38. Jahrestreffen Deutscher Katalytiker

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Investigation of Structural Transformations during Synthesis of MoVTeNb mixed oxide catalysts

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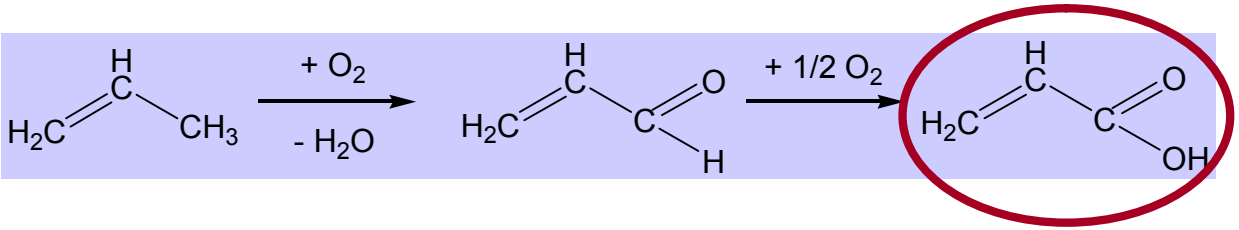
See also P89, P93, P98

Acknowledgements: S. Knobl, D. Niemeyer, V. Makwana, J. Wagner, U. Wild

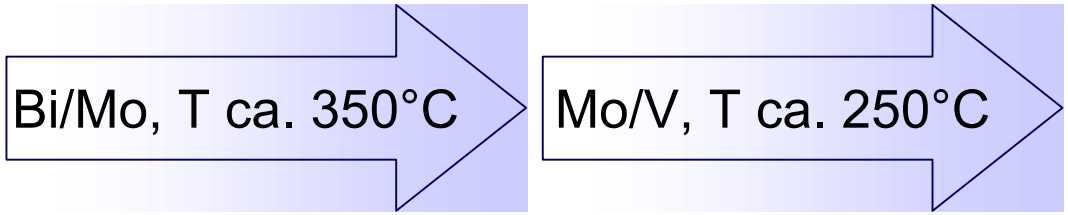
Outline

1. Introduction
2. Preparation of a catalyst for direct oxidation of propane to acrylic acid
3. Raman spectroscopy on aqueous solutions
4. Drying of the precipitate
5. Activation of the catalyst precursor
6. Conclusions

Manufacture of acrylic acid

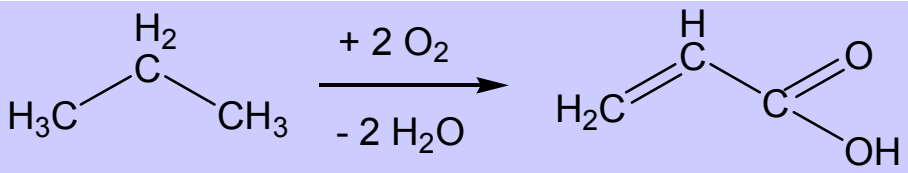


Commercial processes: Two-steps starting from propylene



- Acrylic acid yields up to 87%
- Propene accounts for about 80% of the variable costs
- Alternative raw material: propane
  - Liquified petroleum gas (LPG) from refineries
  - Natural gas liquid (NGL) from gas fields

Catalysts for propane oxidation to acrylic acid

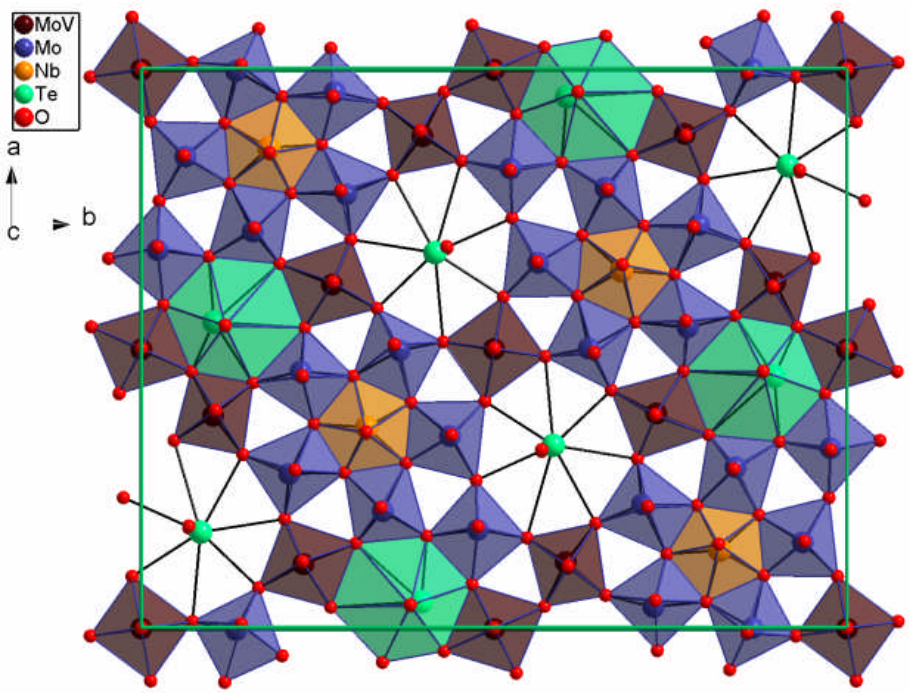


Examples of catalysts studied in propane oxidation to acrylic acid

- Modified vanadium pyrophosphate (VPO) catalysts
  - Ce/VPO (Y_{AA} ca. 19%)
  - VPO/TiO_2-SiO_2 (Y_{AA} ca. 13%)
- Heteropoly acids and salts
  - $H_{1.26}Cs_{2.5}Fe_{0.08}P_1V_1Mo_{11}O_{40}$ (Y_{AA} ca. 13%)
- Multi-component metal oxide catalysts
  - **$Mo_1V_{0.3}Te_{0.23}Nb_{0.125}O_x$** ($Y_{AA}$ ca. 48%)
  - ➢ T. Ushikubo, H. Nakamura, Y. Koyasu, S. Wajiki, Mitsubishi Kasei Corporation, US 005380933A (Jan.10, 1995).

Structural aspects of MoVTeNb catalysts

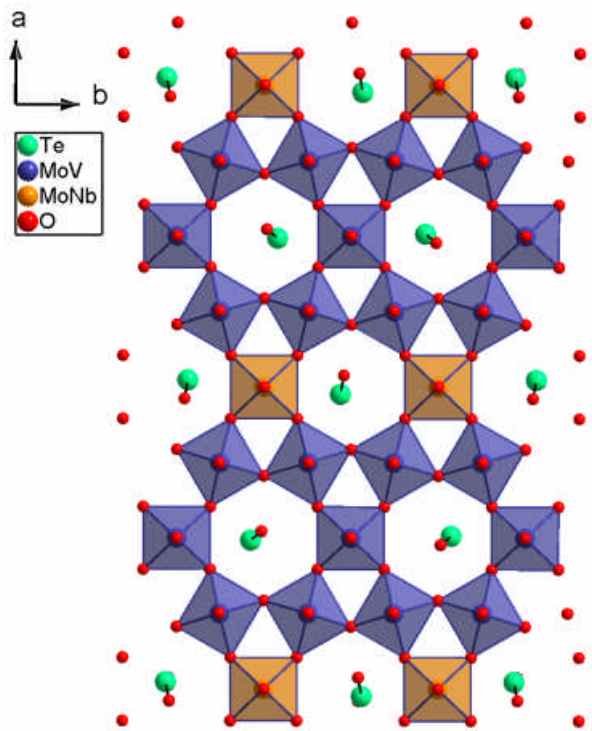
M1



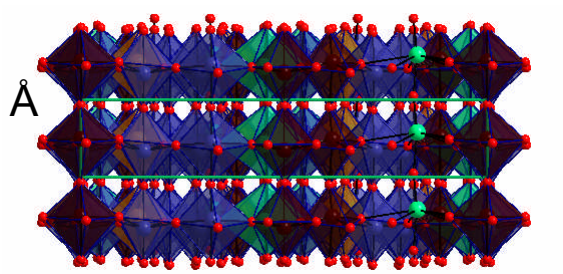
a=21.1 Å

b=26.6 Å

M2



c=4 Å



T. Ushikubo et al. Stud. Surf. Sci. Catal. **112** (1997) 473.

P. De Santo et al. Z. Kristallogr. **219** (2004) 152.

Other phases, e.g.:
- $Mo_{5-x}(V/Nb)_xO_{14}$
- $TeMo_5O_{16}$
- MoO_3, Te

+ amorphous fractions

Objectives and approach

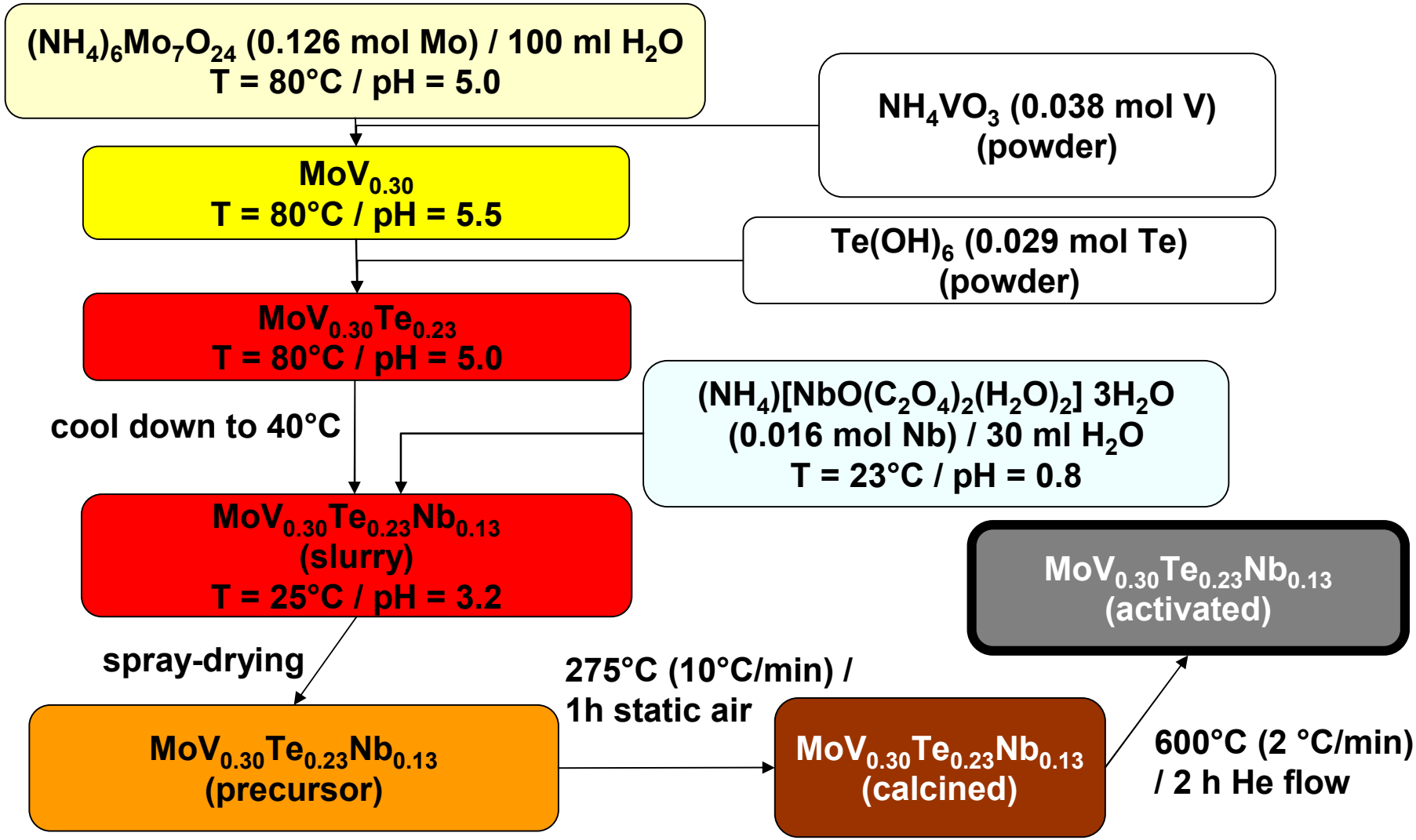
- $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}O_x$ would serve as a basis for a possible commercial process to convert propane directly to acrylic acid
- Described preparation procedure not reproducible (Y_{AA} = 0 – 50%)
- Systematic inspection of the preparation procedure required

↓

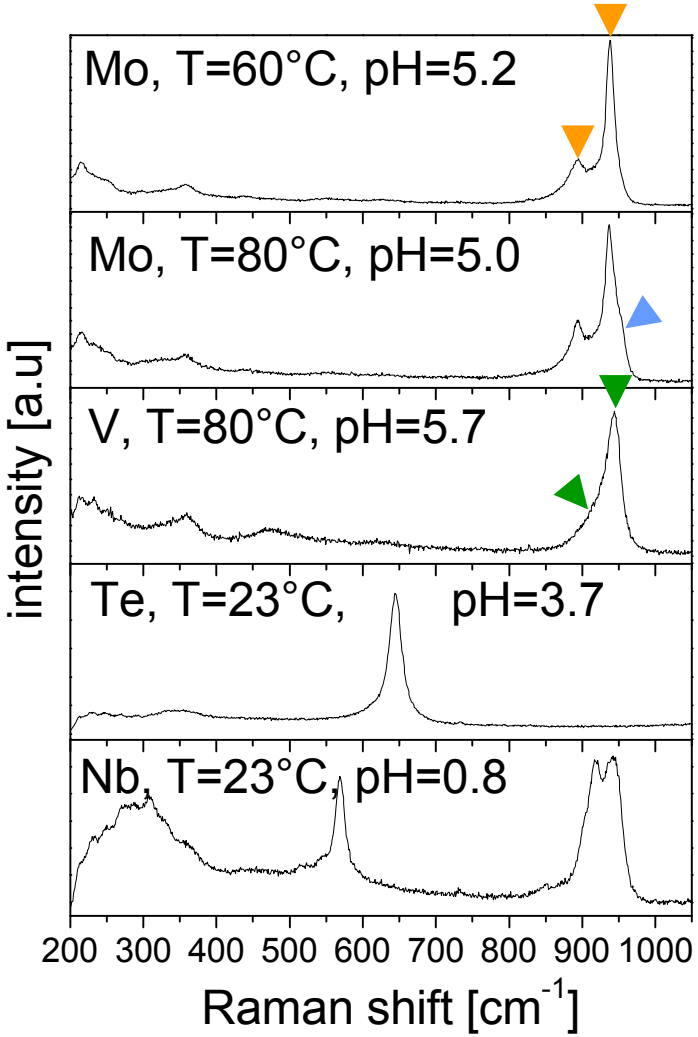
- Which preparation step is crucial for phase distribution in the final catalyst?

in-situ Raman spectroscopy:	Monitoring of formation and rearrangement of molecular building blocks
X-ray diffraction:	Phase composition of precursors and final catalyst
Scanning electron microscopy (SEM):	Microstructure

Preparation of $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}O_x$: „Slurry method“



Raman spectroscopy on individual POM solutions



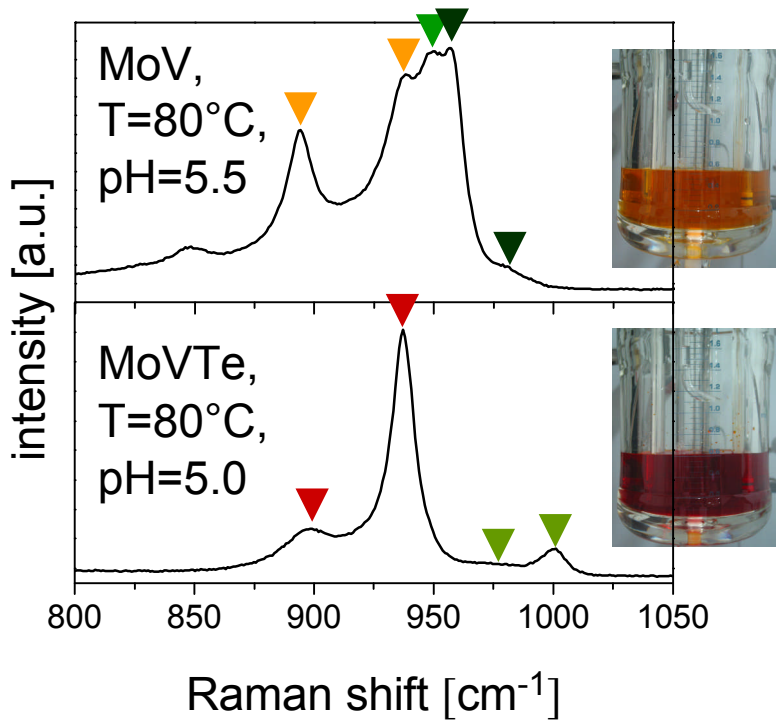
$$7\ MoO_4^{2-} + 8\ H^+ \rightleftharpoons [Mo_7O_{24}]^{6-} + 4\ H_2O$$

$$8\ MoO_4^{2-} + 12\ H^+ \rightleftharpoons [Mo_8O_{26}]^{4-} + 6\ H_2O$$

ν [cm^{-1}]	assignment
937 (s) 893 (m)	ν (Mo=O) $Mo_7O_{24}^{6-}$
955 (sh)	ν (Mo=O) $Mo_8O_{26}^{4-}$
944 (s) 900 (sh)	ν (V=O) $[VO_3]_n^{n-}$
644 (s)	ν (Te-O)
570 (m) 942 (s) 919 (s)	ν (Nb-O) ν (Nb=O)

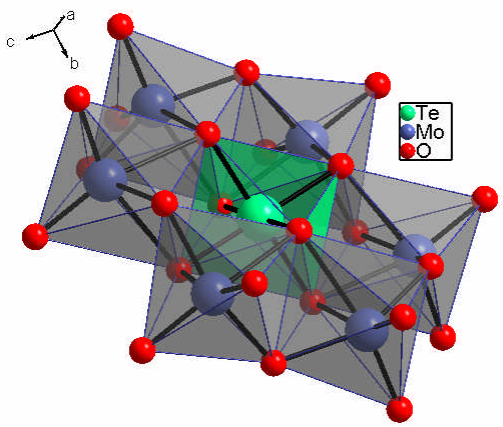
M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer Verlag, Berlin 1983.

Raman spectroscopy on mixed solutions



ν [cm^{-1}]	assignment
937 (s) 893 (m)	ν (Mo=O) $Mo_7O_{24}^{6-}$
950 (sh)	ν(V=O) $[VO_3]_n^{n-}$
980 (s) 956 (m)	ν (V=O) $[V_{10}O_{28}]^{6-}$
848 (m)	ν (V-O-V) or ν (Mo-O-V)
1000 (m) 975 (vw)	ν (V=O) $[H_xV_{10}O_{28}]^{(6-x)-}$ or ν (M=O) $[TeMo_5VO_{24}]^{7-}$
937 (s) 899 (m)	ν (Mo=O) $[TeMo_6O_{24}]^{6-}$

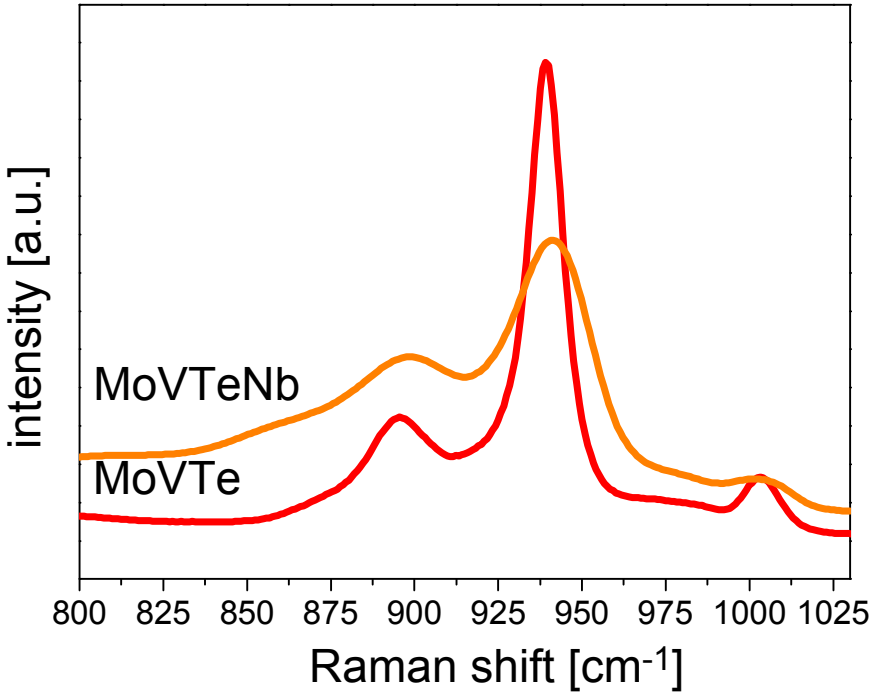
$TeMo_6$ = 0.126 mol Mo + 0.021 mol Te + 0.008 mol residual $Te(OH)_6$



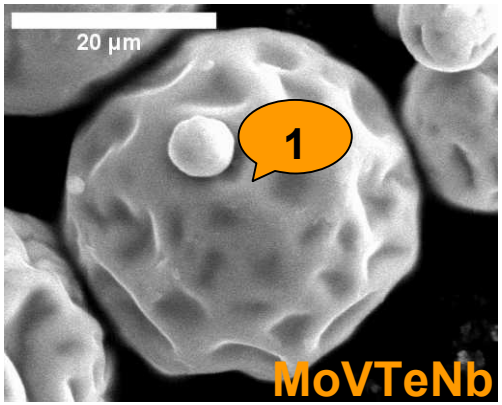
$[TeMo_6O_{24}]^{6-}$

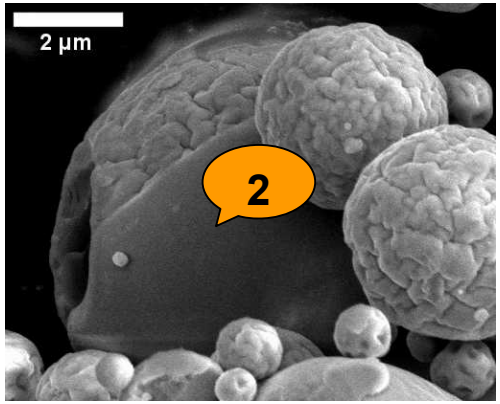
I.L. Botto et al. Mater. Chem. Phys.47 (1997) 37.

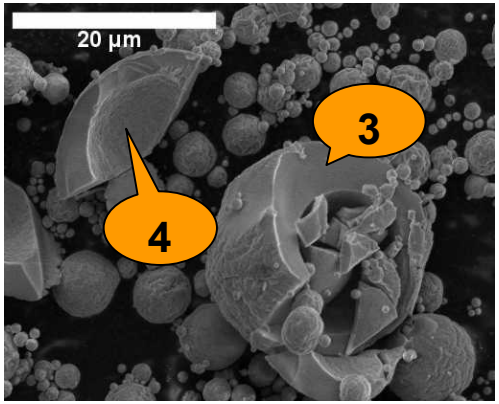
Raman spectra of spray-dried precursors



SEM images of the spray-dried precursor





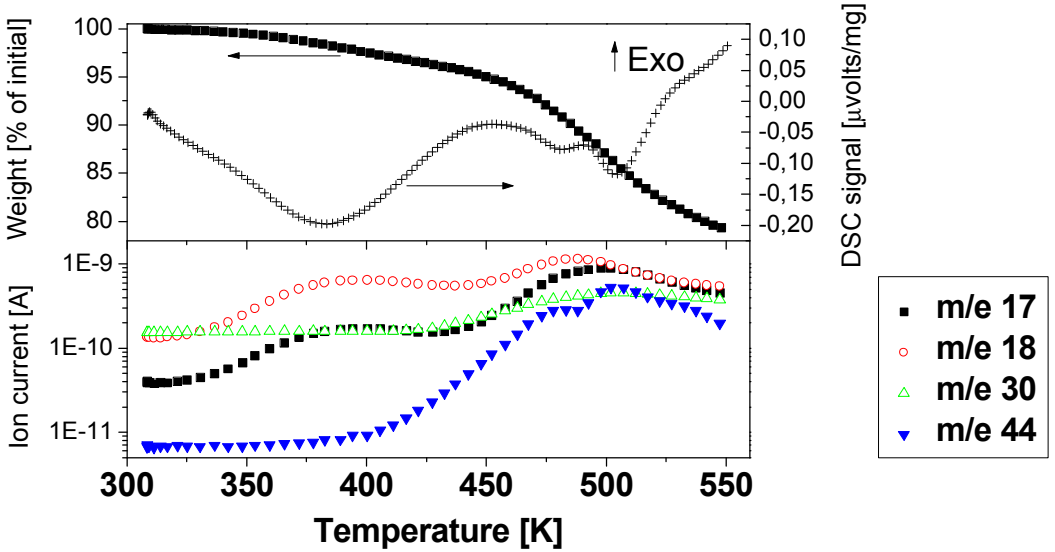


	Molar ratios of elements normalized to Mo from EDX				
	spot 1	**spot 2**	**spot 3**	**spot 4**	**synthesis**
Mo	1	1	1	1	1
V	0.30	0.33	0.28	0.35	0.3
Te	0.28	0.24	0.25	0.27	0.23
Nb	0.22	0.13	0.20	0.20	0.125

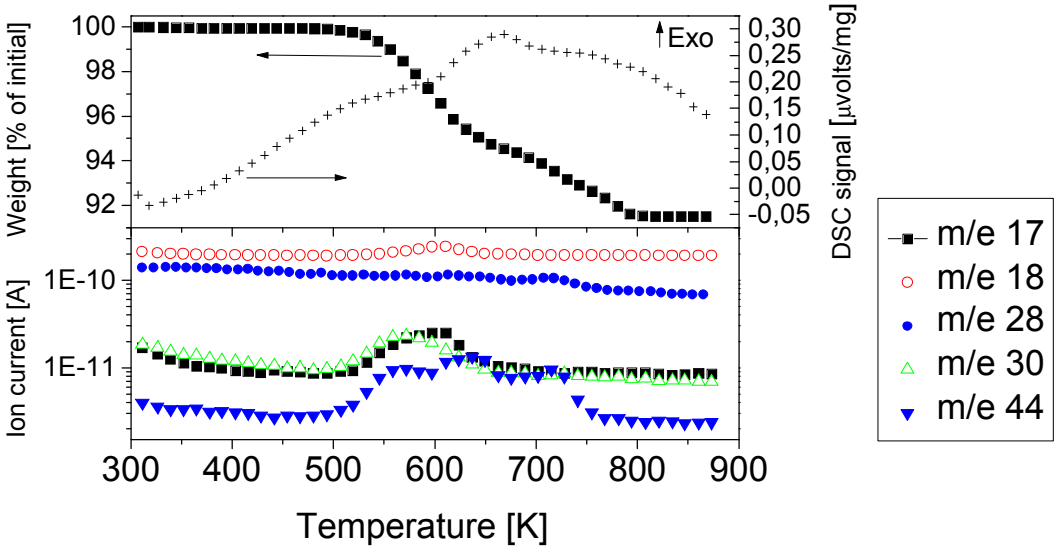
Decomposition of the Anderson-type precursor

Thermogravimetry / Differential Scanning Calorimetry

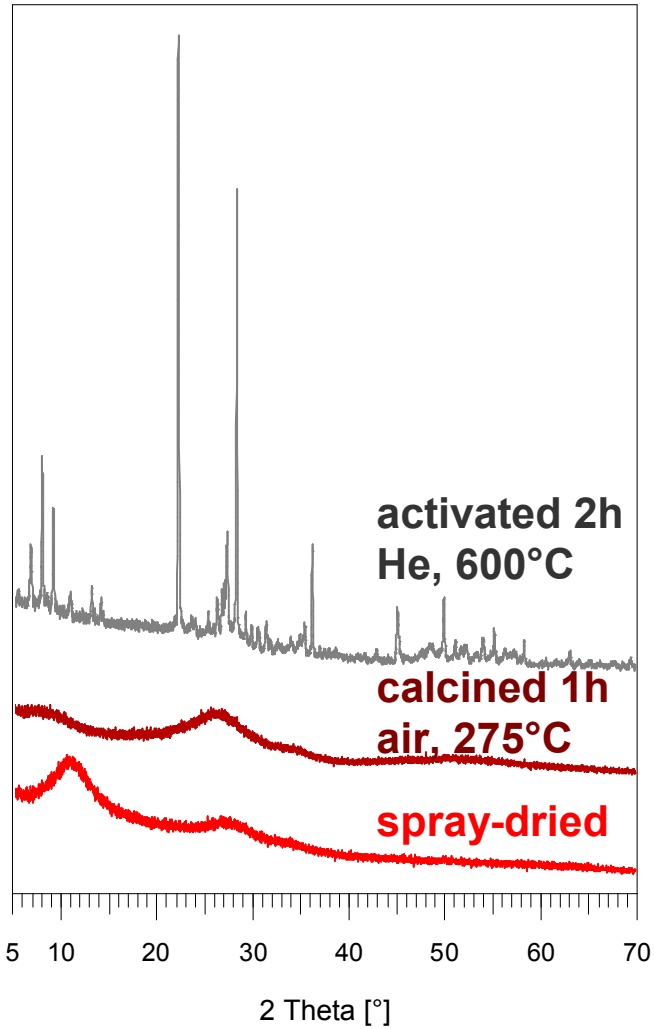
1. Calcination in static air up to 275°C (10°C/min)

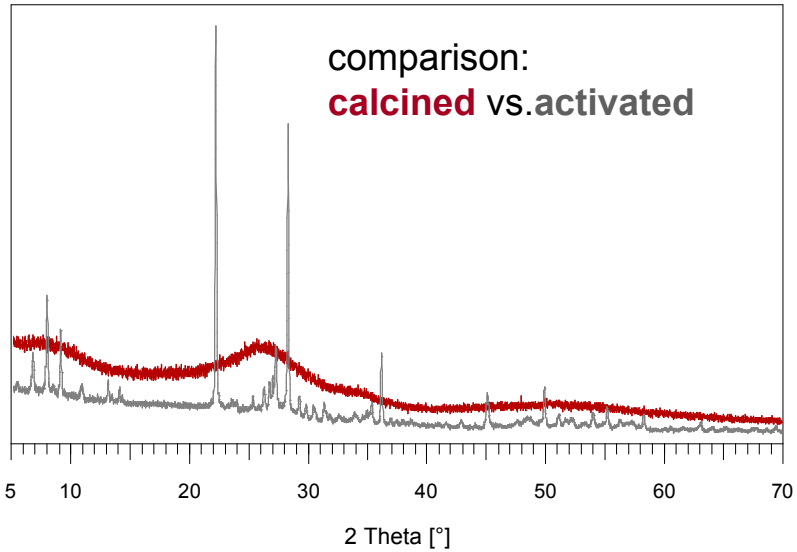


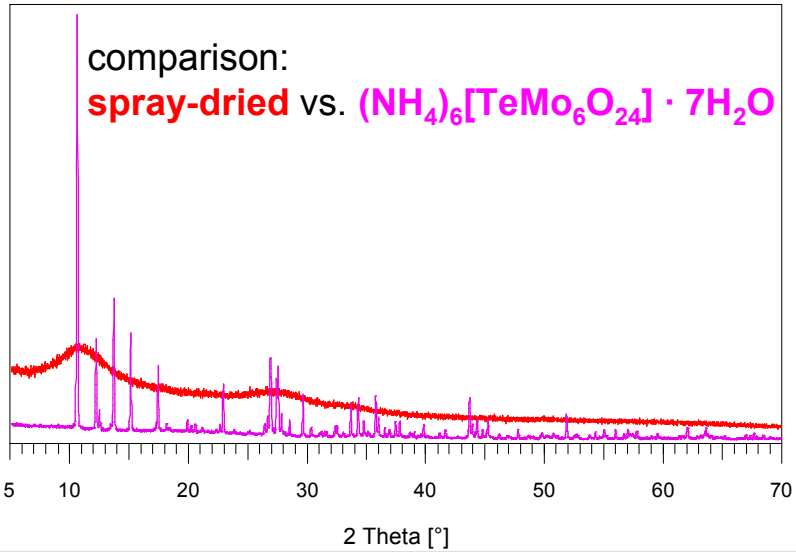
2. Activation in flowing He up to 600°C (2°C/min)



Development of phase structures

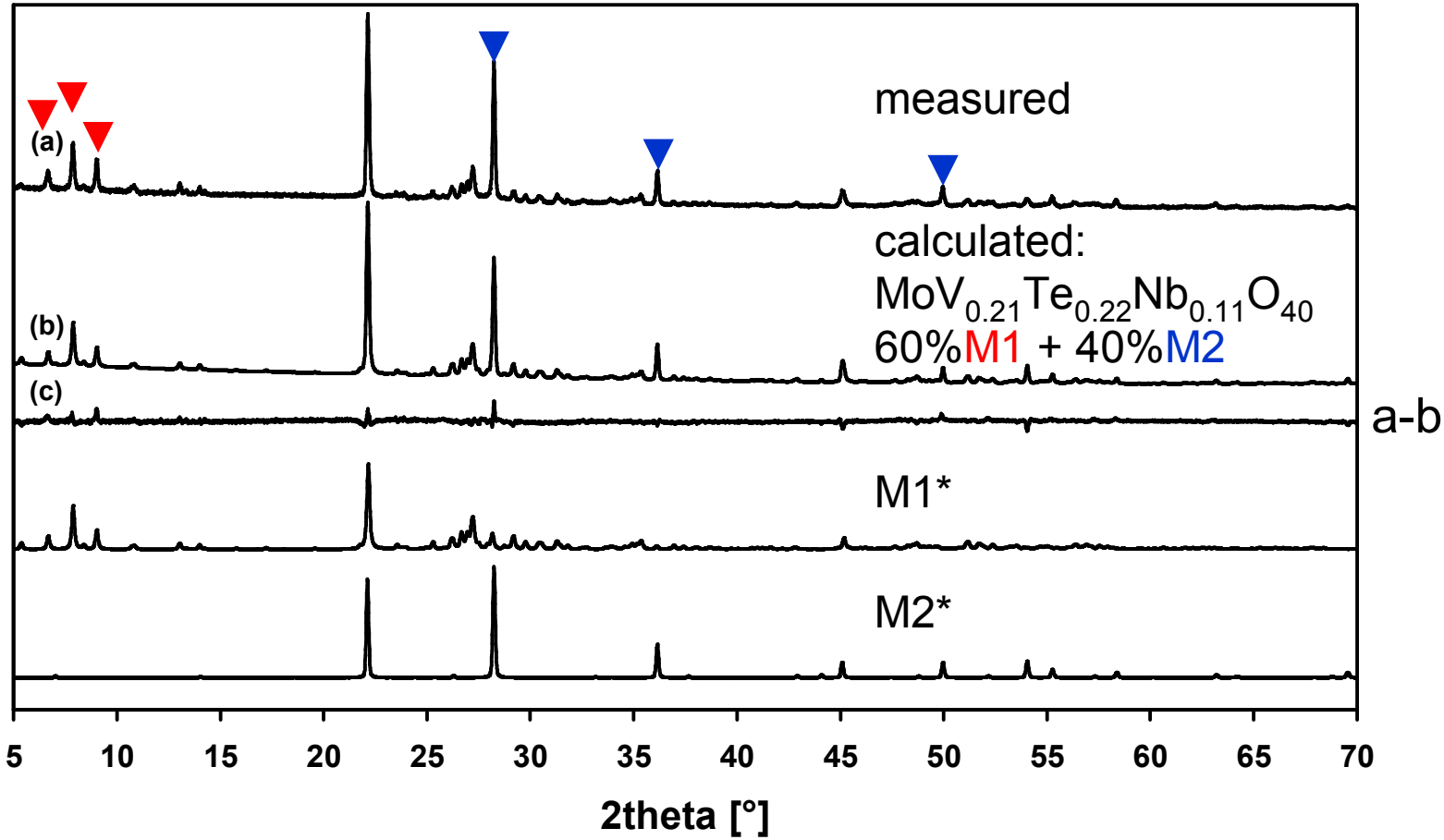






Development of phase structures

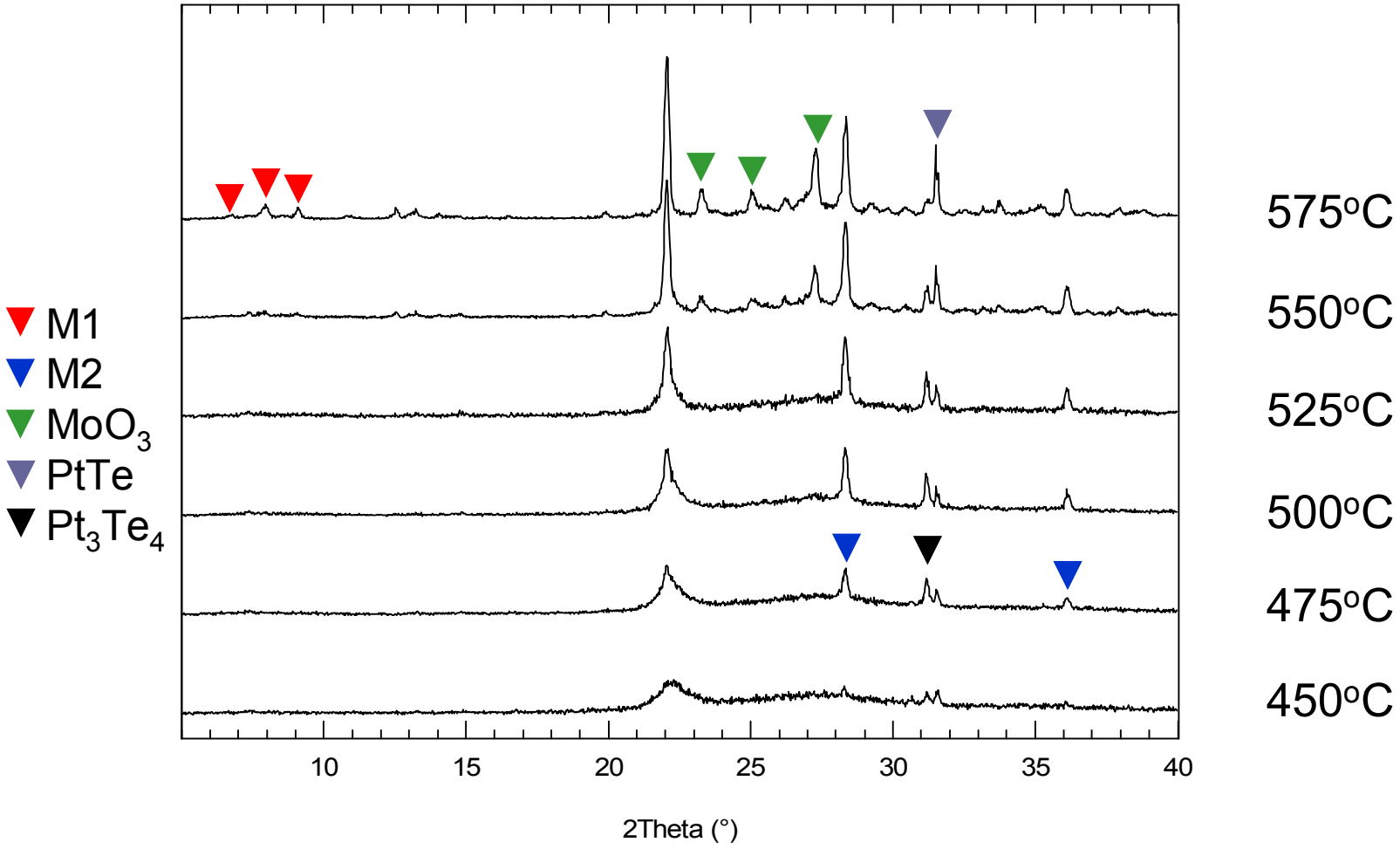
catalyst $MoV_{0.3}Te_{0.23}Nb_{0.125}O_x$ after activation



*simulation based on the model of P. De Santo et al. Z. Kristallogr. **219** (2004) 152.

Development of phase structures

He, 2°C/min:



Conclusions

- An Anderson-type molybdotellurate is formed during preparation of $Mo_1V_{0.30}Te_{0.23}Nb_{0.125}O_x$ in the initial ternary MoVTe solution.
- V mainly coexists with the molybdotellurate as protonated decavanadate.
- Nb does not change the structure of the polyoxometalate species in solution.

- The Anderson-type heteropolyanion is preserved in the spray-dried material.
- Crucial for catalyst activation seems to be the calcination in air at 275°C that results in the decomposition of the Anderson-type species and significant structural rearrangements.
- Thermal treatment in He at 600°C leads to the crystallization of the phases established during calcination and may cause the formation of other phases.