Propane Oxidation over Nanostructured Molybdenum-Vanadium Mixed Oxides: In-situ Studies of the Geometric and Electronic Structure

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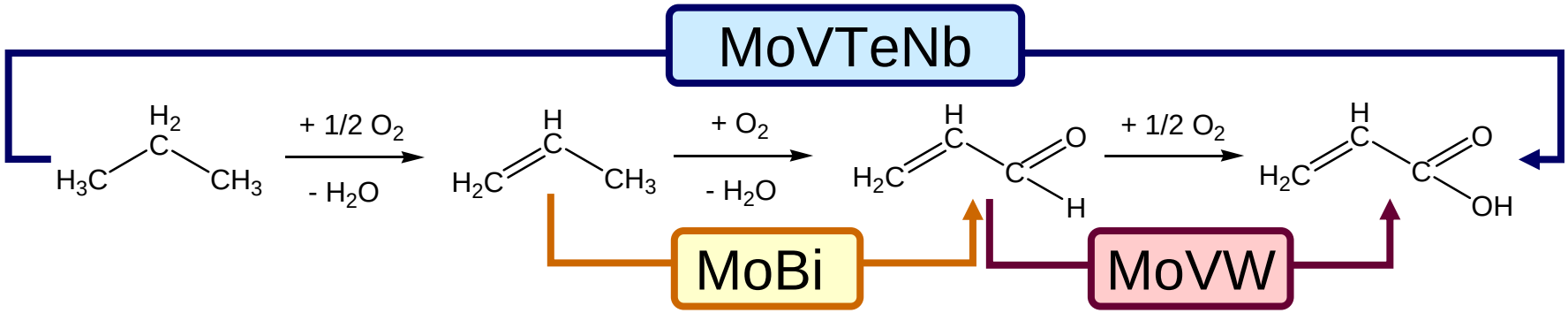
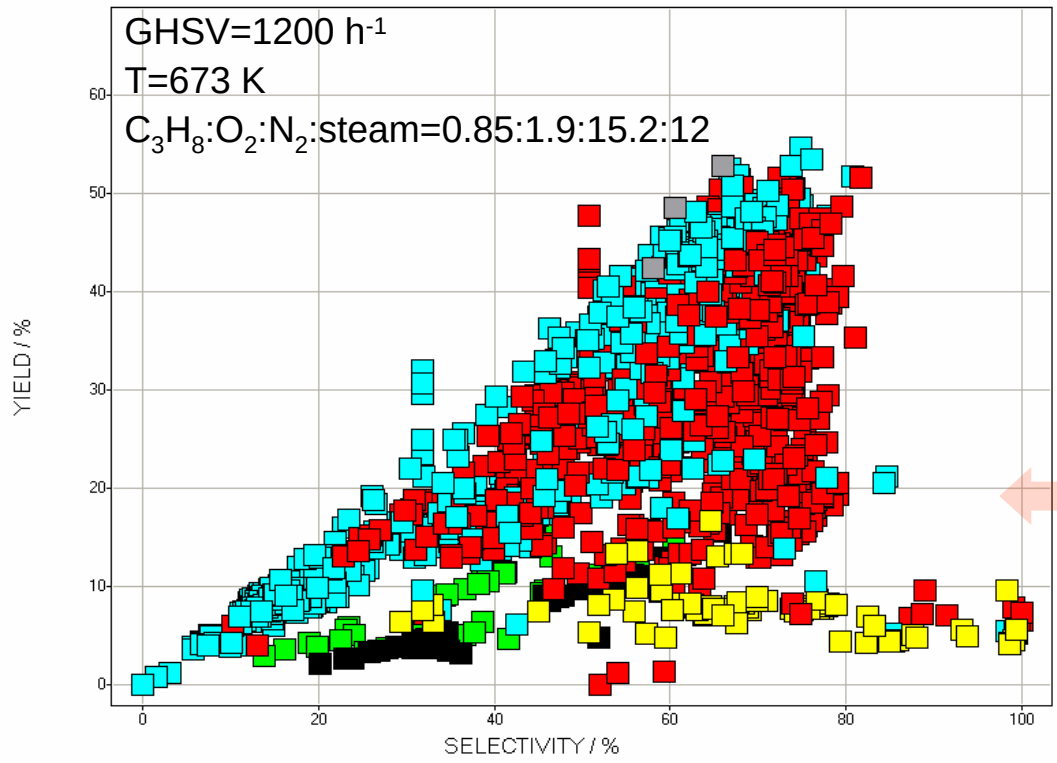
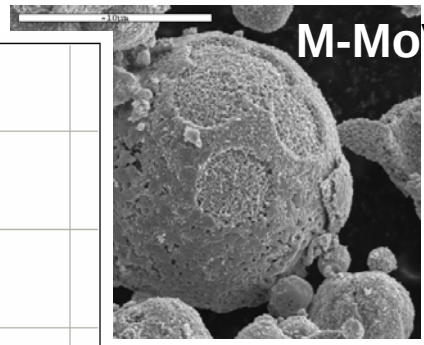
Selective oxidation of propane to acrylic acid





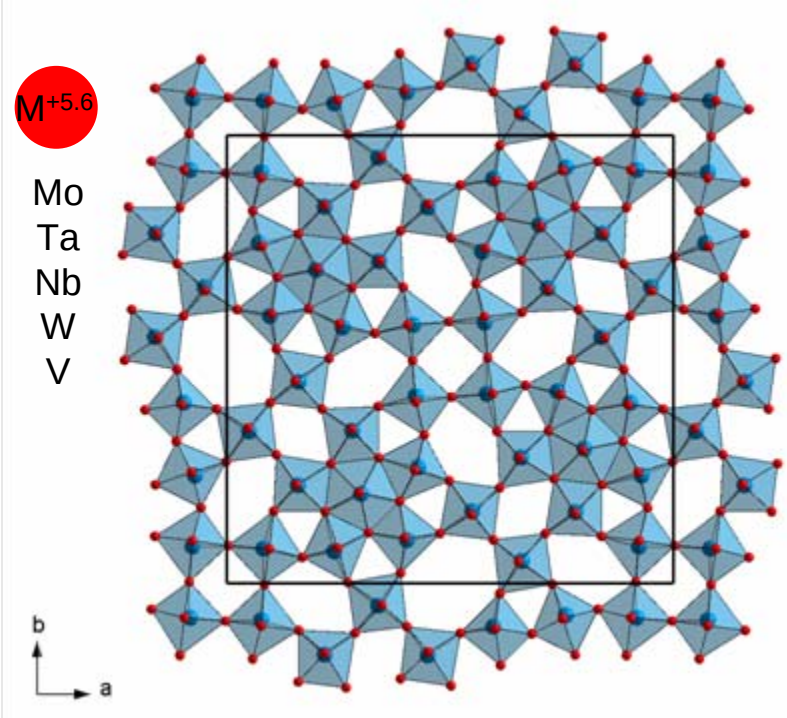


M-MoVTeNb oxide

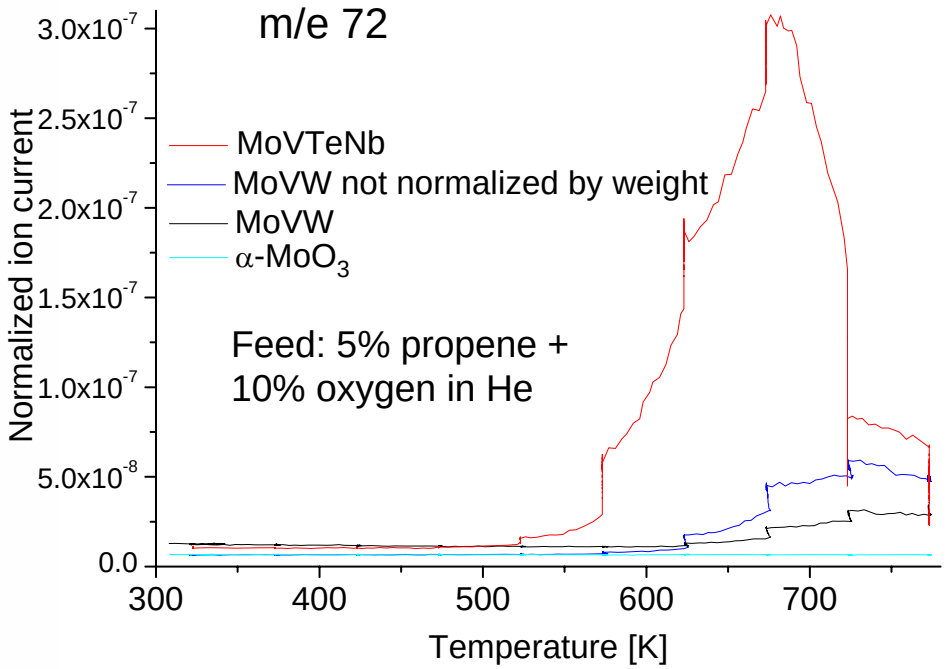
- Phase composition
- Crystallinity
- Surface area
- Chemical composition
- Chemical and electronic nature of the surface
- Presence of nano-structured or amorphous fractions

Model structure and catalytic property in an in-situ cell

Approach:
- Preparation of chemically less complex phase-pure materials consisting of a Mo_5O_{14}-type phase: MoVW and MoV oxides
- In-situ studies during activation and propylene oxidation



Mo_5O_{14} [ICSD 27202]
view along c



Formation of acrylic acid in an in-situ XRD cell monitored by mass spectrometry

Lars Kihlborg, Ark. Kemi, 21(40) 427, 1963; Space group: P 4/mbm

Preparation

Spray-drying of aqueous metal salt solutions

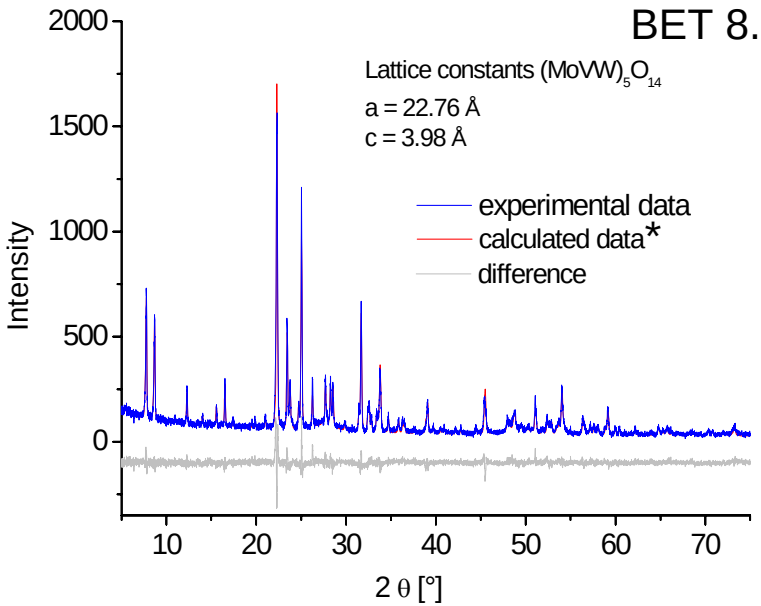
ammonium heptamolybdate
ammonium metatungstate
vanadyl oxalate

20%O_2 in N_2, 623 K, 2h

He, 713 K, 2h

$(Mo_{0.68}V_{0.23}W_{0.09})_5O_{14}$

BET 8.6 m^2/g



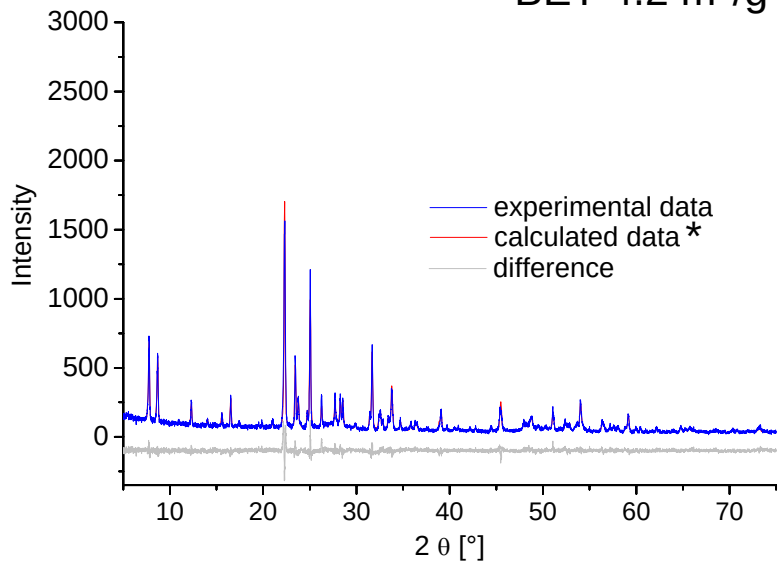
He, 773 K, 4h

purification

He, 773 K, 4h

$(Mo_{0.91}V_{0.09})_5O_{14}$

BET 4.2 m^2/g

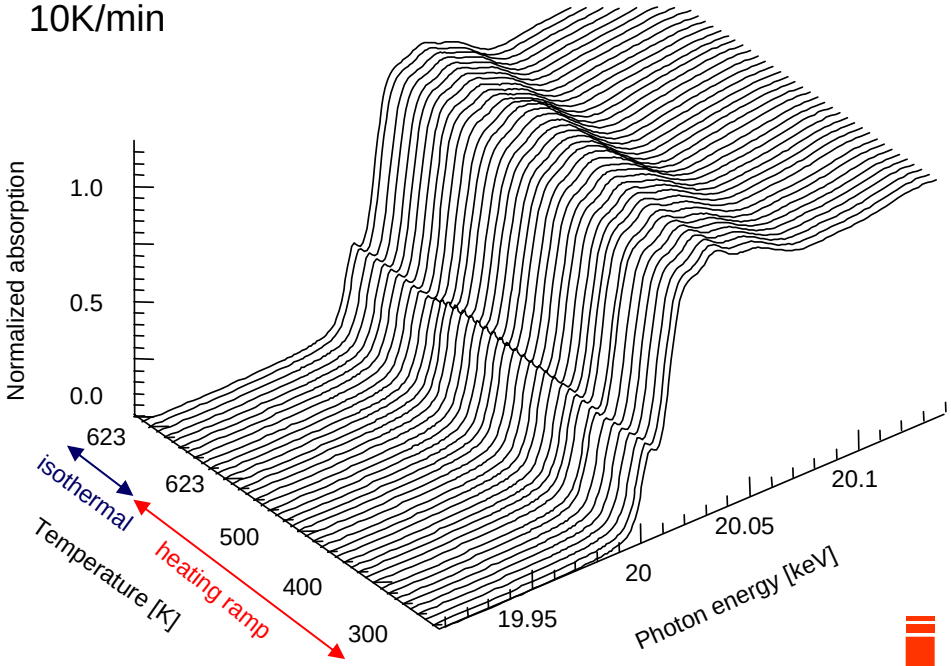


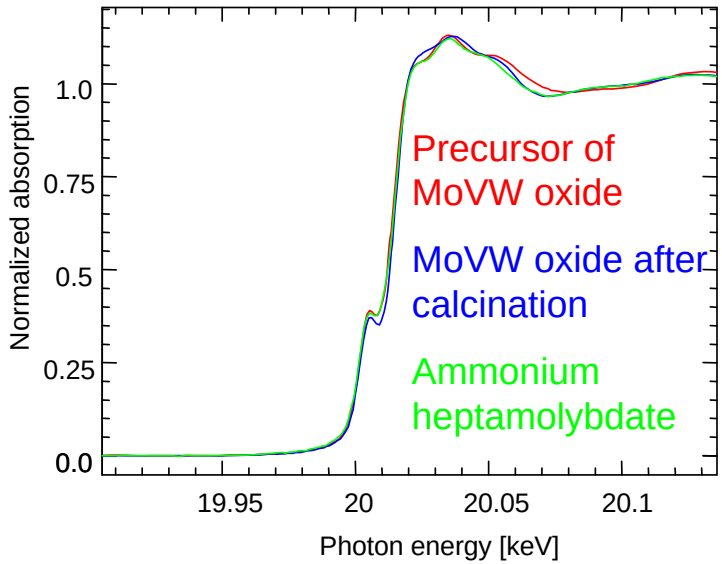
**Lars Kihlborg, Ark. Kemi, 21(40) 427, 1963; Space group: P 4/mbm*

Calcination at the Mo K edge: XANES

$(Mo_{0.68}V_{0.23}W_{0.09})_5O_{14}$

20% oxygen in He
10K/min



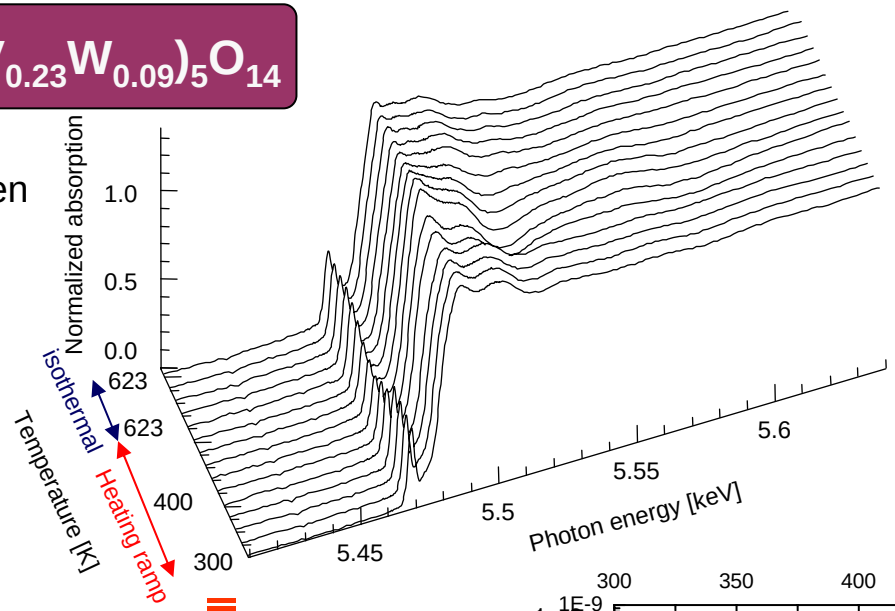


- XANES of the (MoVW)oxide precursor is similar to ammonium heptamolybdate
- XANES of the calcined material looks like crystalline $(MoVW)_5O_{14}$

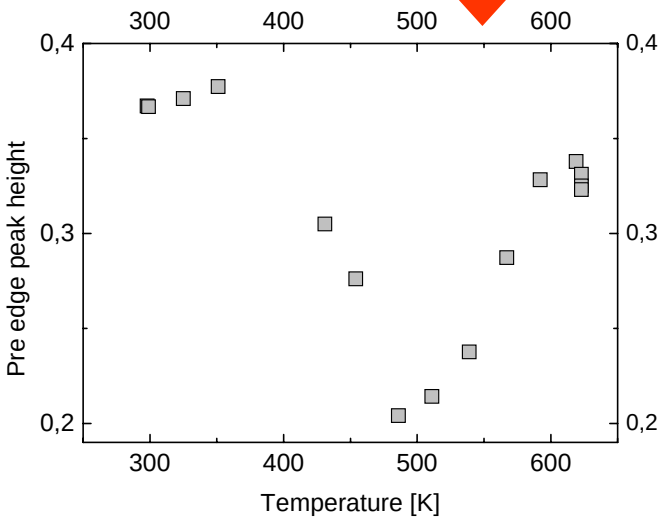
Calcination at the V K edge

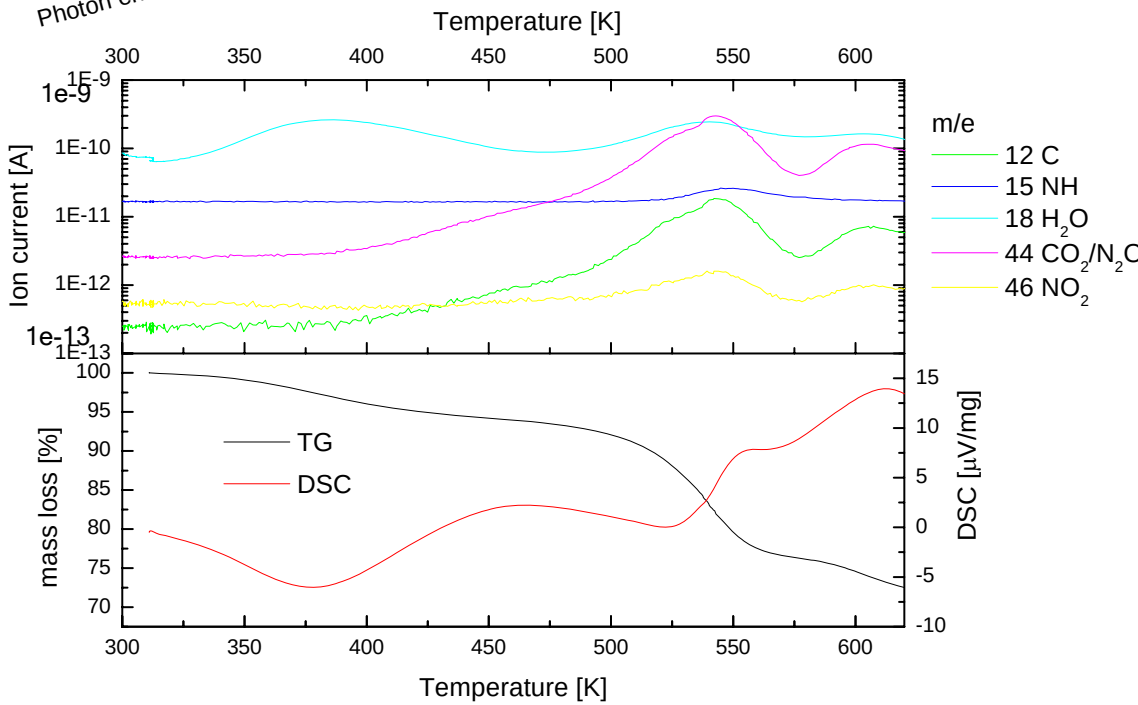
$(Mo_{0.68}V_{0.23}W_{0.09})_5O_{14}$

20% oxygen
in He
10K/min



- Pre-edge peak height goes through a minimum: significant changes in the V coordination





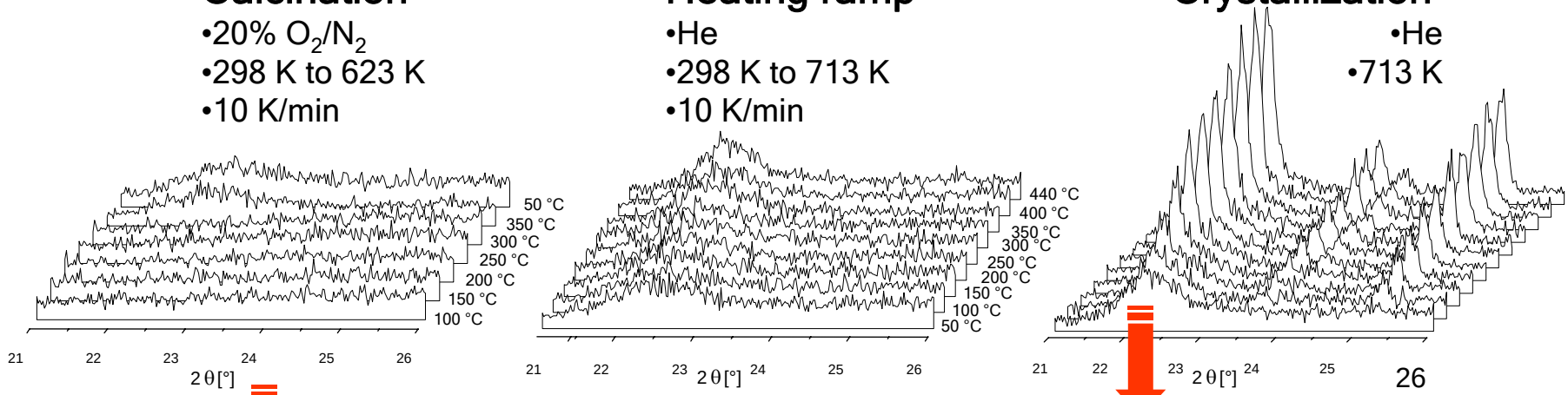
Phase formation

$(Mo_{0.68}V_{0.23}W_{0.09})_5O_{14}$

Calcination
- 20% O_2/N_2
- 298 K to 623 K
- 10 K/min

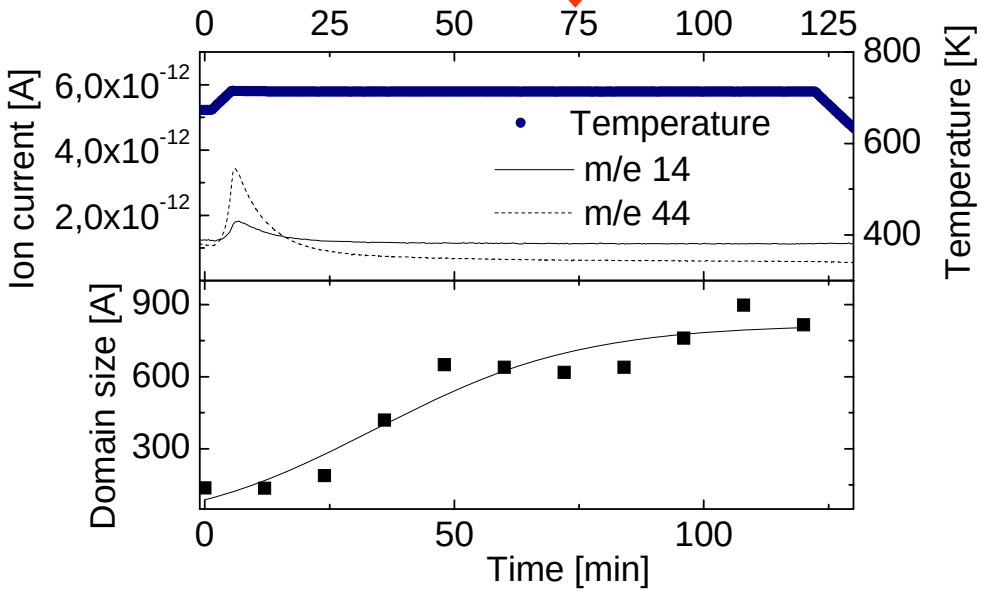
Heating ramp
- He
- 298 K to 713 K
- 10 K/min

Crystallization
- He
- 713 K



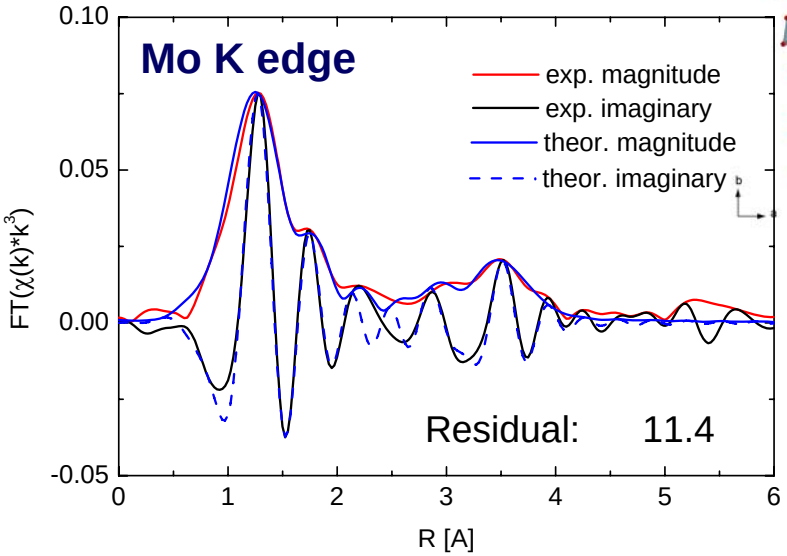
- linkage of precursor units

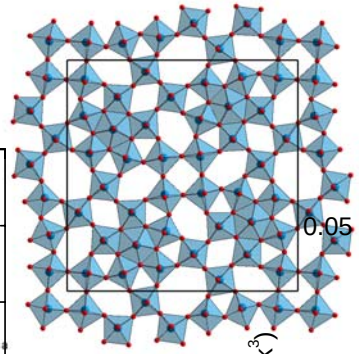
- growth in domain size is detected after complete decomposition of the counter ions in the precursor material.

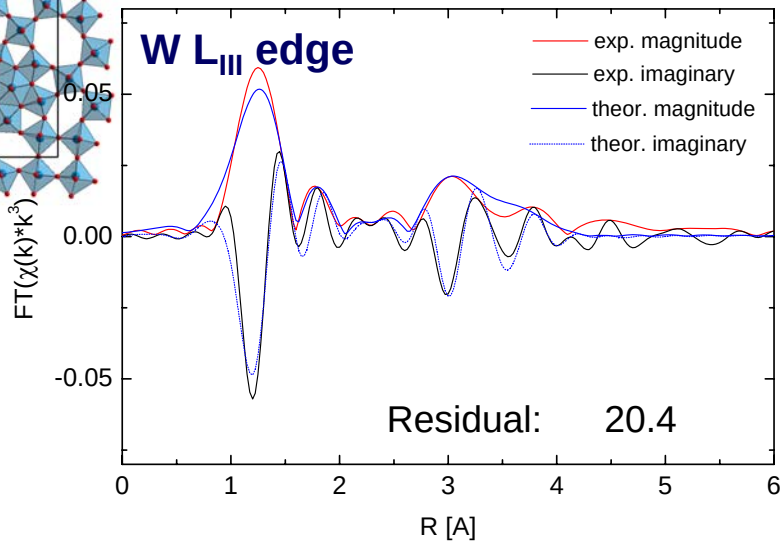


Local environment of Mo and W atoms in the crystalline material

$(Mo_{0.68}V_{0.23}W_{0.09})_5O_{14}$







	Mo c.n.	R [Å]	α-MoO_3 ICDS [35076]
Mo-O	1	1.634	1.671
Mo-O	1	1.724	1.734
Mo-O	2	2.070	1.948
Mo-O	1	2.291	2.251
Mo-O	1	2.482	2.332

- distorted octahedral environment like in α-MoO_3

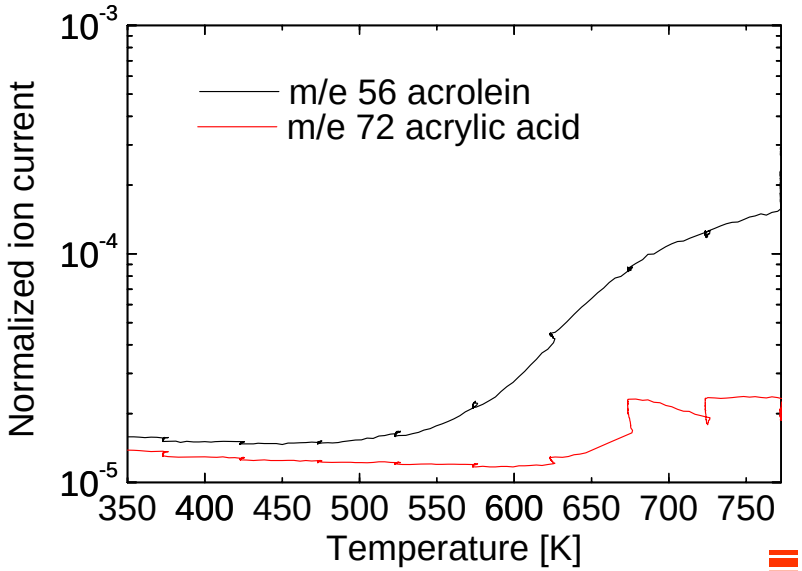
	W c.n.	R [Å]	WO_3 ICSD[1620]
W-O	2	1.71538	1.751; 1.753
W-O	2	1.84121	1.827; 1.951
W-O	2	2.02622	2.055; 2.212

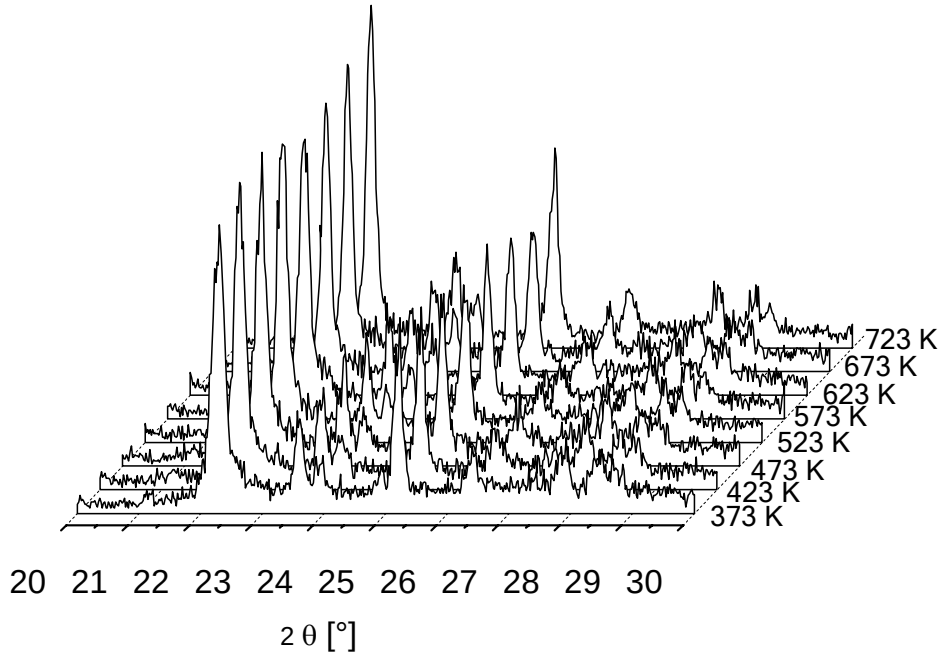
- regular coordination of W comparable to WO_3
- no extraordinary distortions due to presence of Mo and V

XRD under reaction conditions

$(Mo_{0.68}V_{0.23}W_{0.09})_5O_{14}$

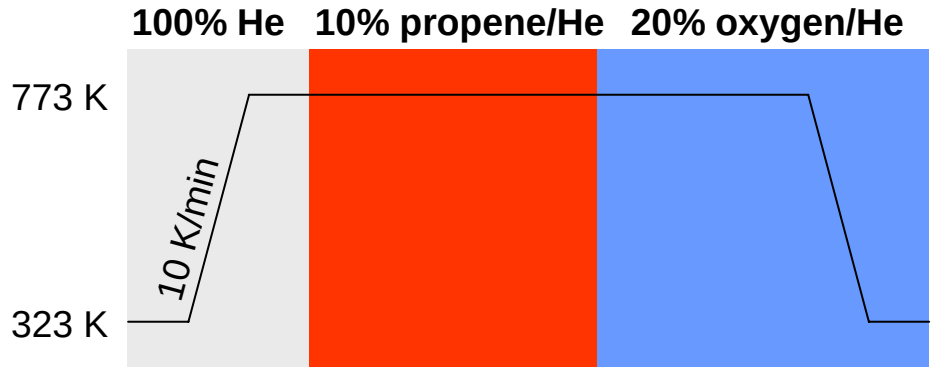
5% propene + 10% oxygen in He
Stepwise heating; ramp 10 K/min





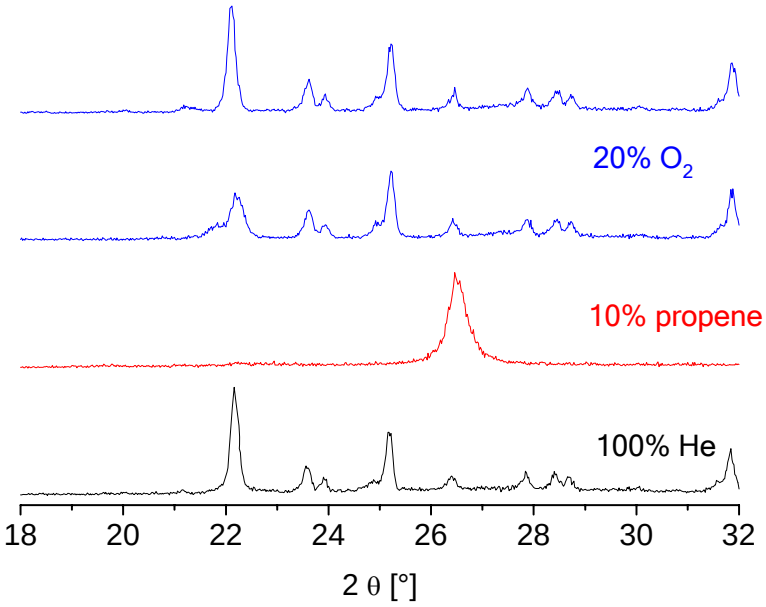
- high stability of the Mo_5O_{14}-type phase in the feed at reaction temperatures

Redox behaviour of MoVW and MoV



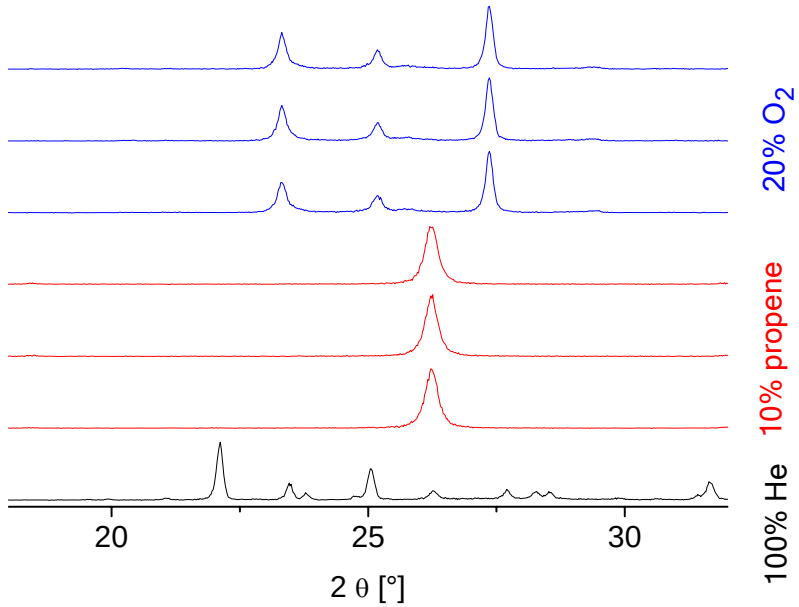
$(Mo_{0.68}V_{0.23}W_{0.09})_5O_{14}$

isothermal treatment at 773 K



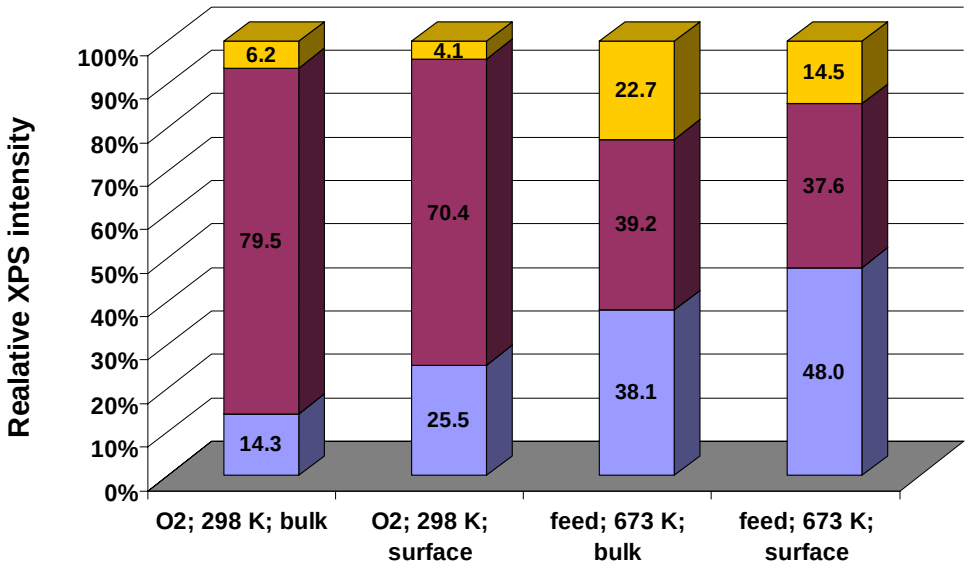
$(Mo_{0.91}V_{0.09})_5O_{14}$

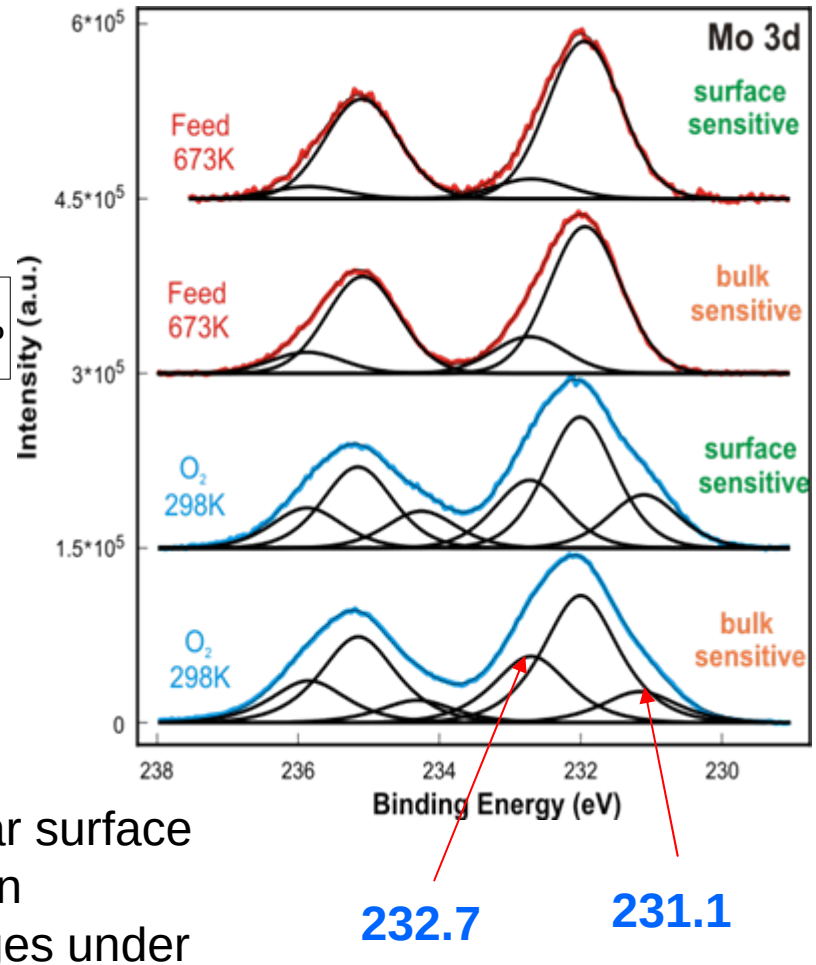
isothermal treatment at 773 K



Near surface composition and electronic structure

$(Mo_{0.68}V_{0.23}W_{0.09})_5O_{14}$



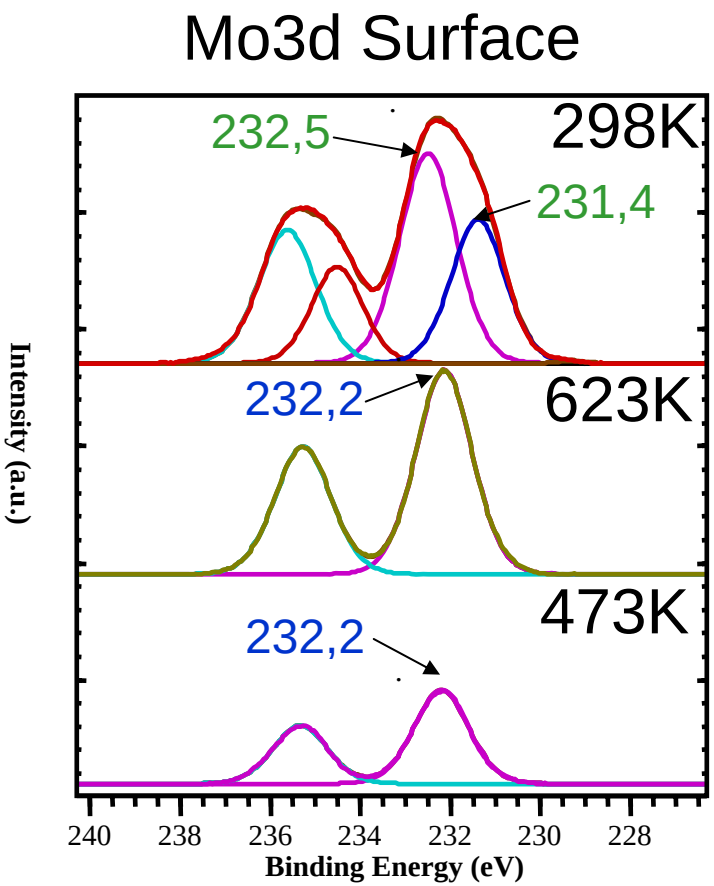


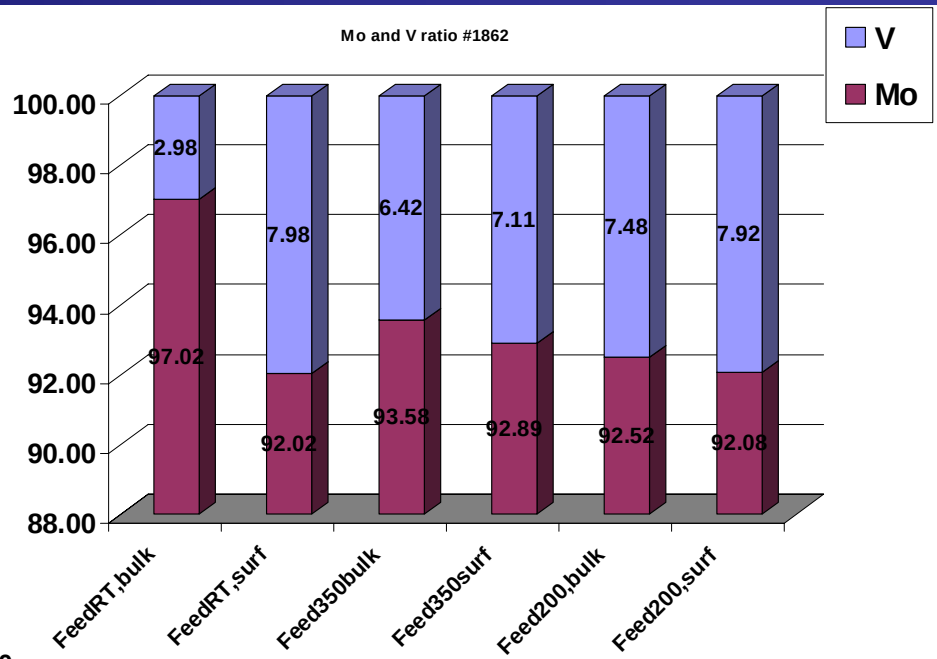
„feed“: molar ratio $C_3H_6 : O_2 = 1:2$
p = 0.5 mbar

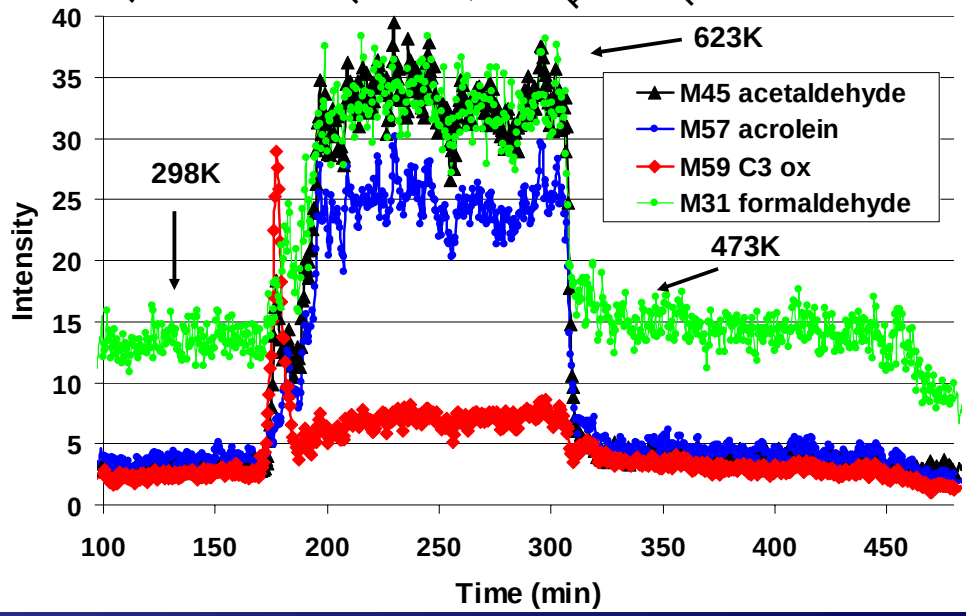
- depth profiles in presence of reactants: near surface composition is different from bulk composition
- Coordination sphere of molybdenum changes under reaction conditions

Electronic structure and near surface composition

$(Mo_{0.91}V_{0.09})_5O_{14}$







„feed“: molar ratio $C_3H_6 : O_2 = 1:2$
p = 0.5 mbar

Conclusions

1. Phase-pure MoVW oxide and MoV oxide model catalysts consisting of a Mo_5O_{14}-type phase have been prepared.
2. The model catalysts show catalytic activity in partial oxidation of C3 hydrocarbons. Under conditions of acrolein and acrylic acid formation the Mo_5O_{14}-type structure was the only phase observed, though, direct correlation to catalytic activity remains to be evidenced.
3. Tungsten stabilizes the Mo_5O_{14}-type structure in MoVW oxide. The material can be reduced to a monoclinic MoO_2-type structure in propene and reoxidized in oxygen to the initial Mo_5O_{14} structure. The reduction behaviour of MoV oxide is similar, however, reoxidation leads to MoO_3.
4. The near surface composition of model catalysts and the oxidation state of the metals strongly depend on temperature and gas phase composition. The surface is enriched in vanadium.
5. We find strong evidences for a dynamic nature of the model catalyst systems.

Persons involved

Preparation and test of propane oxidation catalysts:

M.H. Looi, E.M. Omar, R.M. Salim, R.K. Widi, A. Celaya Sanfiz, S. B. Abd Hamid

Preparation of model catalysts:

O. Timpe, S. Knobl

X-ray Diffraction and EXAFS:

E. Rödel, F. Girgsdies, T. Ressler

XPS:

P. Schnörch, S. Zafeiratos, A. Knop-Gericke

Coordination and presentation:

A. Trunschke

R. Schlögl

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