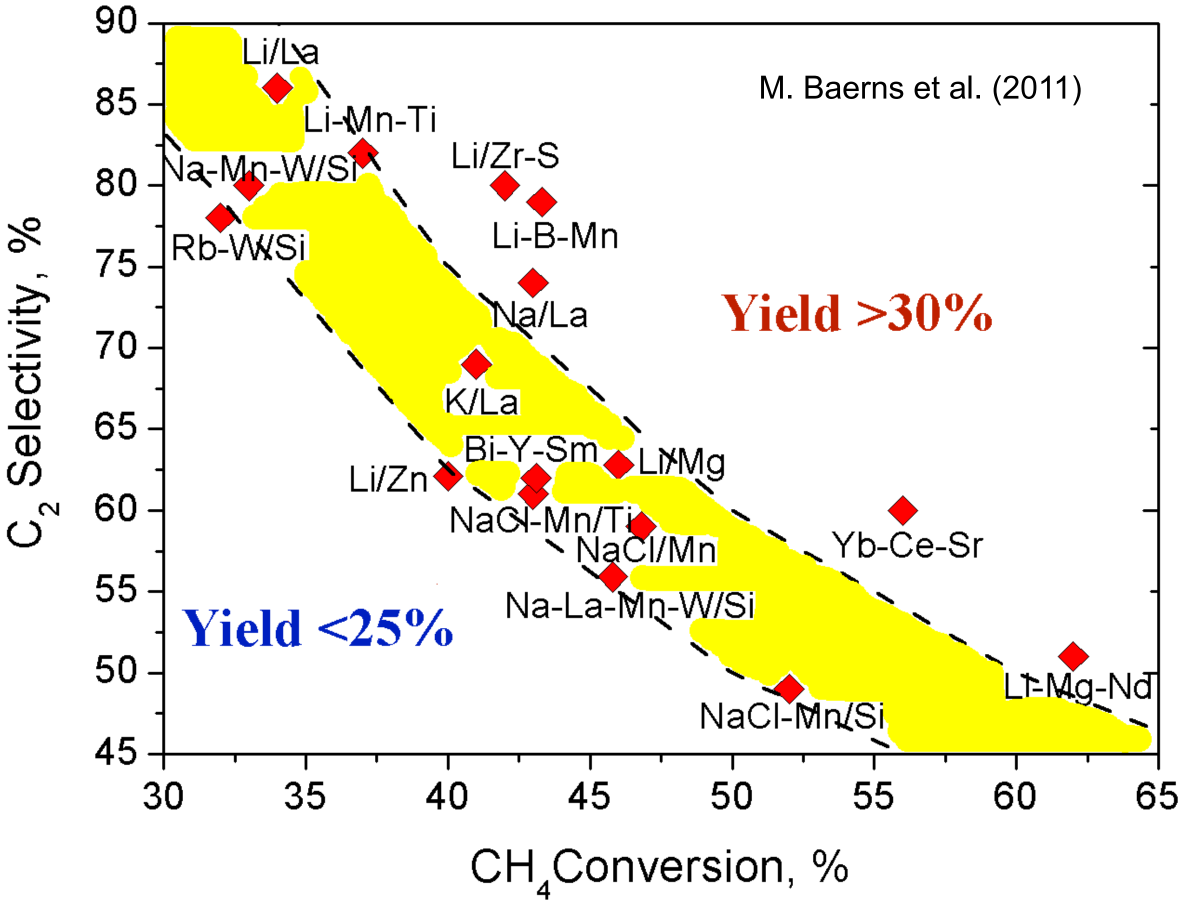

Li/Zn -*Chem. Lett., 1986.*
Li/La, Na/La, K/La - *Eur. Patent, 1986.*
NaCl/Mn - *J. Chem. Soc., 1987.*
Yb-Ce-Sr - *J. Chem. Soc., 1987.*
NaCl-Mn/Ti - *Prepr. Pacifichem, 1989.*
Li/Mg - *Appl. Catal.,1990.*
Li-Mg-Nd – *Chinese J. Catal.,1990.*
Li-Mn-Ti - *Chinese J. Catal.,1990.*
Li-B-Mn - *Appl. Catal. 1991.*
NaCl-Mn/Si - *Austr. Patent.,1990.*
Li/Zr-S – *Chem. Com., 1997.*
Na-Mn-W/Si – *J. Catal.,1998.*
Rb-W/Si - *Catal. Lett., 2000.*
Bi-Y-Sm – *Appl. Catal. 2001.*
Na-La-Mn-W/Si – *Appl. Catal. 2007.*

Reaction conditions: fixed-bed reactor, atmospheric pressure

T: 970 – 1220 K
$P(CH_4)/p(O_2)$: 2 - 5
Contact time: 0.2 – 8.0 s

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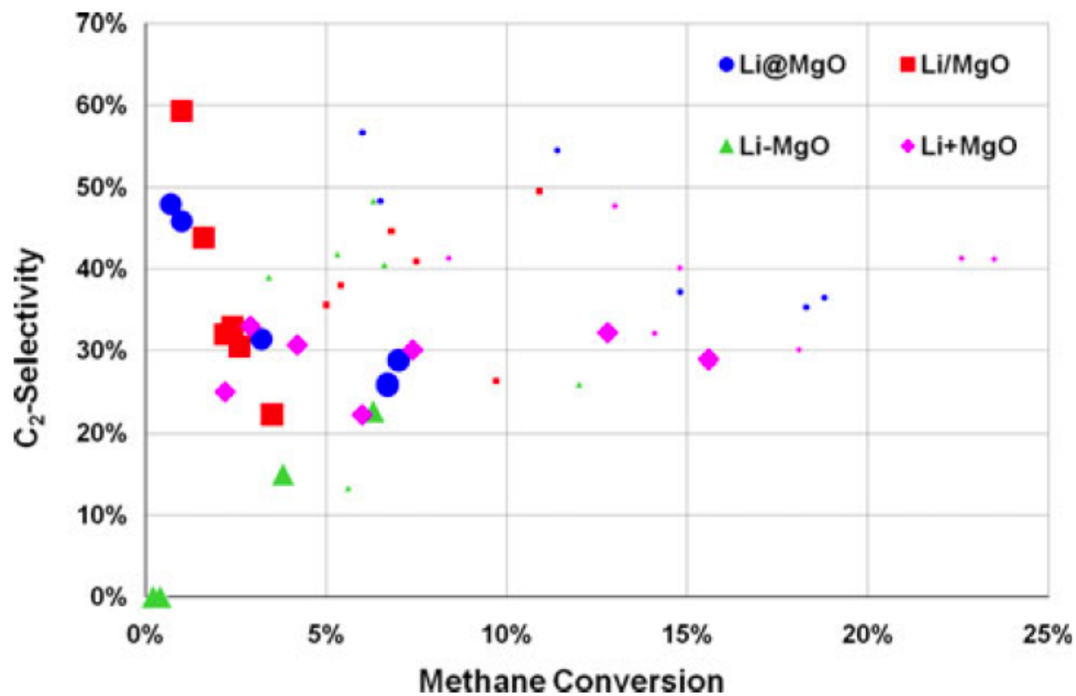
Is Li/MgO a stable OCM catalyst? Lunsford mechanism: Li^+O^- as active site

No.	Preparation	Abbreviation
1	Single source precursors	Li@MgO
2	Wet impregnation	Li/MgO
3	Precipitation	Li–MgO
4	Mixed milling	Li+MgO

Different systems with same Li content but different intimacy of contact Li-MgO

At steady state strong deactivation and poor performance: least-mixed sample best catalyst: Li^+O^-?



S. Arndt et al. (2011)

What is active in Li/ MgO?
Only MgO !

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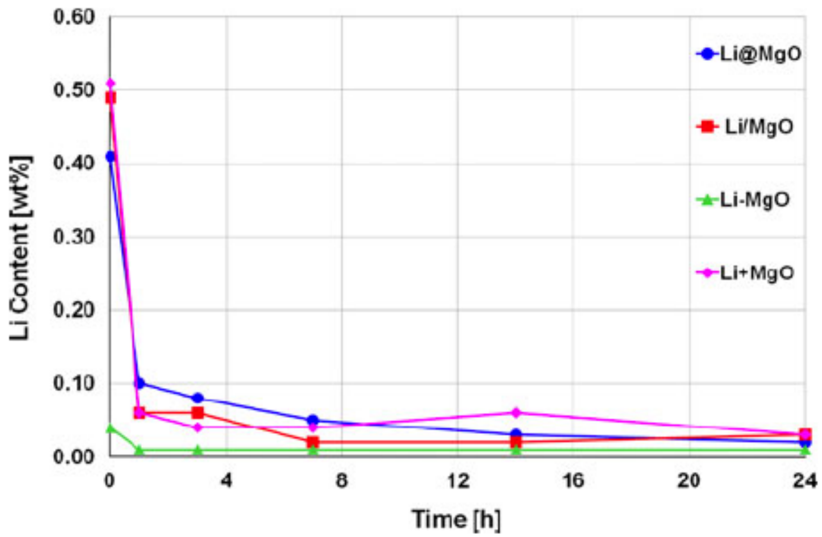
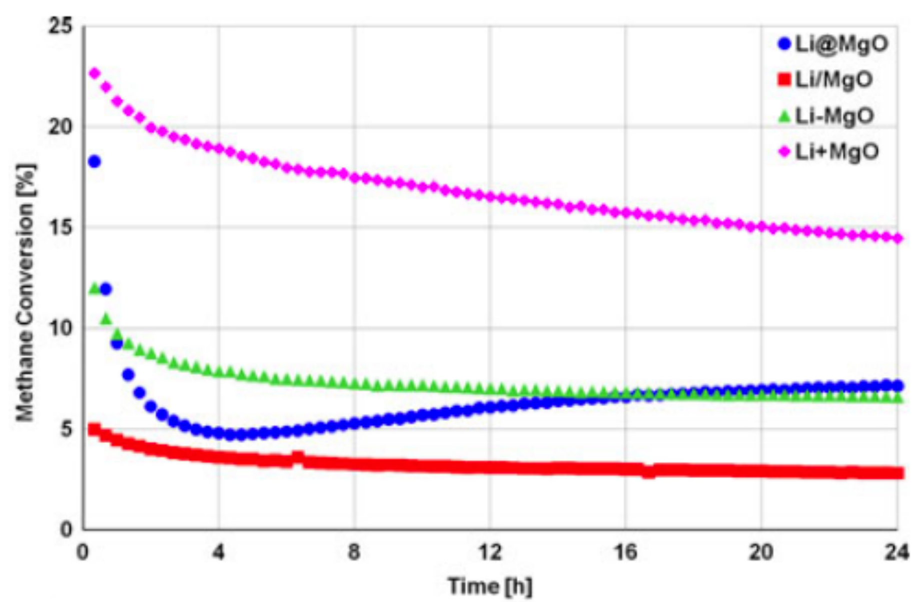


All samples exhibit dramatic loss in Li content: cannot be part of active site

S. Arndt et al. (2011)



No relation of Li content and activity:
Also not related to trace metal impurities:
MgO is a structure-sensitive catalyst for OCM.

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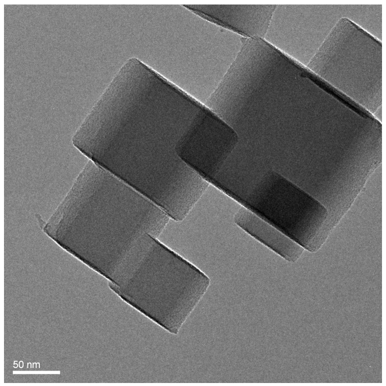
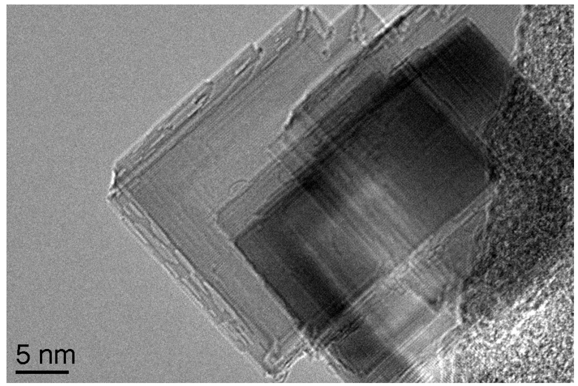
Morphological library of MgO

S-MgO



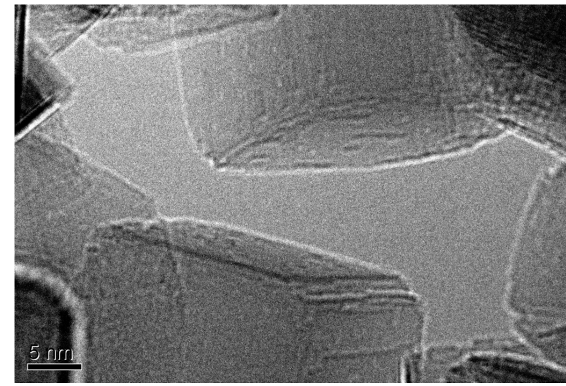
Mg oxidation

C-MgO



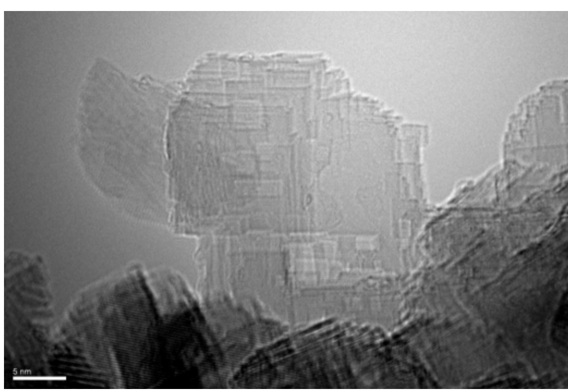
Ultra pure commercial MgO

SG-MgO

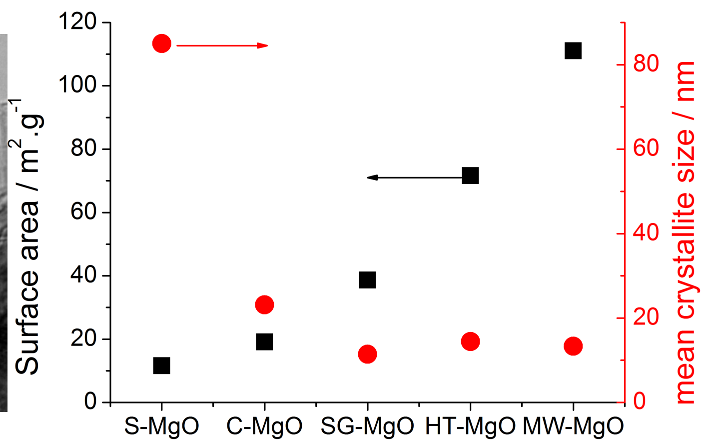


Sol-gel synthesis

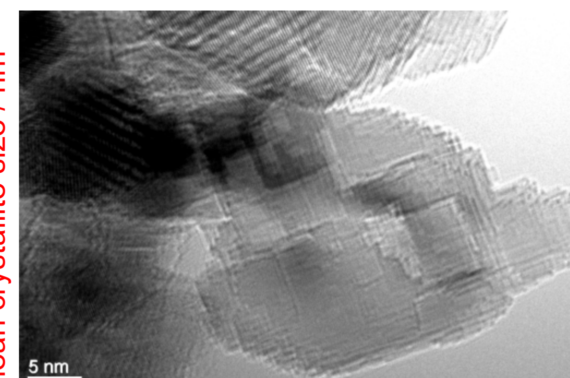
HT-MgO



Hydrothermal post treatment



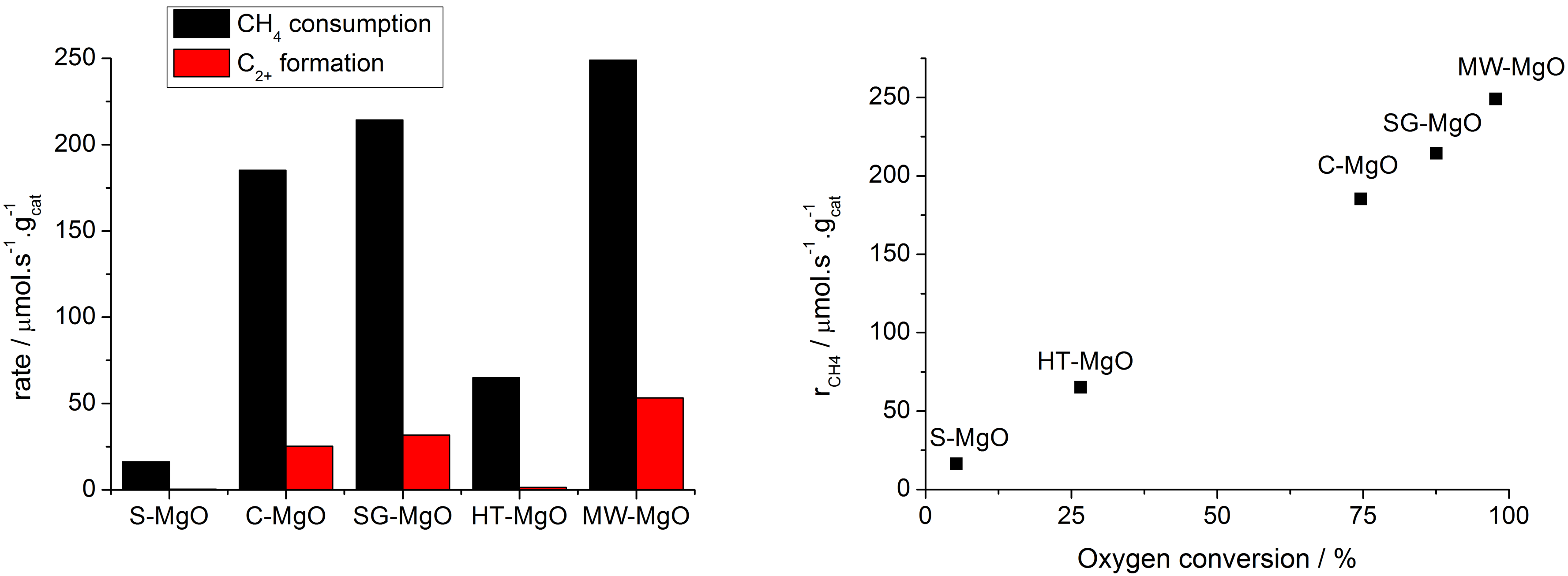
MW-MgO



Hydrothermal post treatment in microwave autoclave

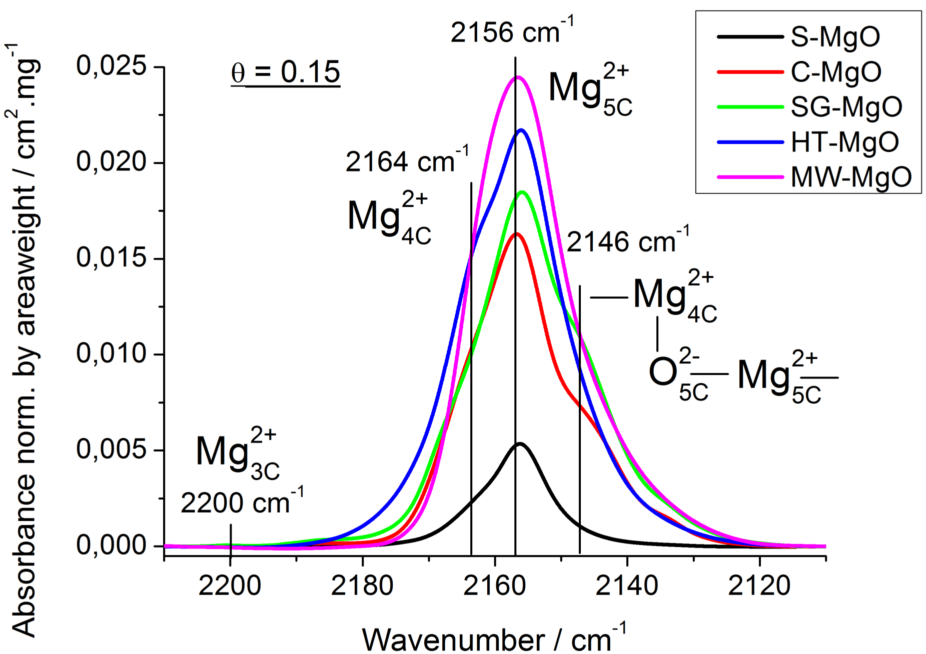
A non-standard mode of redox catalysis for a non-reducible oxide

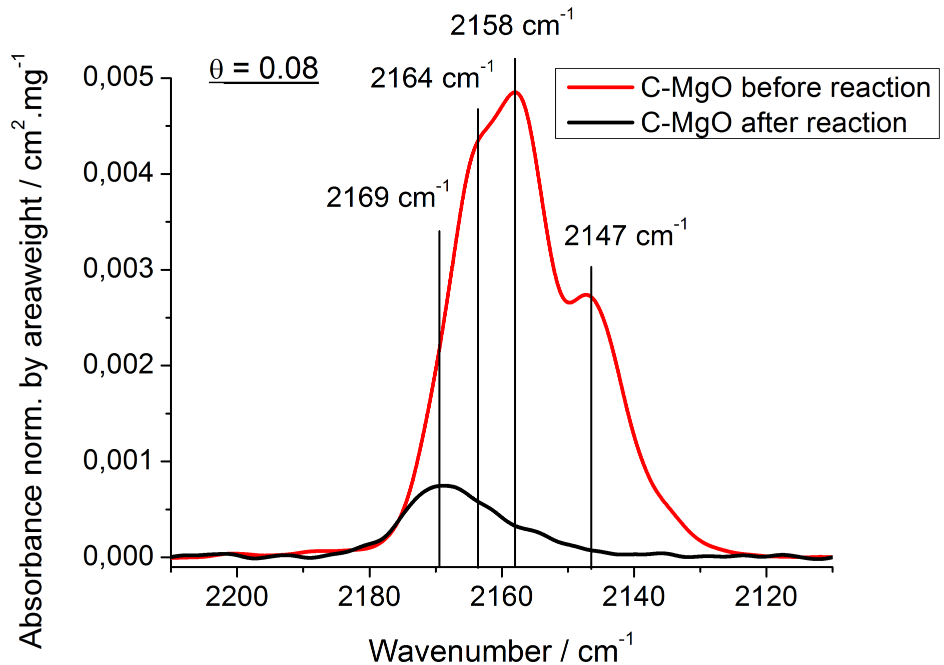
Experimental condition: T = 1023 K, W/F = 0.033 g.s.ml^{-1}, $CH_4/O_2/N_2$ = 3/1/1



Activity for methane conversion scales with ability to activate oxygen:
Is activated methane activating oxygen? (catalyst as „marriage broker“)

CO adsorption as probe for active sites

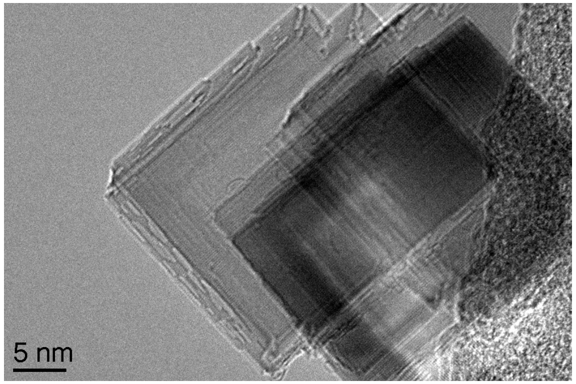




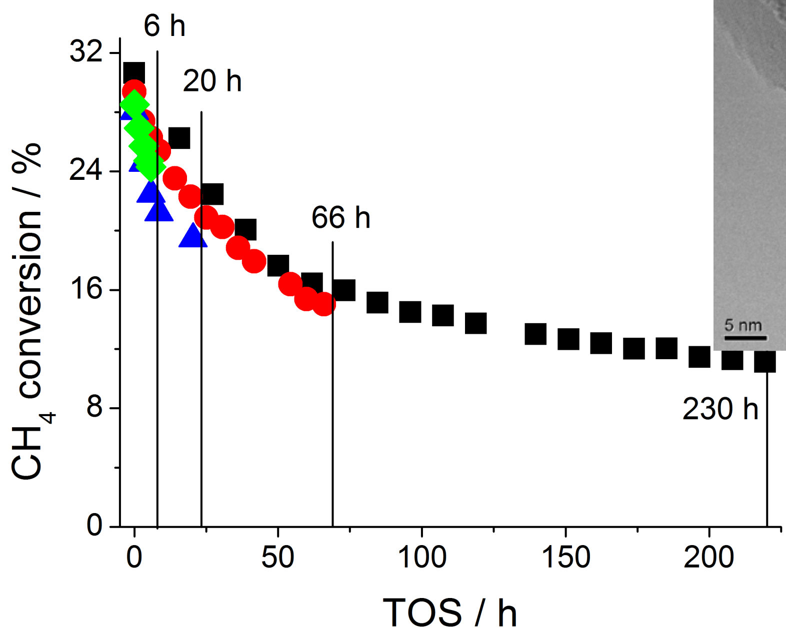
Methane activation scales with abundance of monoatomic steps:
Deacvtivation related to morphological modification.

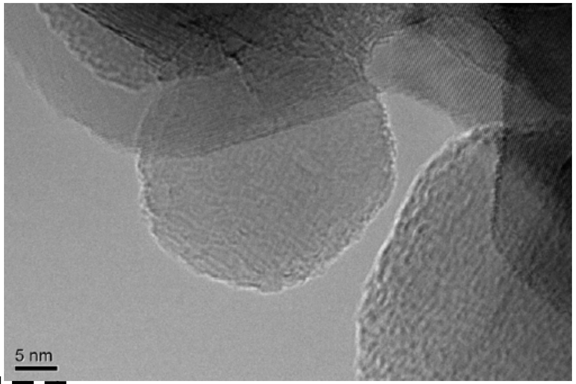
Spoto et al., *Prog. Surf. Sci.*, **2004**, 76, 71-146

Deactivation of C-MgO



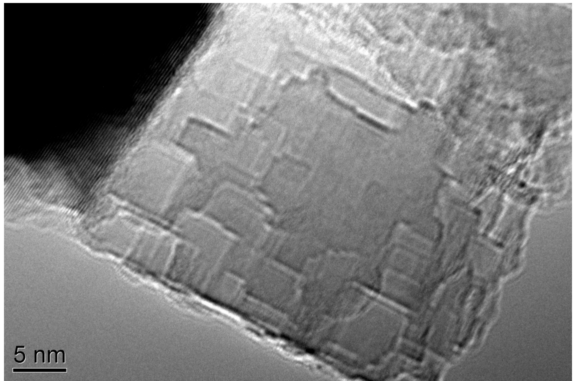
t = 0 h



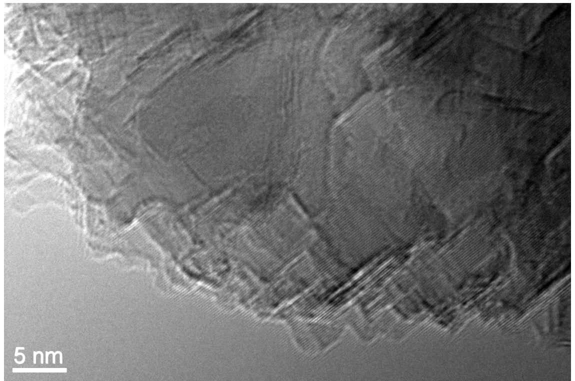


t = 230 h

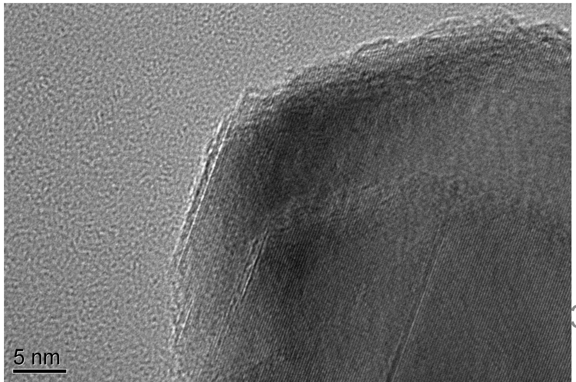
t = 6 h



t = 25 h



t = 66 h



Reactivity of MgO

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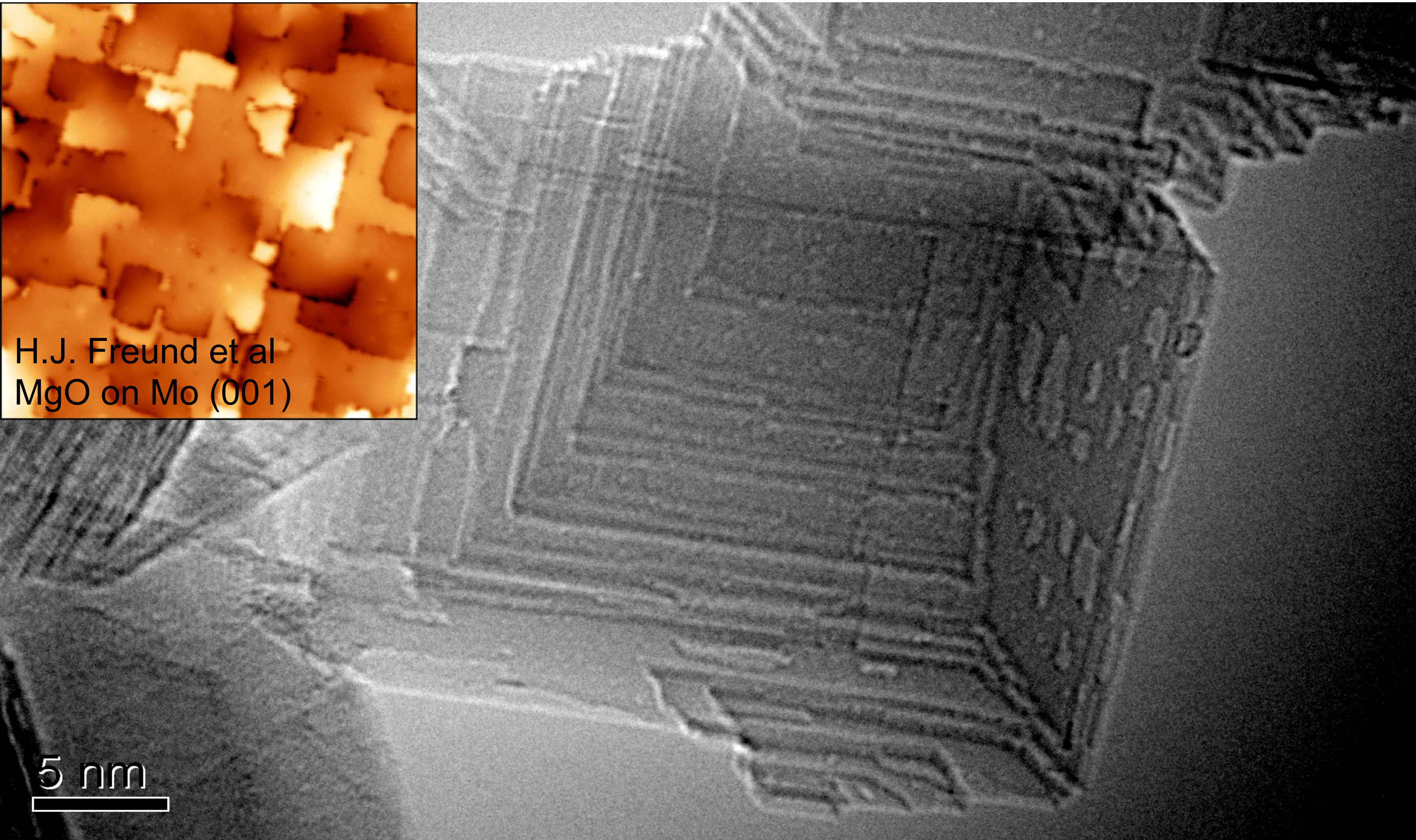

Quenched identification of oxygen anion radicals

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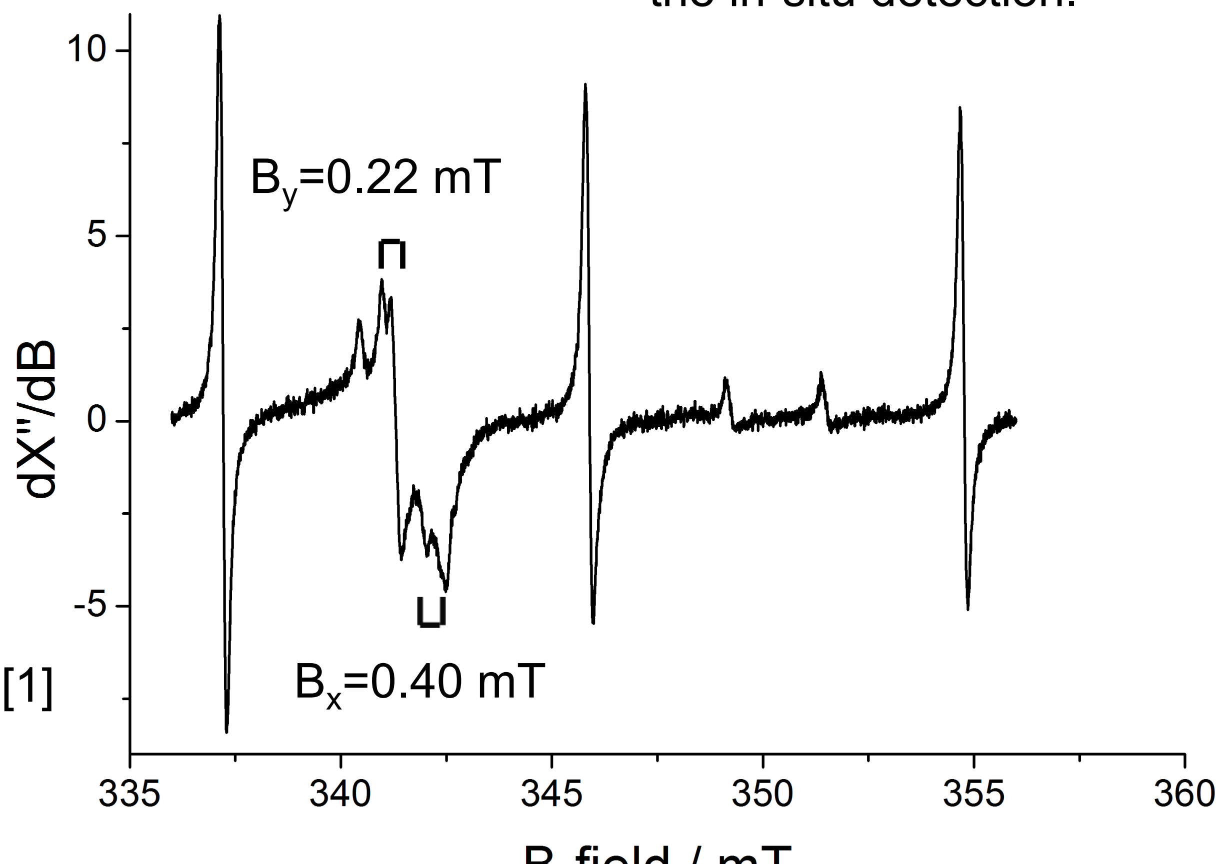
R. Horn et al prepare for the in-situ detection.

Heat treatment at 800 °C in dynamic vacuum
Addition of 100 mbar C + 10 mbar O_2 at RT
Evacuation, EPR measured at 77 K



hyperfine coupling constant [1]
B_z = 0.10 mT
B_y = 0.21 mT
B_x = 0.37 mT

[1] Giamello et al., *J. Chem. Soc. Faraday Trans. 1*, **1989**, 85, 3987

3+1 = 2+2
Catalyst design?

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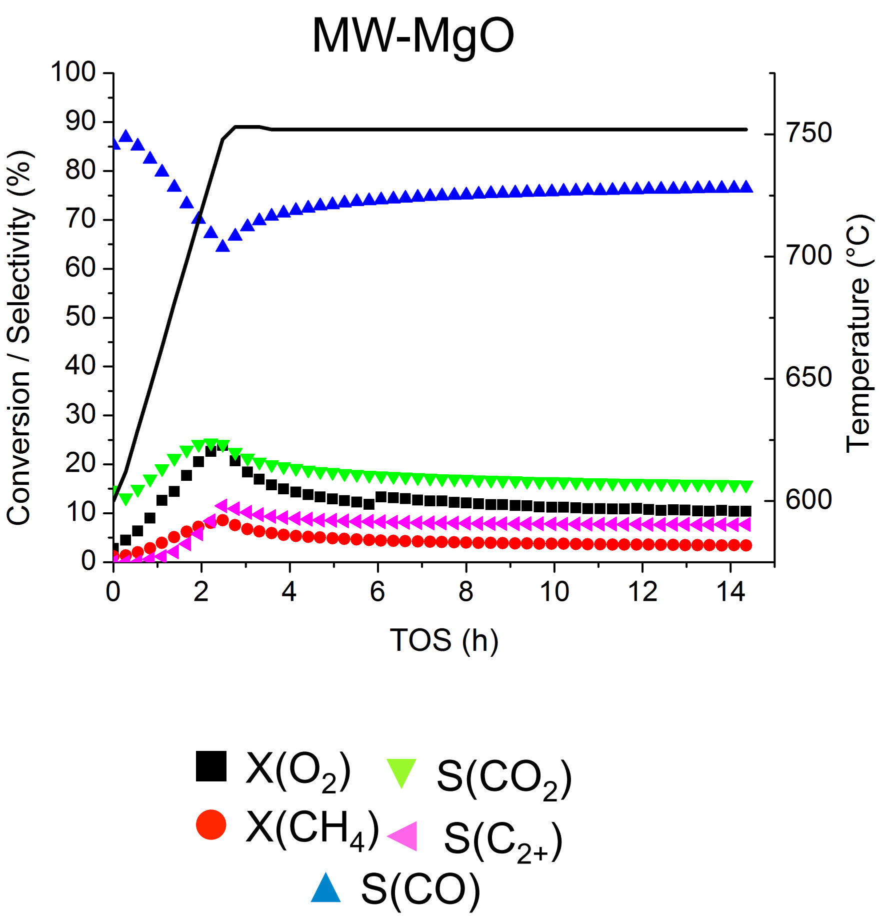
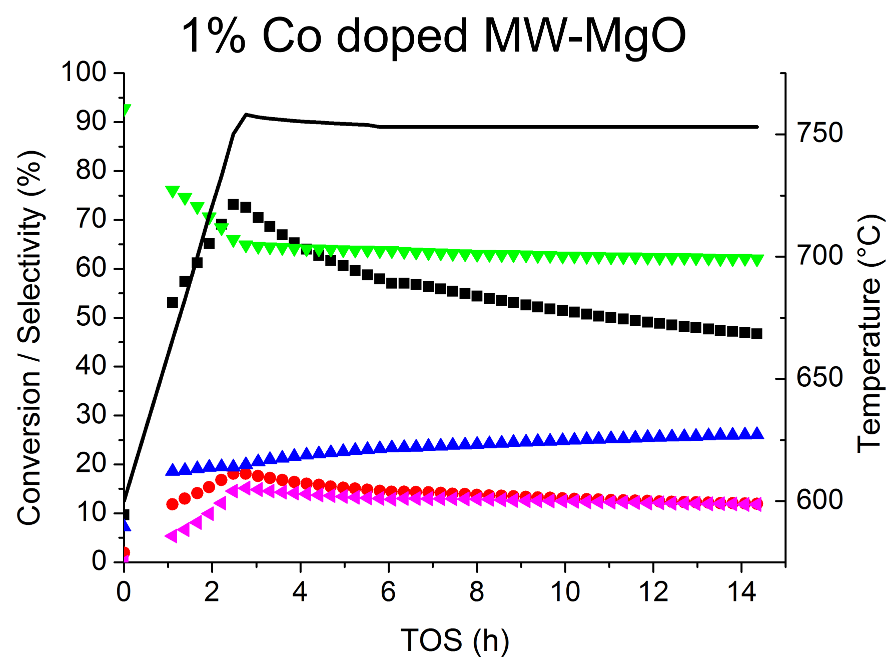
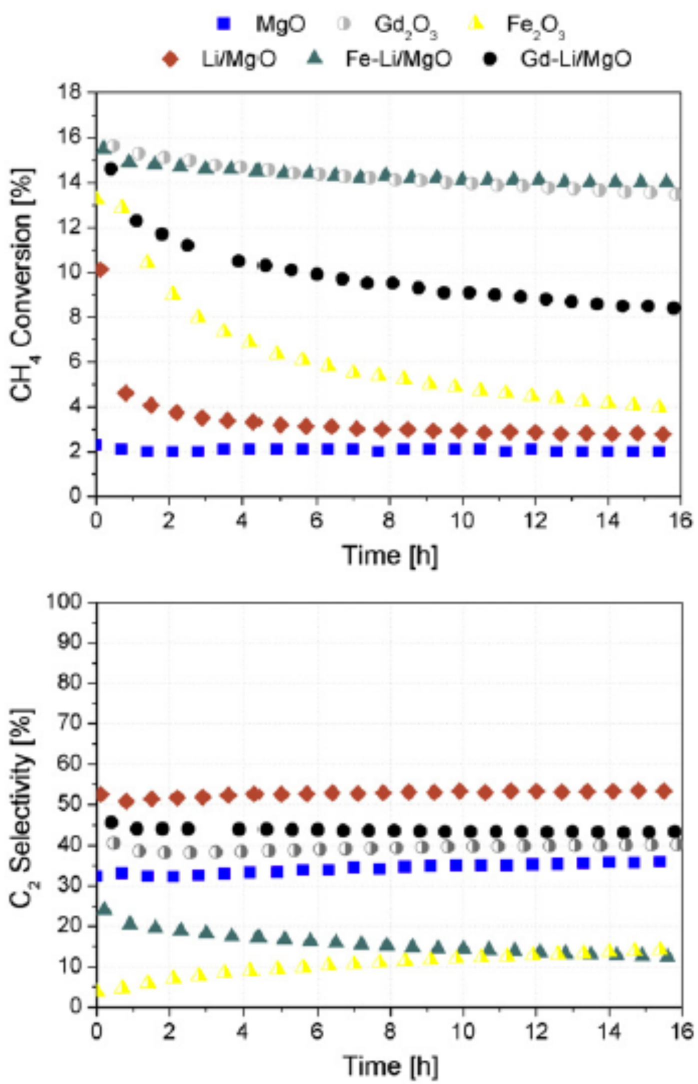




Two concepts.
Hold Li in Mg sites
Add dilute redox ability

3+1 = 2+2
Catalyst design?



U. Simon, K.P Dinse et al(2012)

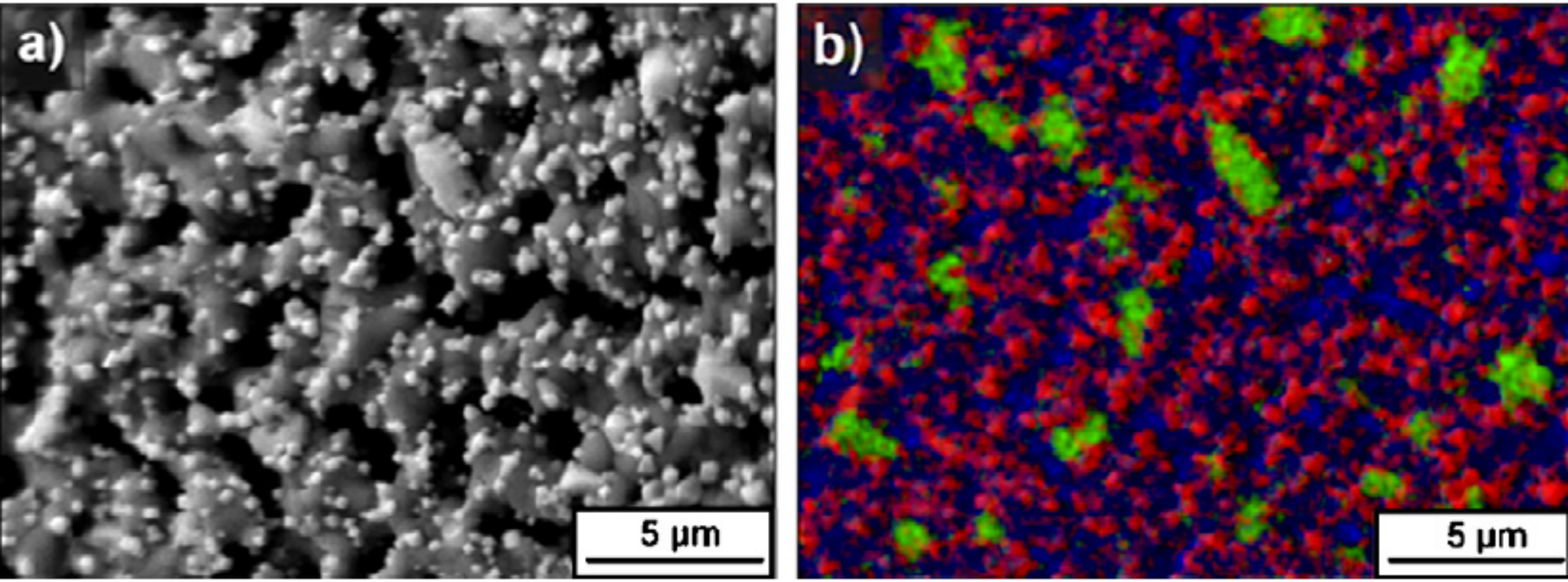
A complex glass chemistry

U. Simon et al. Chem. Eng. J. (2011)

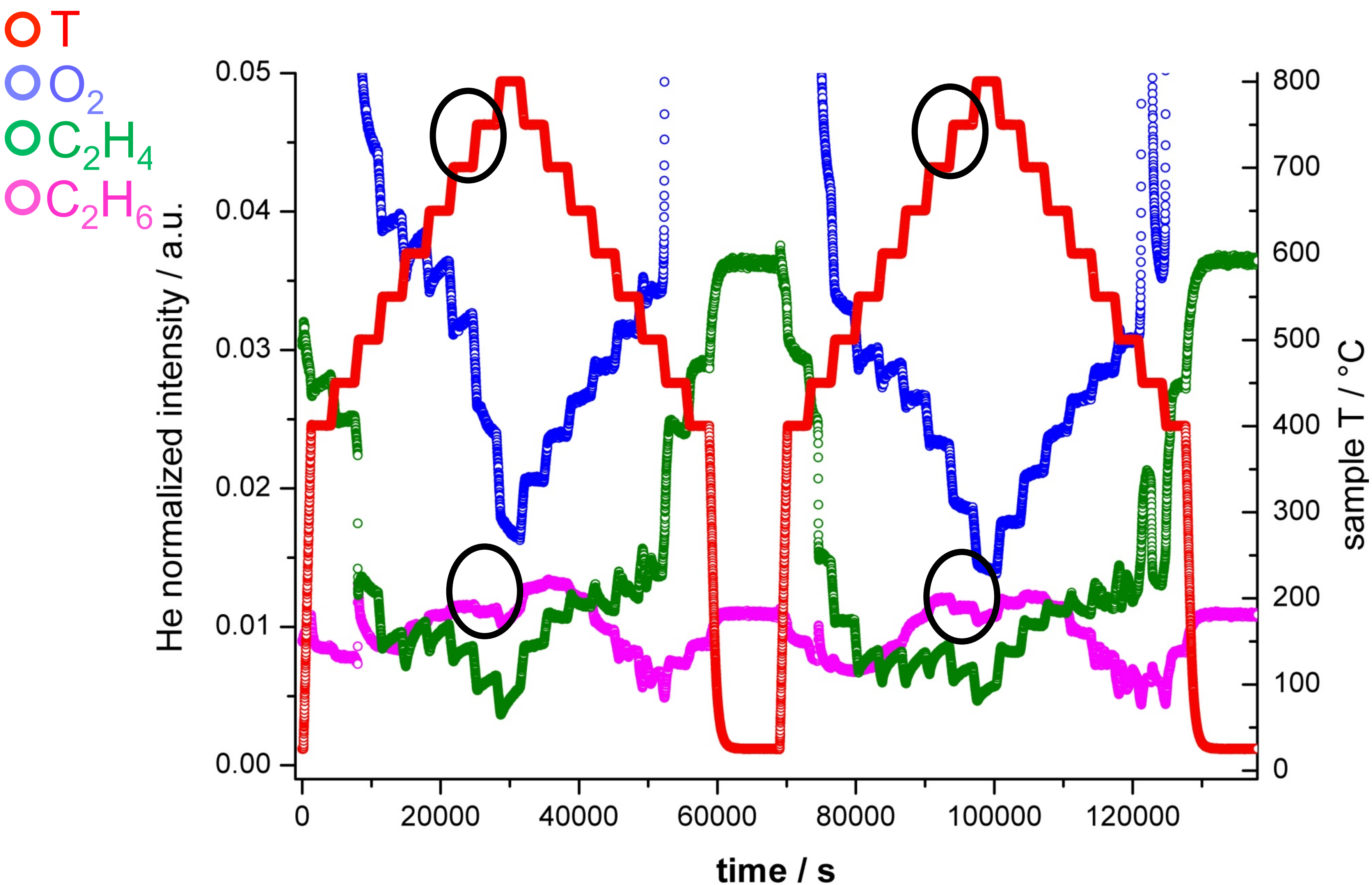
$$Mn(NO_3)_2 \times H_2O + Na_2WO_4 \times H_2O + SiO_2(\text{amorphous}) \xrightarrow{\text{air}} Mn_2O_3 + Na_2WO_4 + \alpha\text{-cristobalite} + xH_2O + xNO_x \quad (1)$$

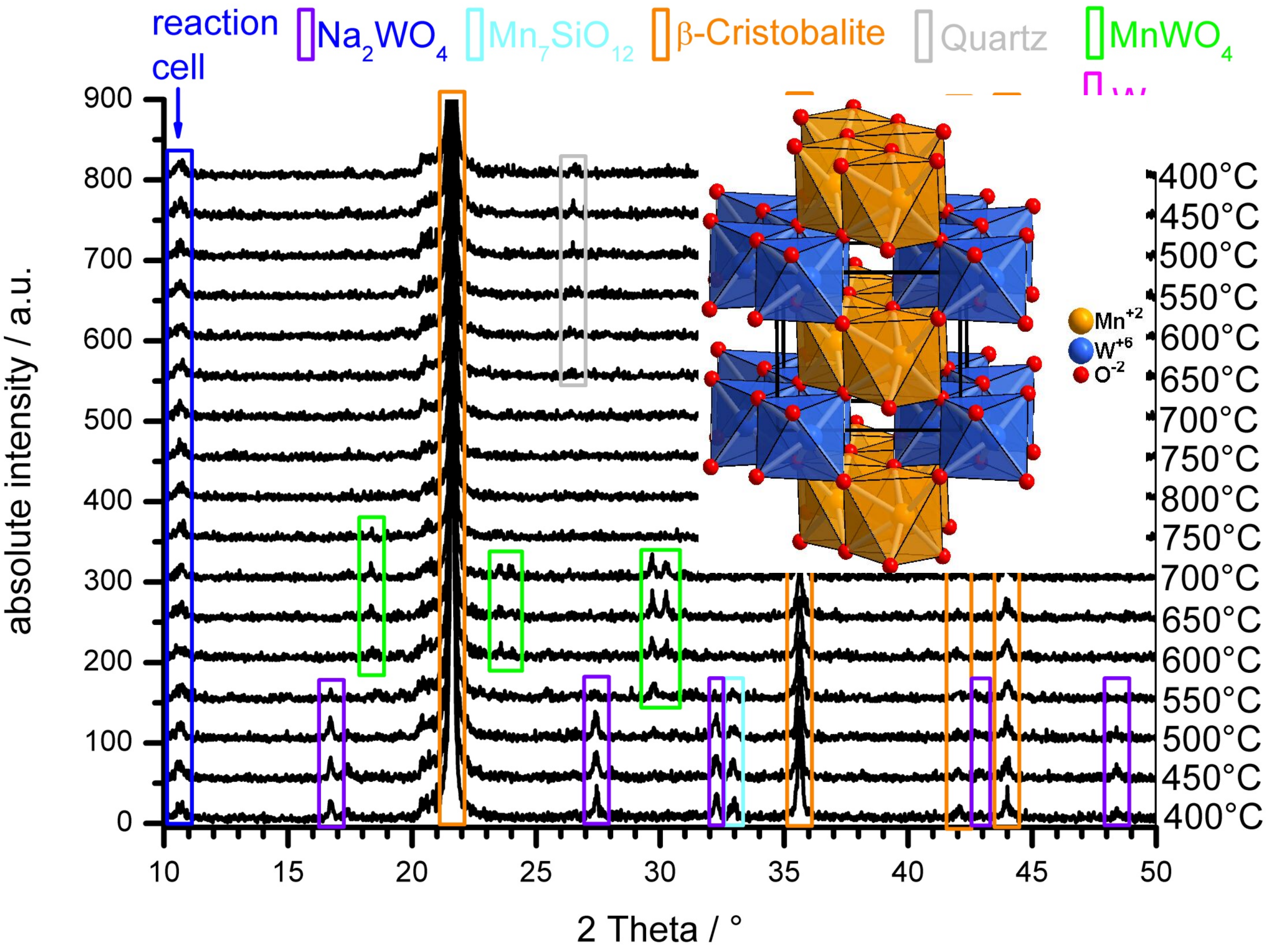
$$\overset{+III}{Mn_2}O_3 + Na_2\overset{+VI}{W}O_4 + \alpha\text{-cristobalite} \xrightarrow{\overset{0}{H_2}} \text{melt} \xrightarrow{\overset{0}{H_2}} \overset{+II}{Mn}\overset{+VI}{W}O_4 + Na_2\overset{+VI}{W}O_4 + \alpha\text{-cristobalite} + x\overset{+I}{H_2}O \quad (2)$$

A complex glass chemistry



In-situ structure: XRD and gas analysis





reaction cell
Na2WO4
Mn7SiO12
β-Cristobalite
Quartz
MnWO4
Mn+2
W+6
O-2
absolute intensity / a.u.
2 Theta / °
400°C
450°C
500°C
550°C
600°C
650°C
700°C
750°C
800°C
750°C
700°C
650°C
600°C
550°C
500°C
450°C
400°C

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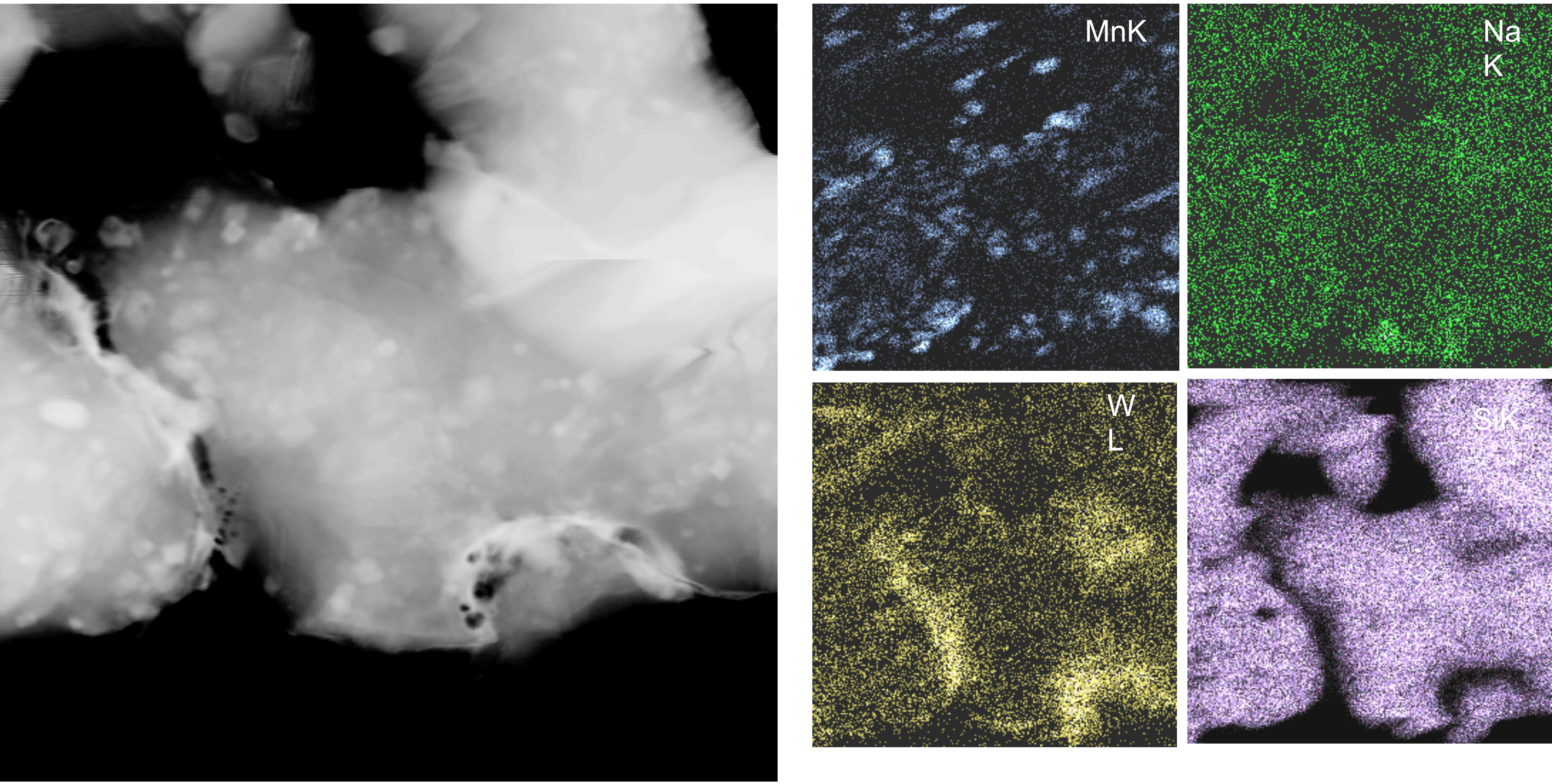
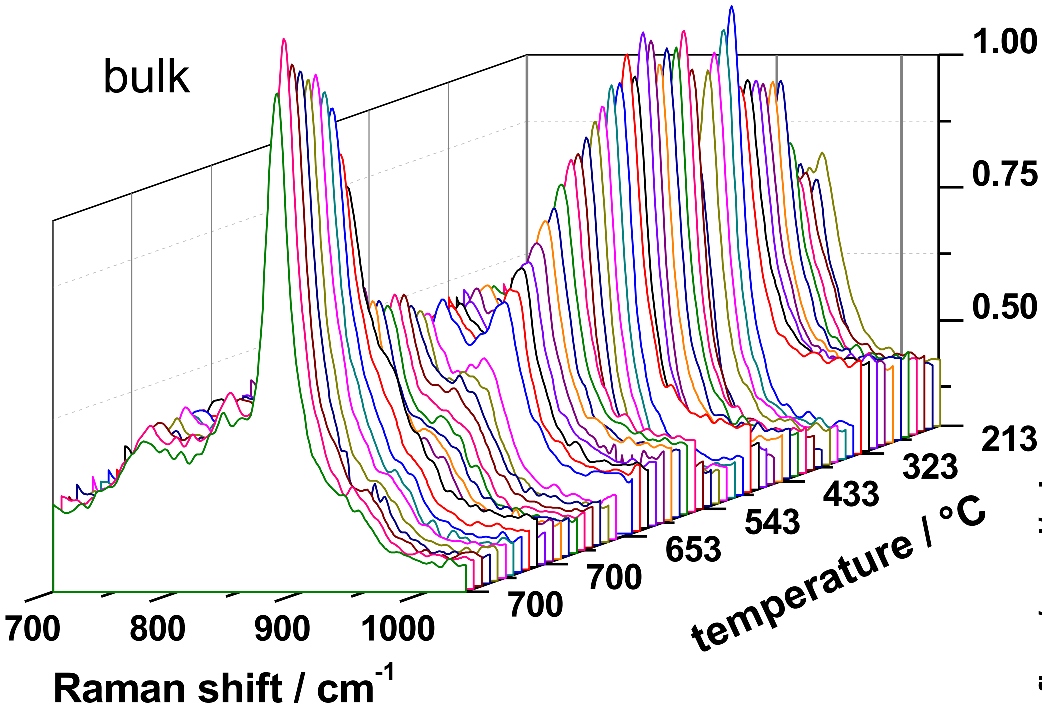
Chemical heterogeneity: active phase?

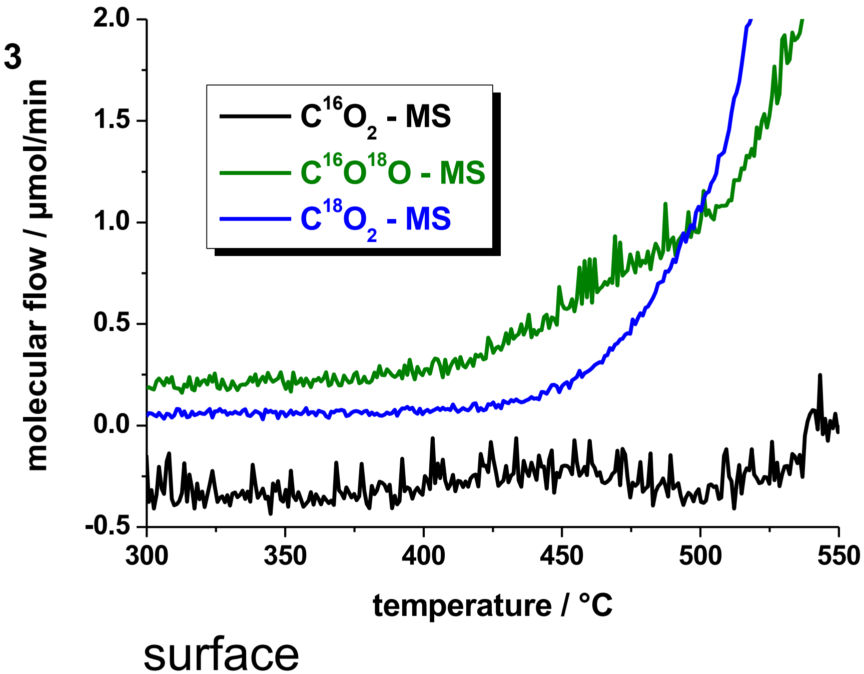


HAADF-STEM after catalysis

Oxygen isotope marking for active species: Is bulk lattice oxygen relevant?

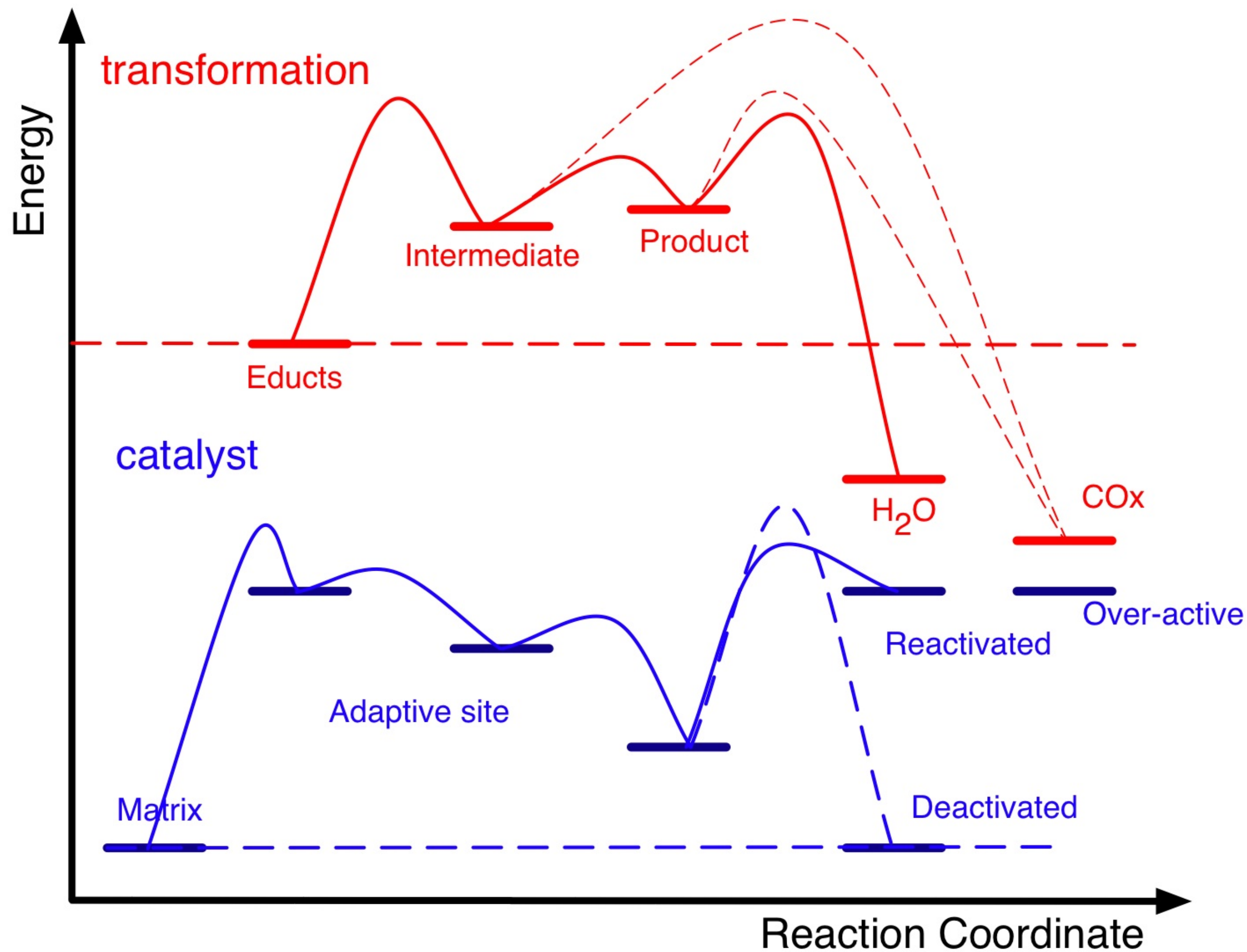


The $W^{16}O_4$ signal is continuously decreasing from about 450 °C on which corresponds well with the onset of the reaction.

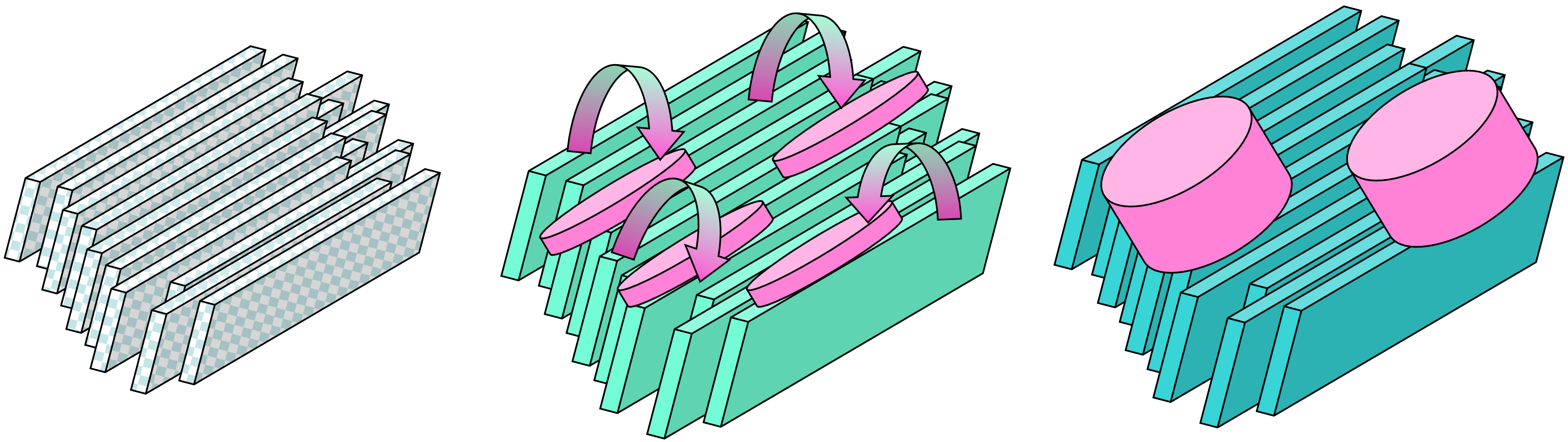


The ^{18}O signal is increasing at about 650 °C and strongly at 700 °C due to excess oxidant following catalyst deactivation.

Selective oxidation: Coupling of transformation and material



Selective oxidation: Coupling of transformation and material



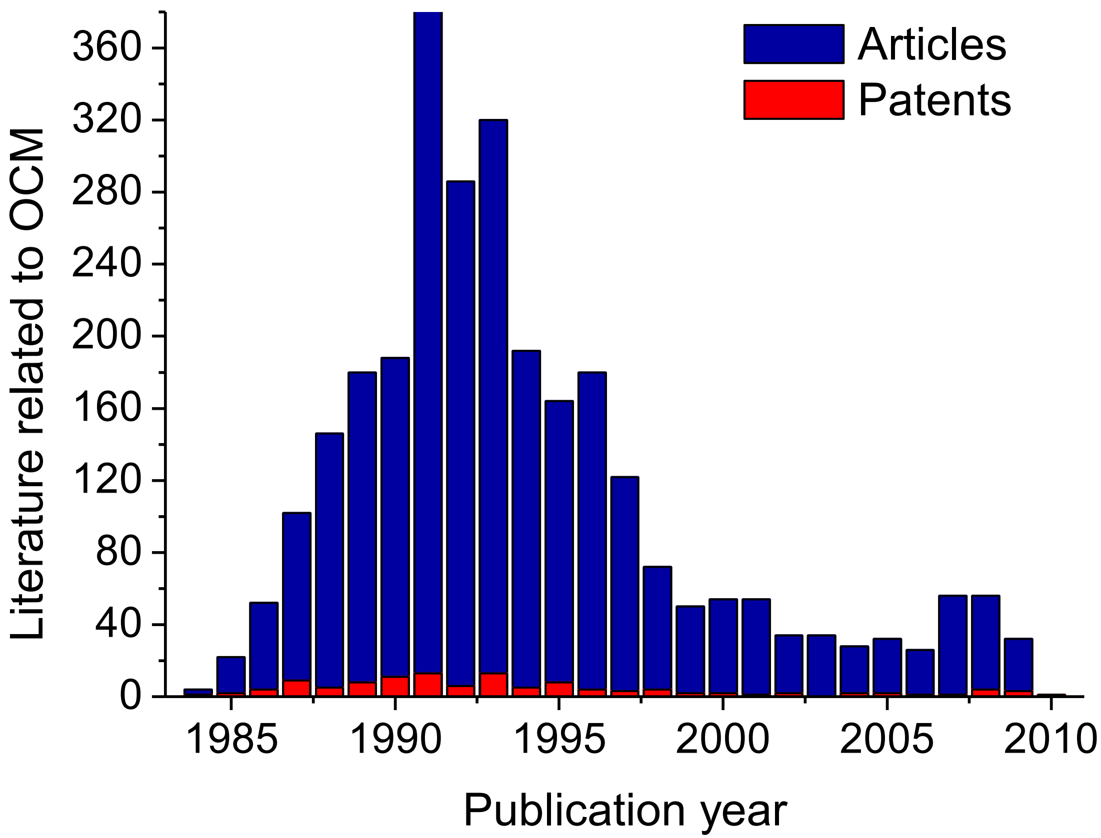
Take home

- Bulk properties of catalytic oxides control surface reactivity under high performance catalysis conditions.
- Non-reducible MgO restructures from highly active (100) step terminations exposing heterolytic reaction sites for methane plus oxygen co-reaction into less active high-indexed sites exposing less active sites for homolytic reaction (“Grignard” intermediate).
- Reducible oxides terminate in a reactive double layer of oxide and adsorbate maintained stable by mechanisms of semiconductor charge exchange. The resulting dynamics creates adaptive sites for selective catalytic transformation.

Dem Anwenden muss das Erkennen vorausgehen

Max Planck

Thank You



C_2 Selectivity		C_2 Yield	
ANO VA	Regr. tree	ANO VA	Regr. tree
Li	Li	Li	Li
Na	Na	Ba	Ba
Sr	Sr	Na	Na
Ba	W	La	Mn
Ca	Ba	Sr	Sr
Pb	Ca	Sm	W
Mo	Pb	W	Ca
W	La	Mg	La
Mg	Nd	Ca	Nd
V	Mg	Nd	Mg

Totally 2588 references (2378 articles and 211 patents) closely related to Oxidative Coupling (Dimerization) of Methane.

Catalysis is a multi-scale phenomenon loose NP are not enough

Catalysis scales with the Avogadro number.

The conversion of few molecules is conceptually very interesting (chemical physics) but chemically insignificant.

Catalysis science is not “applied science” when it cares about all requirements for converting “large” amounts of molecules: 25 ml of converted liquid contain 10^{27} molecules.

Catalysis is a multi-scale phenomenon loose NP are not enough