Investigation of hydrothermally synthesized MoVTeNb mixed oxide catalysts for selective oxidation of propane to acrylic acid

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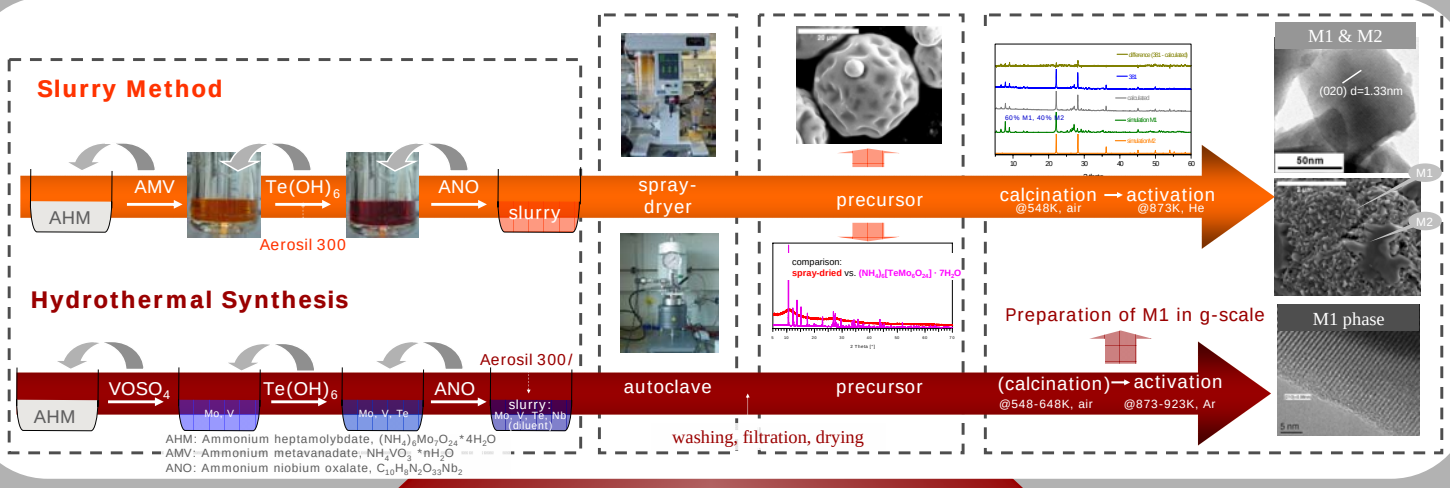
Introduction

- The selective oxidation of propane to acrylic acid has created a great interest due to economic and environmental advantages.
- Currently the best catalyst for this reaction is a Mo-V-Te-Nb [1] oxide mixture, mainly composed of two phases (M1 and M2)[2], prepared by the so-called "slurry method".
- Preparation method as well as activation conditions are crucial for the catalytic performance.
- In order to understand the functionality of MoVTeNb mixed oxide catalysts, single-phase material is needed.
- Hydrothermal synthesis is a well established method for the preparation of single-phase M1 MoVTeNb oxide catalysts[3].

Objectives

- Preparation of pure M1 phase by applying hydrothermal synthesis.
- Study of evolution of homogeneity and morphology of the materials during the different preparation steps.
- Analysis of relations between structural characteristics and catalytic activity.

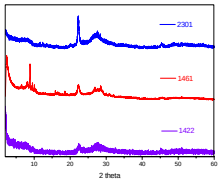
Synthesis



AHM: Ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}*4H_2O$
AMV: Ammonium metavanadate, $NH_4VO_3*nH_2O$
ANO: Ammonium niobium oxalate, $C_{10}H_8N_2O_{33}Nb_2$

SEM & EDX

Fig. 1 XRD patterns of the precursors



❖ Precursors of phase mixtures show sharper reflexes

Fig. 2 SEM & EDX of precursors materials

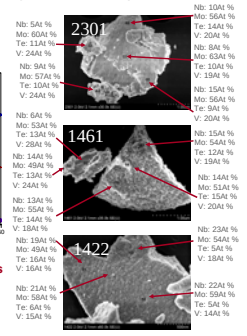


Table 1 average elemental composition of the precursors and activated materials

Precursor	Stochiometry of starting solution, [Mo](mol/l)	Mo	V	Te	Nb
2301	$Mo_1V_{0.33}Te_{0.23}Nb_{0.125}$, 0.2M	64±12.6%	17 ±6.9%	9±4.4%	10±4.7%
1461	$Mo_1V_{0.33}Te_{0.23}Nb_{0.125}$, 0.4M	53±2.5%	22 ±6.0%	14±1.3%	11±4.6%
1422	$Mo_1V_{0.25}Te_{0.23}Nb_{0.125}$, 0.256M	54 ±4.1%	16 ±1.5%	7 ±4.2%	24 ±4.5%
Catalyst	Phases				
2430	M1=55.7 % M2 29.9% Mo_5O_{14}=6.4 % $V_{0.95}Mo_{0.97}O_5$ =8.0 %	52 ±10.5%	26 ±10.3%	12 ±6.5%	10 ±6.9%
1464	M1=58% M2=42%	52 ±4.4	23 ±5.7	15 ±2.8	10±3.5
939	M1= 100%	51 ±4.3%	15 ±1.3%	11 ±2.8%	23±5.1%

❖ Phase-pure samples show significantly higher Nb content.
❖ The homogeneity decreases with increasing phase variety.
❖ These trends are not generally reflected in the precursor.

Fig. 3 SEM & EDX of activated materials

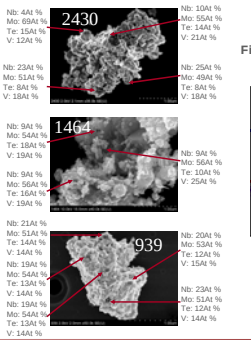
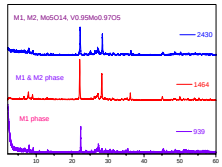


Fig.4 XRD patterns of the activated materials



✓ Phase-pure M1 material can be prepared by hydrothermal synthesis applying a Mo/V/Te/Nb molar ratio of 1/0.25/0.23/0.125.
✓ The final phase composition and chemical homogeneity of the activated catalyst is not generally determined by the nanostructure and homogeneity of the precursor.
✓ Despite phase purity, catalysts show strikingly different catalytic properties.
✓ The M1 phase is stable against reduction in 2 % hydrogen at the reaction temperature.

Catalytic Properties

Reaction conditions

- $C_3:O_2:N_2$:steam (% molar): 0.85:1.9:15.2:12
- T = 673K
- GHSV = 1200 h^{-1}
- mass balance: ± 10 %

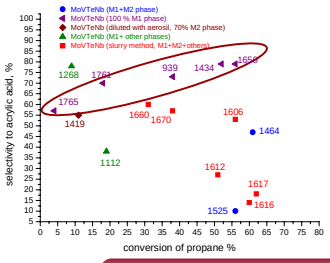


Table 2 heat treatments and catalytic test of pure M1 phase samples

Composition of initial solution: $Mo_1V_{0.25}Te_{0.23}Nb_{0.124}$

precursor code	catalyst code	heat treatments	BET (m^2/g)	X_{C3H8}	S_{AA}	Y_{AA}
929	939	(without calcination) Ar, 873K, 2 h	2.2	38	73	28
1422	1434	air, 598K, 1 h Ar, 923K, 2 h	3.9	52	79	41
	1650	air, 598K, 1 h Ar, 923K, 2 h	n.d.	56	79	44
1760	1761	air, 528K, 1 h Ar, 873K, 2 h	n.d.	18	70	13
	1765	air, 598K, 1 h Ar, 923K, 2 h	n.d.	4	57	4

❖ Activity of MoVTeNb oxides shows no correlation with a certain phase.
❖ Pure M1 phase leads to similar selectivity but to a very different conversion of propane.

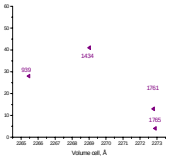


Table 3 lattice parameters of the pure M1 phase samples

Code	a / Å	b / Å	c / Å	V / Å³	Crystallite size / nm Lorentzian	Gaussian
939	21.2044(23)	26.6785(30)	4.00466(33)	2265.45(40)	75.5(27)	130(13)
1434	21.1954(36)	26.6981(49)	4.00977(50)	2269.03(64)	89.2(52)	163(32)
1765	21.2270(49)	26.7330(69)	4.00538(67)	2272.90(87)	69.0(37)	135(26)
1761	21.2320(67)	26.7445(93)	4.00255(86)	2272.8(12)	57.4(35)	115(26)

❖ There appears to be an optimal unit cell volume for high yields of acrylic acid.

TPR

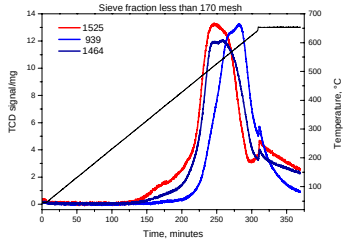


Table 4 hydrogen consumption at temperature reaction

sample	phases	moles hydrogen	mg of oxygen /mg sample
939	M1=100%	7,50	0,10
1525	M1=63% M2=37%	8,23	0,13
1464	M1=58% M2=42%	7,53	0,12

❖ At reaction temperature (673K) the degree of reduction is lower for the phase-pure M1 material.
❖ By 923K the overall hydrogen consumption is the lowest for the phase-pure M1 sample.
❖ The selectivities to acrylic acid are inversely related to the reducibility at reaction temperature.

[1] M. Hatano and A. Kayou, United States Patent No. 5,049,692, (1991).
[2] T. Ushikubo, K. Oshima, A. Kayou, M. Hatano, Stud. Surf. Sci. Catal. 112 (1997) 473.
[3] W. Ueda, K. Oshihara, Appl. Catal. A-Gen 200 (2000) 135.