Investigation of the structural transformations during synthesis of MoVTeNb mixed oxide catalysts

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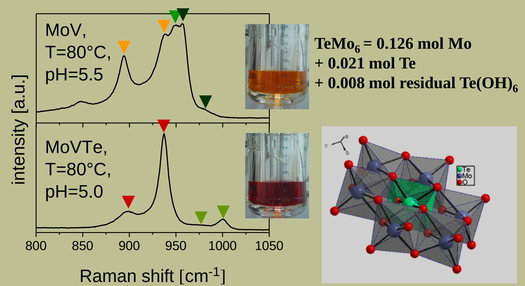
Introduction & Motivation

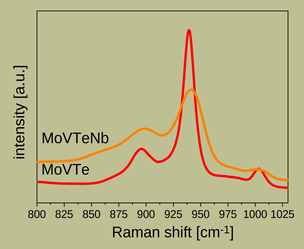
To understand the physico-chemical characteristics of a catalyst a detailed knowledge of the active structure is essential. However, heterogeneous catalysts represent a class of material of great complexity and the strategy of catalyst preparation in industry in part still remains to trial and error, leading to "mysterious" compositions and making a structure-activity analysis of the final catalyst almost impossible. Traces of many elements are present in most of the working molybdenum oxide catalysts in industry and in many cases it is still unclear whether these additional metals form active centres themselves, or act only as structural promoters for an active molybdenum oxide phase. By following each step in the preparation of a complex oxide catalyst, the structural transformations leading to the final active material can be revealed. Only if we understand the essential structural characteristics of a good catalyst we can develop new synthetic strategies to further improve systems, that are already pushed to the activity and selectivity limits after years of trial and error.

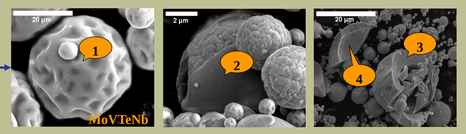


$TeMo_6$ = 0.126 mol Mo + 0.021 mol Te + 0.008 mol residual $Te(OH)_6$

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

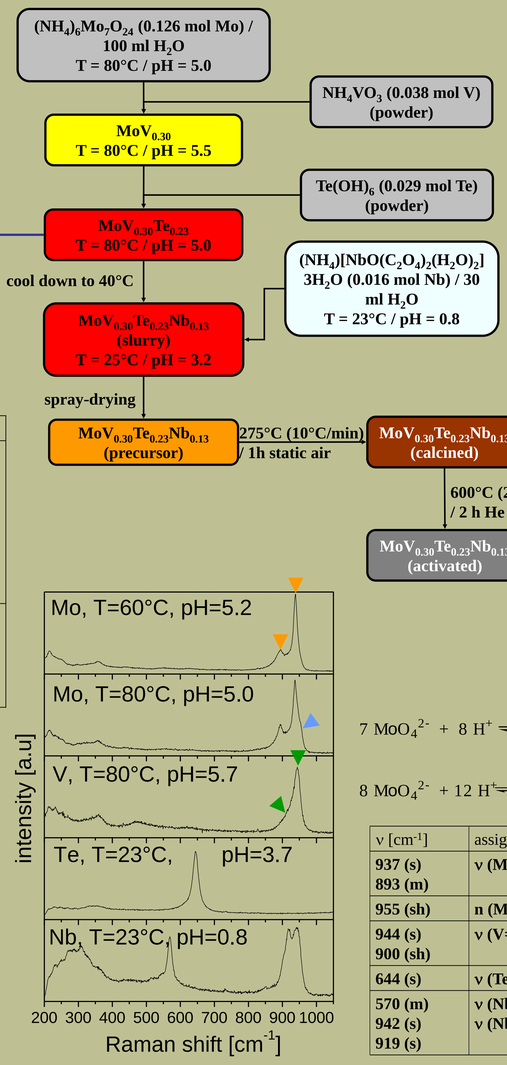
I.L. Botto et al. Mater. Chem. Phys.47 (1997) 37.

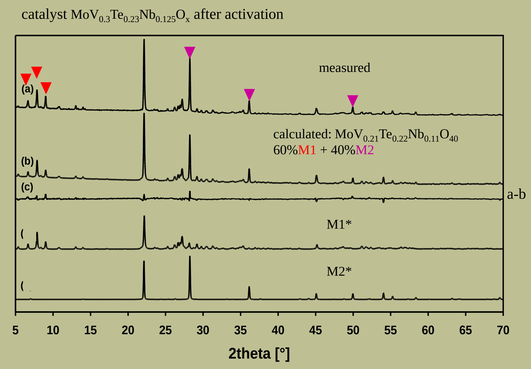




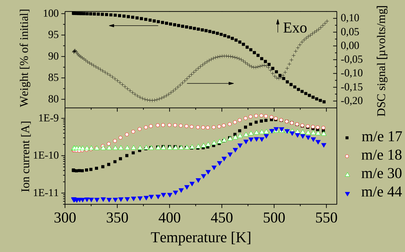
Molar ratios of elements normalized to Mo from EDX

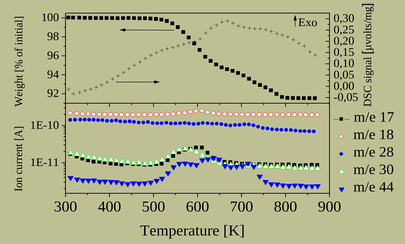
	spot 1	spot 2	spot 3	spot 4	synthesis
Mo	**1**	**1**	**1**	**1**	**1**
V	**0.30**	**0.33**	**0.28**	**0.35**	**0.3**
Te	**0.28**	**0.24**	**0.25**	**0.27**	**0.23**
Nb	**0.22**	**0.13**	**0.20**	**0.20**	**0.125**



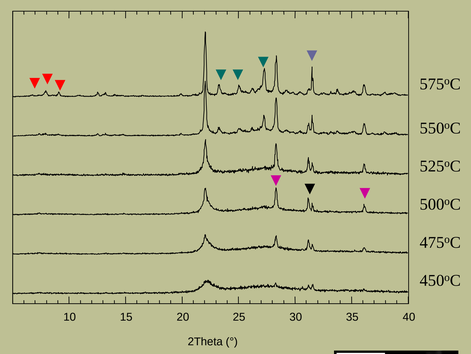


*simulation based on the model of P. De Santo et al. Z. Kristallogr. **219** (2004) 152.





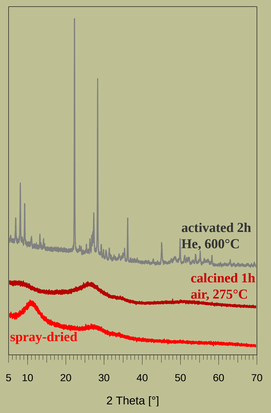
He, 2°C/min:

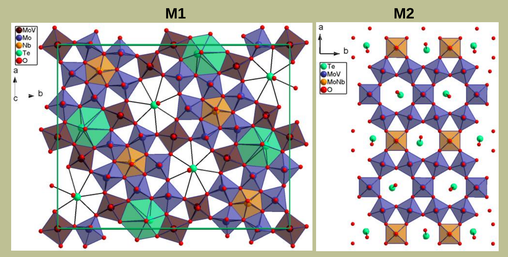


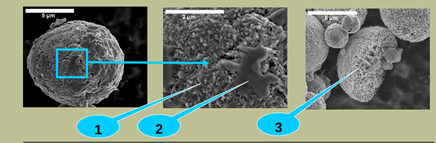
$7\ MoO_4^{2-} + 8\ H^+ \rightleftharpoons [Mo_7O_{24}]^{6-} + 4\ H_2O$

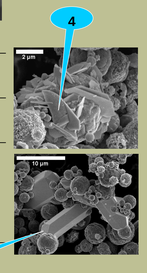
$8\ MoO_4^{2-} + 12\ H^+ \rightleftharpoons [Mo_8O_{26}]^{4-} + 6\ H_2O$

ν [cm^{-1}]	assignment
937 (s) 893 (m)	**ν (Mo=O)** $Mo_7O_{24}^{6-}$
955 (sh)	**n (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)**









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

Conclusions

An Anderson-type molybdo-tellurate is formed in the initial ternary MoVTe solution. This structural module is preserved in the spray-dried material. Hence, the role of tellurium in the MoVTeNb synthesis could be described as a structural promoter that arranges molybdenum and tellurium by forming the stable Anderson phase. This close contact of Mo and Te is fundamental for the formation of the required mixed oxide phases during calcination because it presumably prevents the formation of larger amounts of undesirable MoO_2 and MoO_3. However, the Raman spectra have shown that large fractions of vanadium and niobium as well as a small amount of tellurium are not transformed in solution and therefore hinder, after calcination and thermal treatment, the formation of a homogeneous phase composition. Some of the phases observed might be either inactive, or favour deep oxidation. The contribution of amorphous components existing on top and in between the crystalline particles has to be taken into consideration as well. Therefore, there remains much more room for optimization. In fact, a novel strategy for a knowledge based preparation routine is likely to yield better material with increased activity for partial oxidation catalysis. Finally, the stability of a specific phase under reaction conditions must be accounted for when brought into discussion.