Nanostructured Molybdenum Oxide Catalysts for the Selective Oxidation of C3 Hydrocarbons

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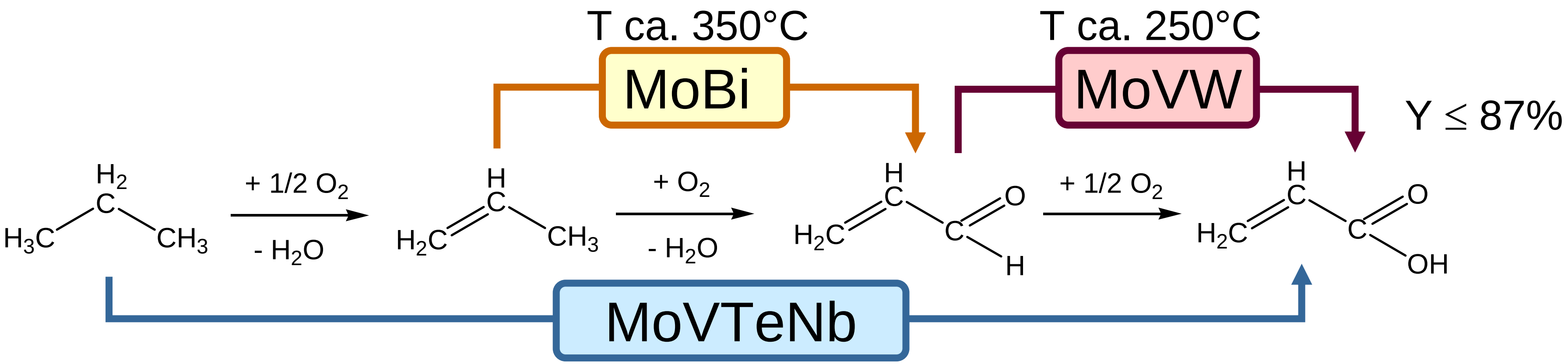


Examples of catalysts studied in propane oxidation to acrylic acid

- 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).

Preparation of $MoVTeNbO_x$

$(NH_4)_6Mo_7O_{24}$
(0.126 mol Mo) / 100 ml H_2O
T = 80°C / pH = 5.0

NH_4VO_3 (0.038 mol V)
(powder)

$MoV_{0.30}$
T = 80°C / pH = 5.5

$Te(OH)_6$ (0.029 mol Te)
(powder)

$MoV_{0.30}Te_{0.23}$
T = 80°C / pH = 5.0

cool down to 40°C

$(NH_4)[NbO(C_2O_4)_2(H_2O)_2]\ 3H_2O$
(0.016 mol Nb) / 30 ml H_2O
T = 23°C / pH = 0.8

$MoV_{0.30}Te_{0.23}Nb_{0.13}$
(slurry)
T = 25°C / pH = 3.2

spray-drying

$MoV_{0.30}Te_{0.23}Nb_{0.13}$
(precursor)

275°C (10°C/min) /
1h static air

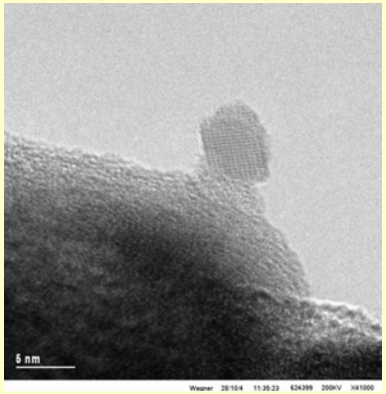
$MoV_{0.30}Te_{0.23}Nb_{0.13}$
(calcined)

600°C (2 °C/min) /
2 h He flow

$MoV_{0.30}Te_{0.23}Nb_{0.13}$
(activated)

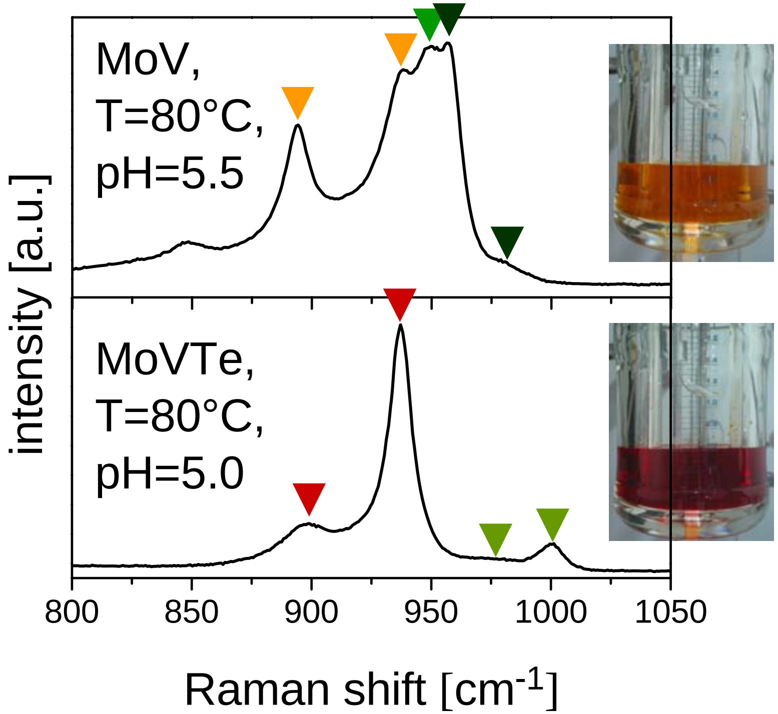
Further synthetic strategies:

- Hydrothermal synthesis
- Addition of diluents
- Addition of noble metals



Ru-[PMo]-$MoVTeNbO_x$

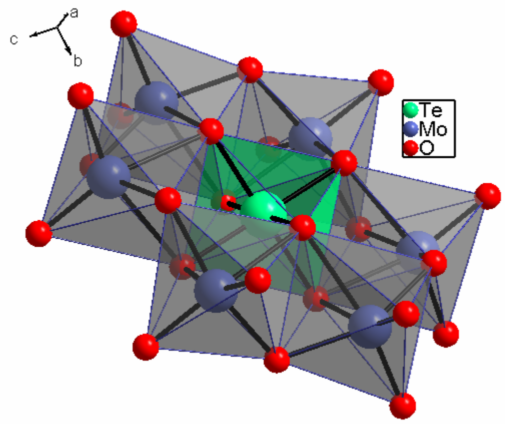
Raman spectroscopy on mixied solutions



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

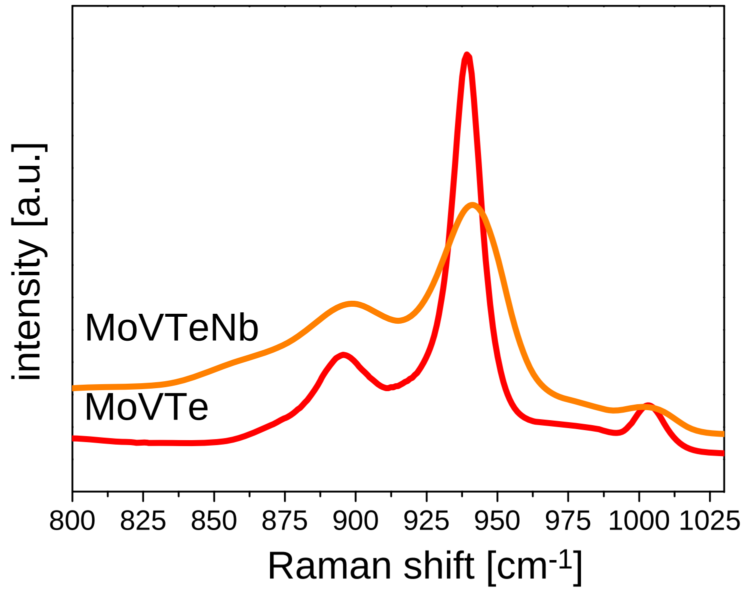
$TeMo_6$ = 0.126 mol Mo + 0.021 mol Te
residual 0.008 mol $Te(OH)_6$ not detectable

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

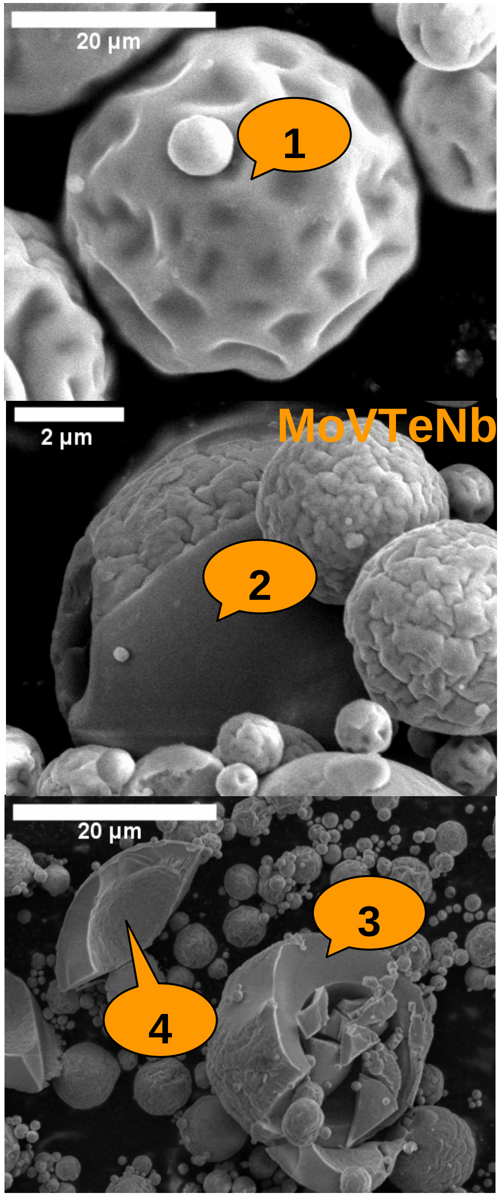


$[TeM_6O_{24}]^{6-}$
M=Mo, V

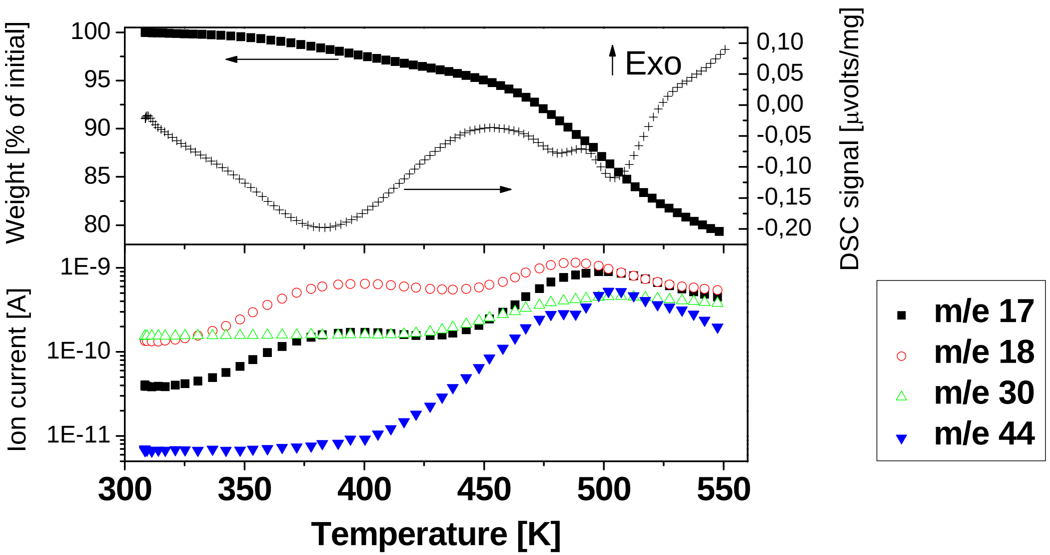
Spray-dried precursor



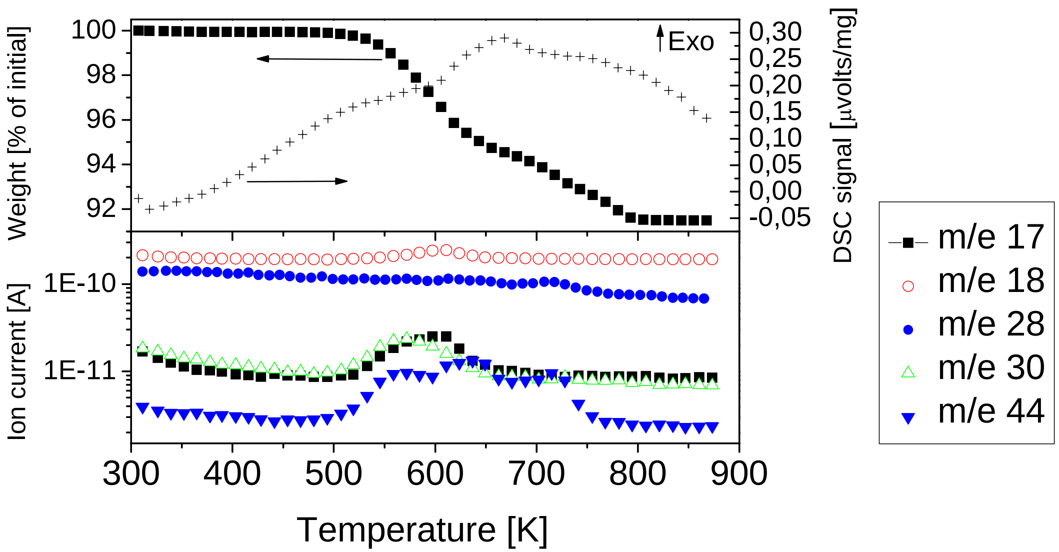
Molar ratios of elements normalized to Mo from EDX					
	spot 1	spot 2	spot 3	spot 4	synthesis
Mo	1	1	1	1	1
V	0.30	0.33	0.28	0.35	0.3
Te	0.28	0.24	0.25	0.27	0.23
Nb	0.22	0.13	0.20	0.20	0.125



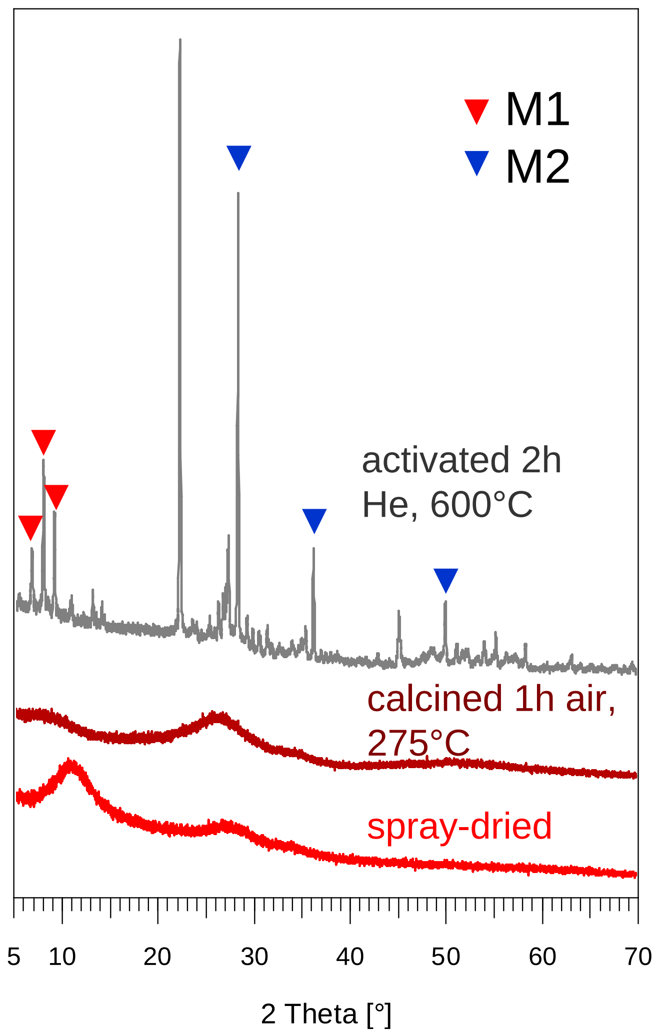
1. Calcination in static air up to 275°C (10°C/min)

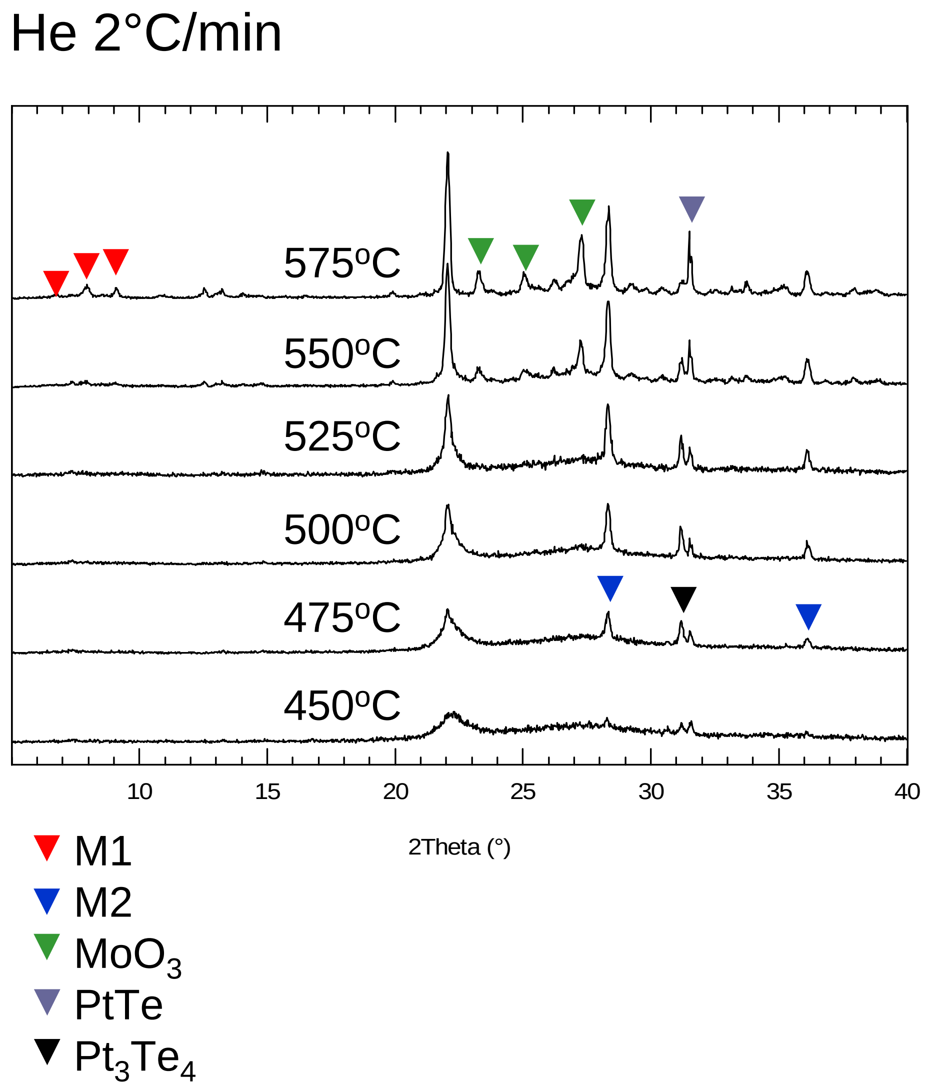


2. Activation in flowing He up to 600°C (2°C/min)

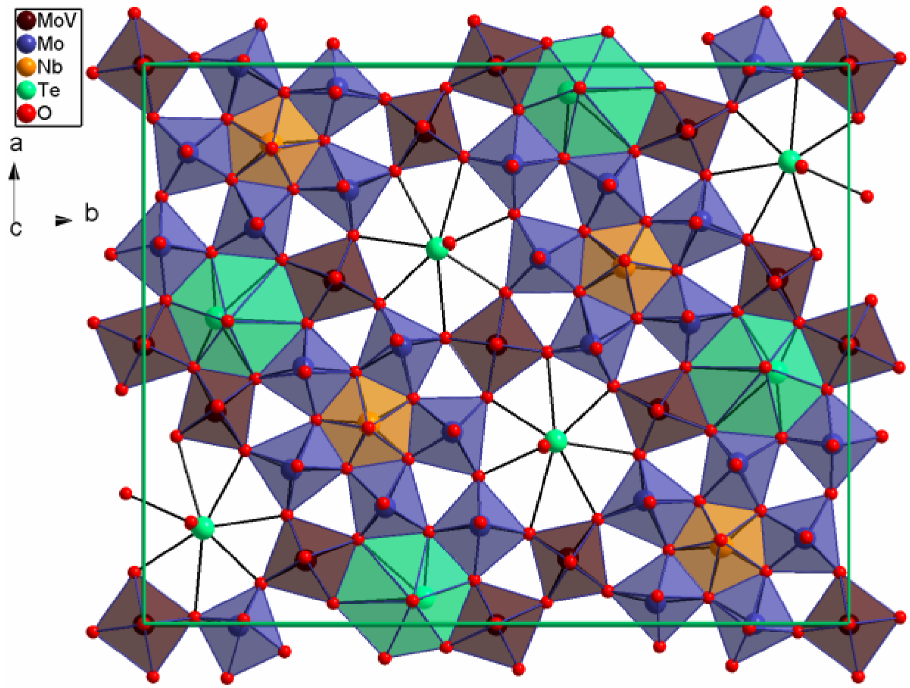


Development of the phase structure





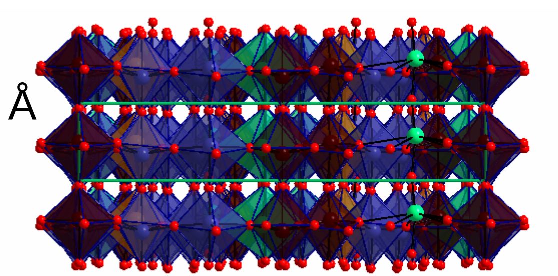
M1



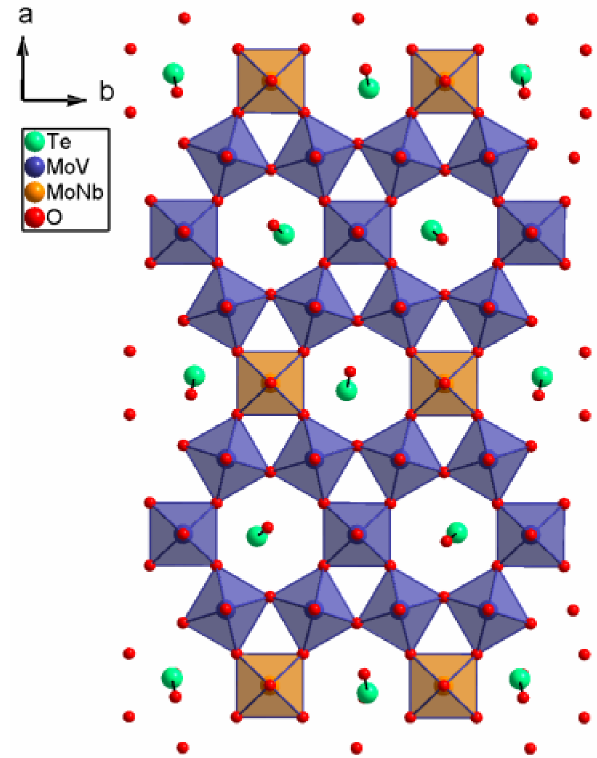
a=21.1 Å

b=26.6 Å

c=4 Å



M2



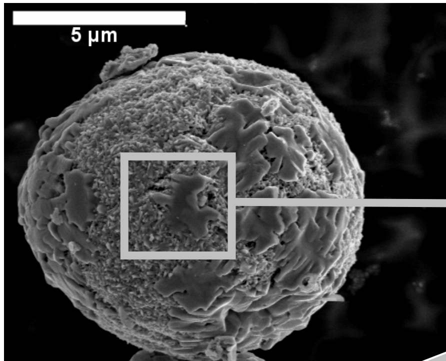
T. Ushikubo et al. Stud. Surf. Sci. Catal. **112** (1997) 473.

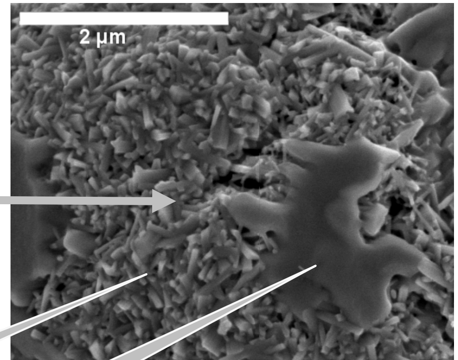
P. De Santo et al. Z. Kristallogr. **219** (2004) 152.

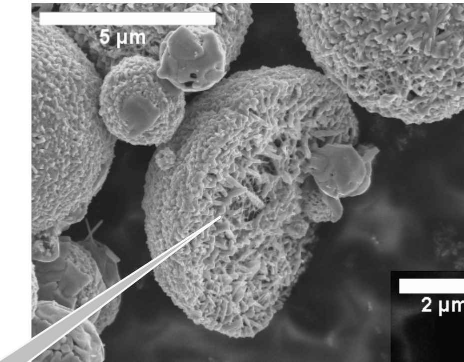
Other phases, e.g.:

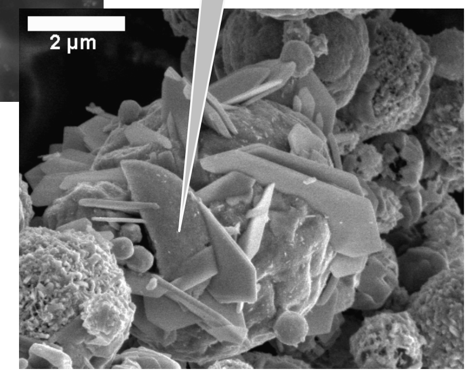
- $Mo_{5-x}(V/Nb)_xO_{14}$
- $TeMo_5O_{16}$
- MoO_3, Te

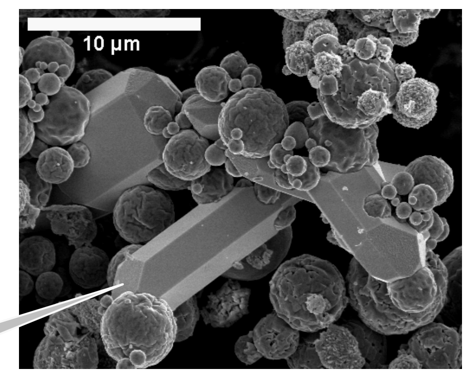
+ amorphous fractions







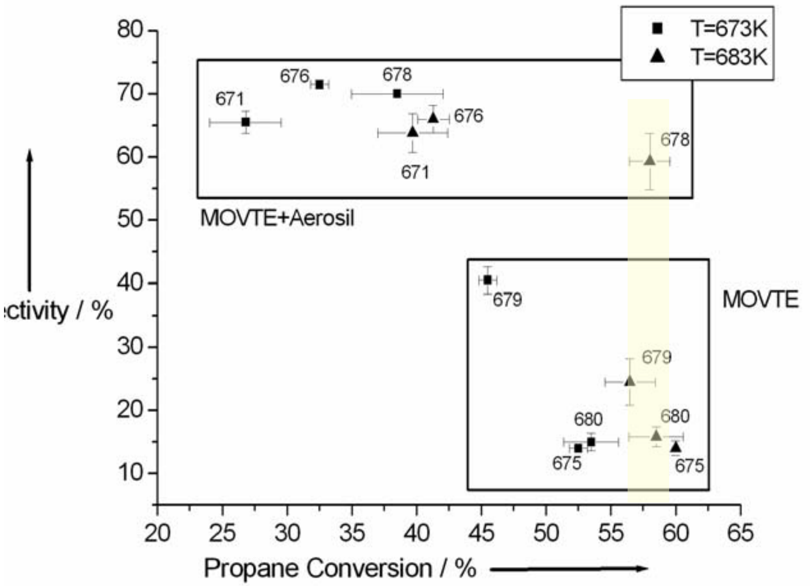




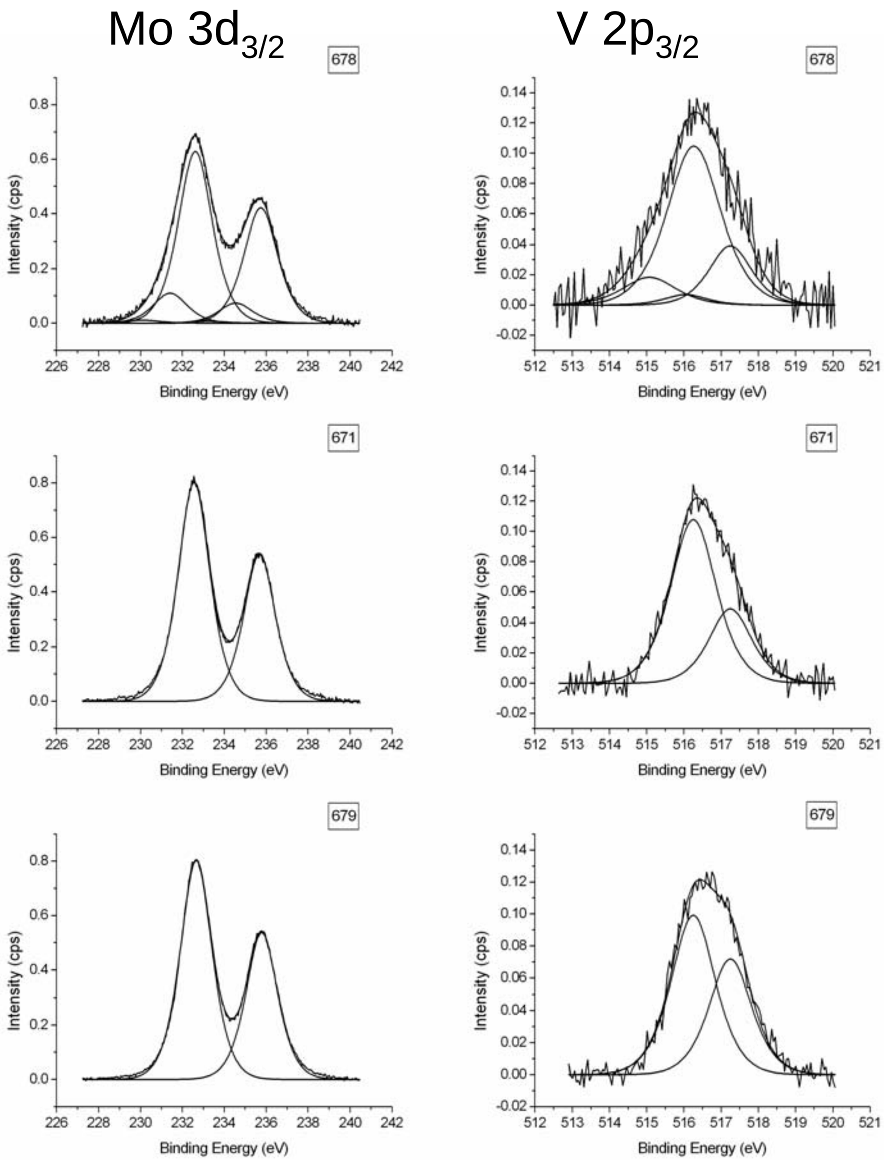
	Molar ratio of elements normalized to Mo from EDX					
	spot 1	**spot 2**	**spot 3**	**spot 4**	**spot 5**	**M1**	**M2**
Mo	1	1	1	1	0	1	1
V	0.28	0.35	0.31	0.33	0	0.15	0.32
Te	0.12	0.39	0.14	0.32	1	0.12	0.42
Nb	0.11	0.12	0.22	0.09	0	0.13	0.08

XPS: $Mo_1V_{0.19}Te_{0.19}Nb_{0.14}O_x$

Electronic structure / surface composition and catalytic properties



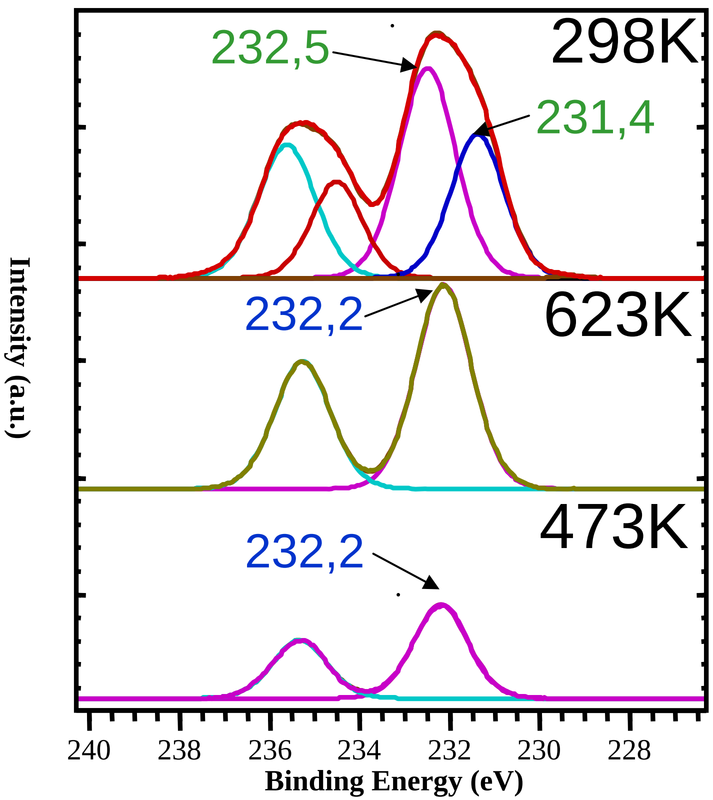
Catalyst	Atomic percentage (XPS) normalized to Mo				V oxida-tion state
	Mo	V	Te	Nb	5+/red.
678	1	0.24	042	0.11	23/77
671	1	0.20	0.24	0.15	30/70
679	1	0.21	0.24	0.15	41/59
nominal	1	0.30	0.23	0.13	
M1	1	0.15	0.12	0.13	

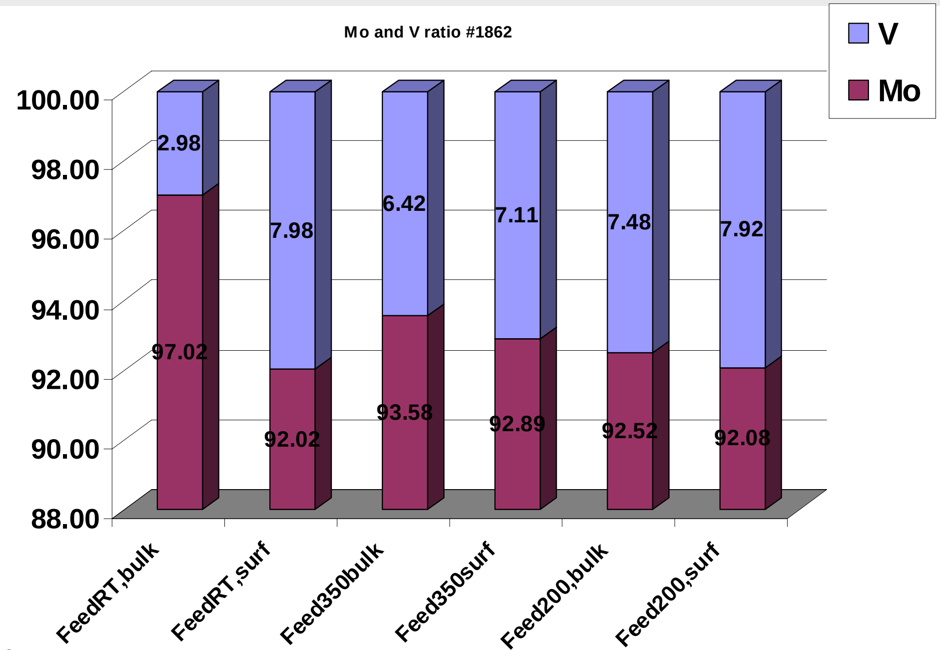


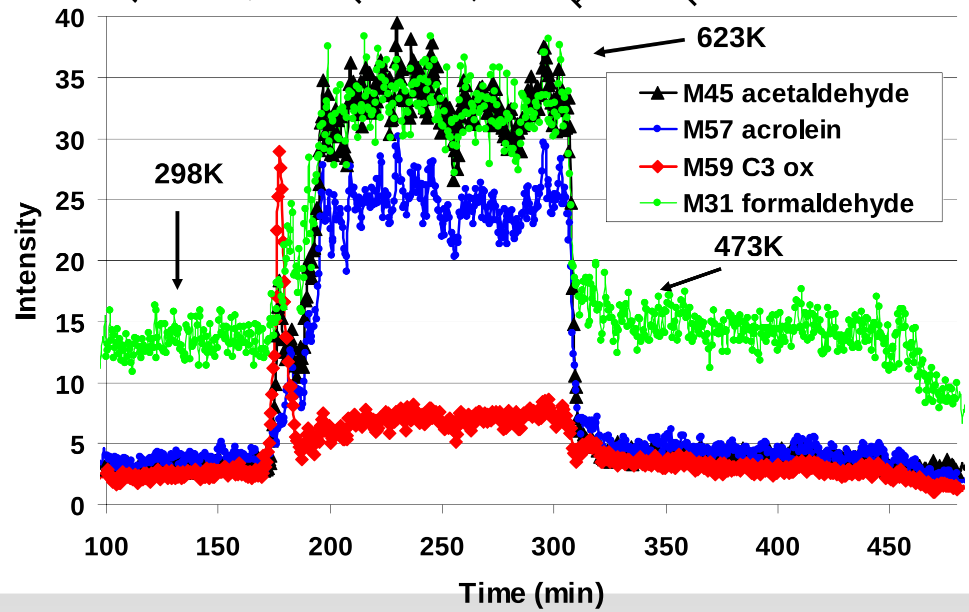
Electronic structure / surface composition of a model catalyst

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

Mo3d Surface



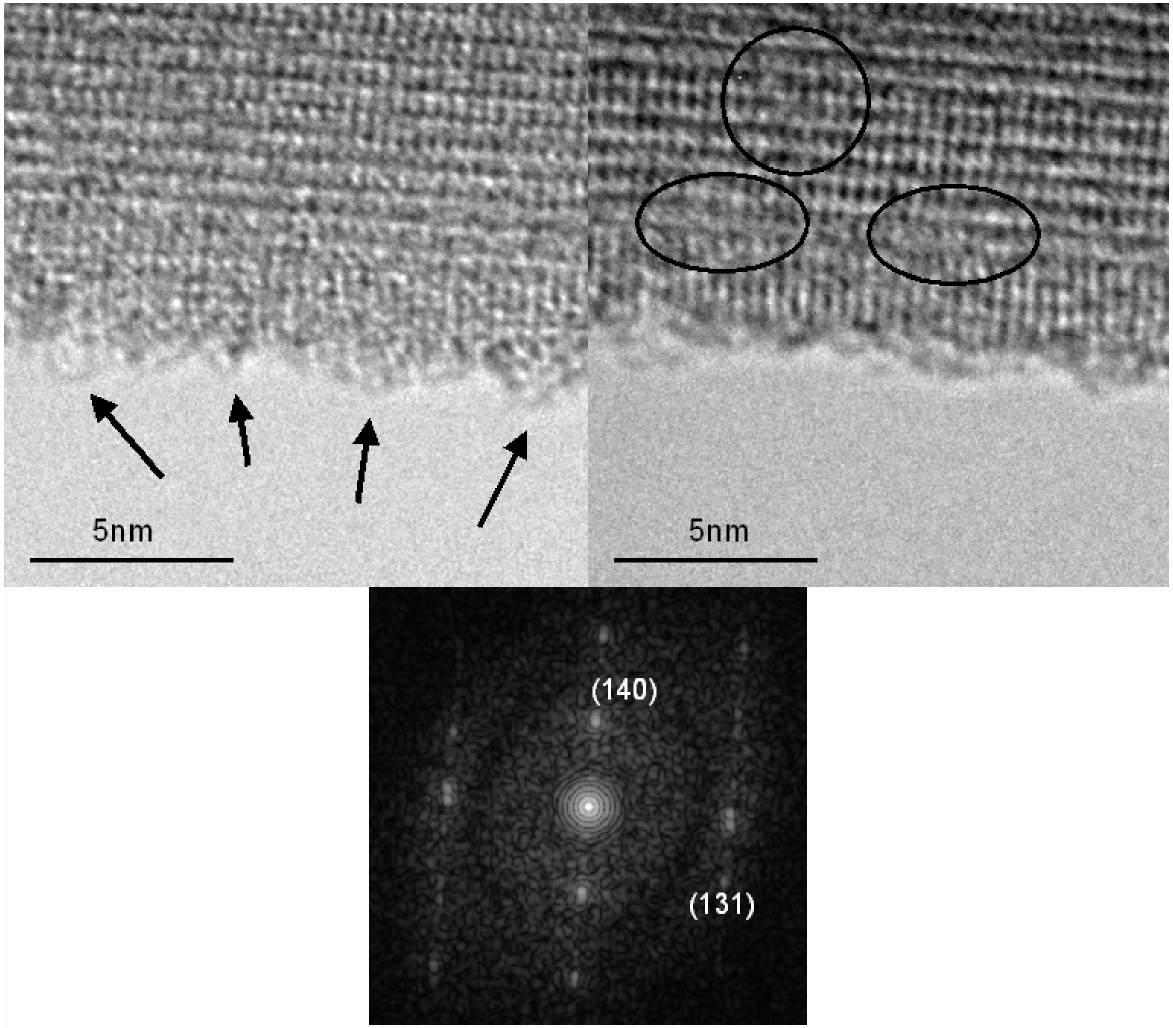




„feed“: molar ratio $C_3H_6 : O_2 = 1:2$

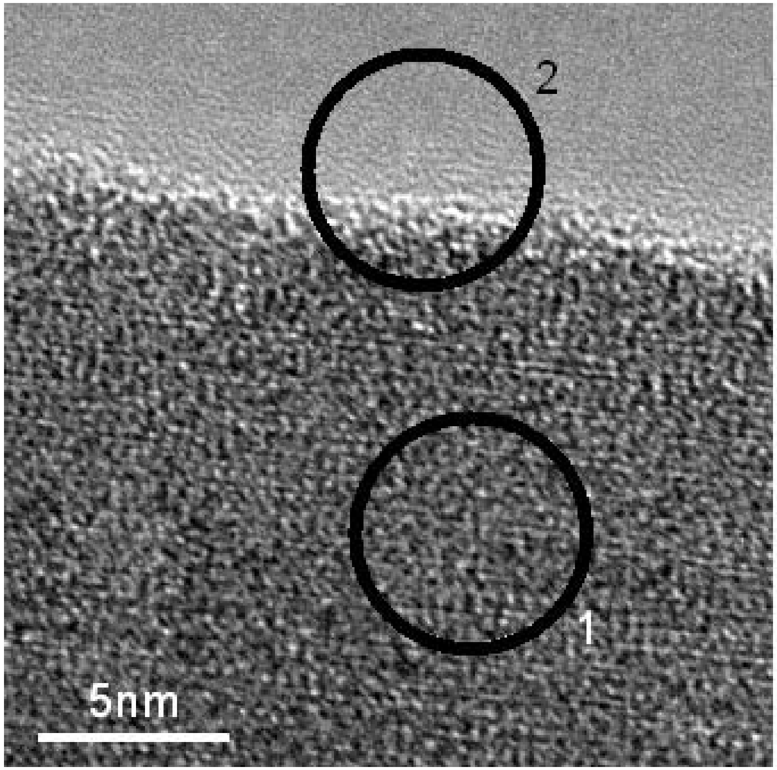
p = 0.5 mbar

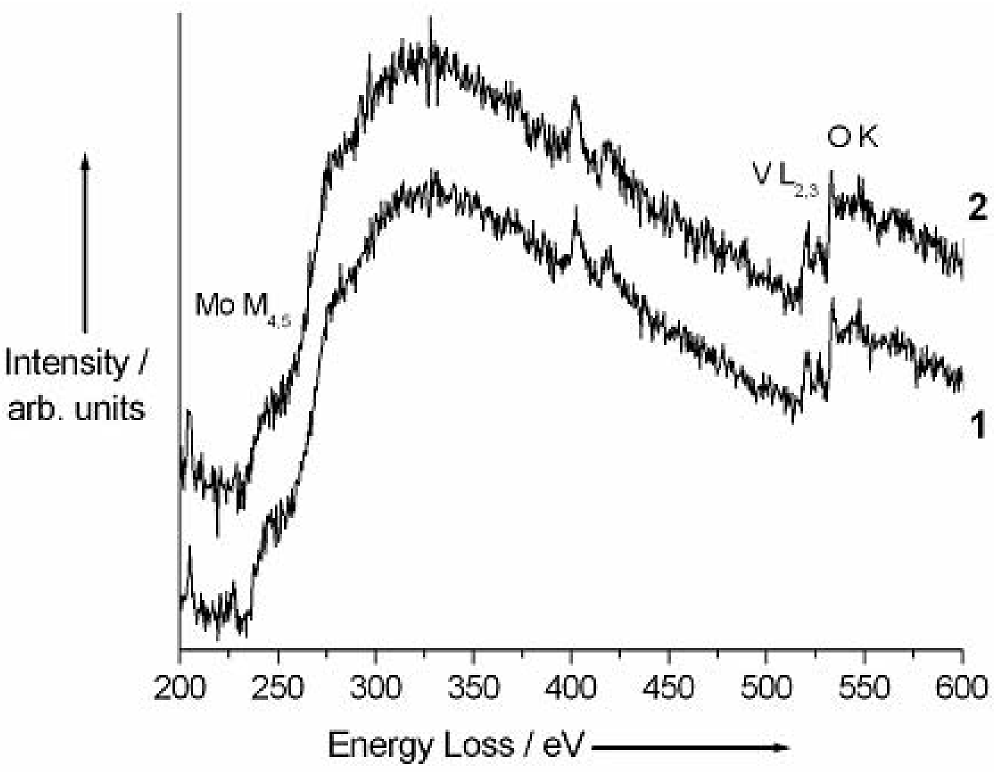
Surface texturing



Surface texturing of M1 phase viewed along the [4] zone-axis.

Composition of the structural ill-defined region





Summary

- The preparation routine for the multi metal oxide $Mo_1V_{0.30}Te_{0.23}Nb_{0.125}O_x$ used as catalyst for the selective oxidation of propane to acrylic acid was investigated.
- Anderson-type heteropoly anions $[TeM_6O_{24}]^{6-}$, M=Mo, V, and protonated decavanadate species $[H_xV_{10}O_{28}]^{(6-x)-}$ coexist in solution. These species are preserved after spray-drying.
- Calcination of this X-ray amorphous material seems to be an essentiall step, leading to a re-arrangement of the tellurate building blocks and generating amorphous precursors of the crystalline phases.
- The chemical composition of the surface of the catalyst differs from the bulk. The near surface composition of model catalysts and the oxidation state of the metals strongly depend on temperature and gas phase composition.
- Surface texturing of catalyst particles is revealed by high-resolution TEM.
- Area confined EELS measurements reveal Mo, V, and O at the surface as well as in the bulk material.

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