

Mo-V-Te-Nb-O mixed metal oxides – “diluted” and “undiluted”- prepared by Hydrothermal Synthesis for selective oxidation of propane to acrylic acid

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Introduction

- The selective oxidation of propane to acrylic acid has provoked a great interest due to the economical and environmental advantages.
- Nowadays the best catalyst for this reaction is the $\text{Mo}_{0.1}\text{-V}_{0.33}\text{-Te}_{0.23}\text{-Nb}_{0.125}\text{-O}$ mixed metal oxide developed by Mitsubishi Chemicals.
- Application of Hydrothermal Synthesis instead of the conventional method, “Slurry method”, has the advantage of producing a material with higher crystallinity.
- Preparation method as well as activation conditions are crucial for the catalytic performance.

Objectives

Investigation of the influence of preparation parameters on structure and morphology of the materials

- type and concentration of Mo-starting material
- addition of diluent
- parameter of heat treatment

Experimental

Preparation of slurry-precursor

- AHM, VOSO_4 , $\text{Te}(\text{OH})_6$, $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_{33}\text{Nb}_2$
- $\text{Mo}_{0.1}\text{-V}_{0.33}\text{-Te}_{0.23}\text{-Nb}_{0.125}$ / $\text{Mo}_{0.1}\text{-V}_{0.25}\text{-Te}_{0.13}\text{-Nb}_{0.124}$
- $T_{\text{synthesis}} = 80^\circ\text{C}$
- diluent: Aerosil 300



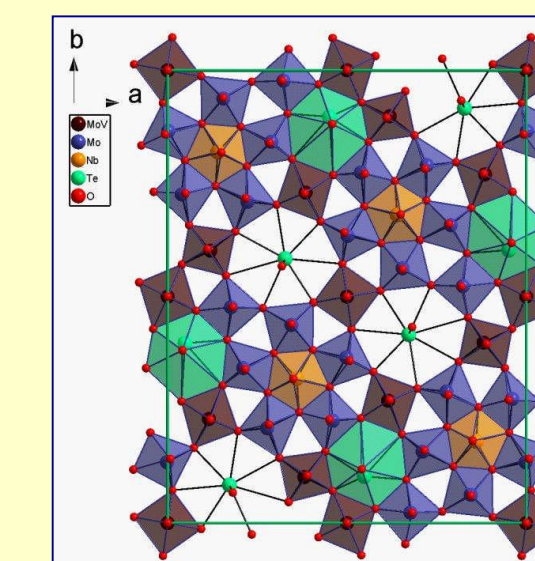
Hydrothermal Synthesis

- $T = 175^\circ\text{C}$
- $P = 13\text{ bar}$
- $t_{\text{synthesis}} = 48\text{ h}$

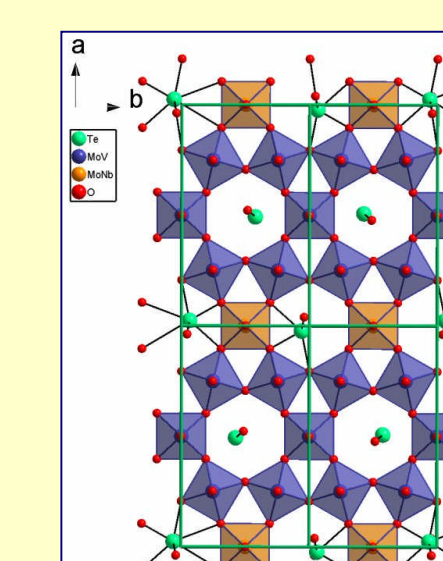
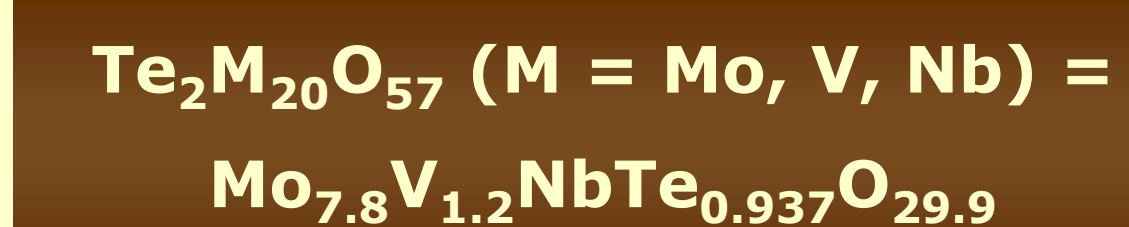
Activation (heat treatment)

- calcination (air, $T = 275$ or 325°C)
- heat treatment (N_2 , $T = 600$ or 650°C)

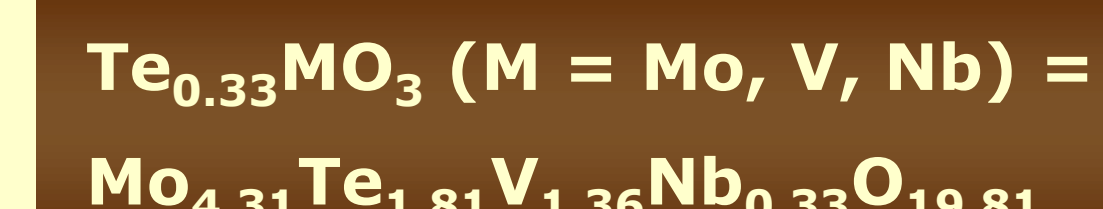
Structure



M1 phase (Ushikubo)¹⁾



M2 phase (Ushikubo)¹⁾



Present working hypotheses:

- M1 is the active phase²⁾
- phase cooperation between M1 and M2³⁾

Results

Table 1 preparation conditions and BET surface areas of the samples 939 and 1434.

$\text{Mo}_{0.1}\text{V}_{0.25}\text{Te}_{0.13}\text{Nb}_{0.124}$				
code	[Mo] (=) M	Molybdenum-compound	heat treatment	BET surface area (m^2/g) activated samples
939	0.2	AHM	in N_2 , 600°C , 2 h (without previous calcination)	2.03
1434	0.2	AHM	in air, 325°C , 1 h in N_2 , 650°C , 2 h	3.88

Table 2 preparation conditions and BET surface areas of the samples 1525, 1464 y 1419.

$\text{Mo}_{0.1}\text{V}_{0.33}\text{Te}_{0.23}\text{Nb}_{0.125}$					
code	[Mo] (=) M	Molybdenum-compound	diluent	BET surface area (m^2/g)	
				no activated samples	activated samples
1525	0.2	$\text{Mo}_{36}\text{O}_{112}^{8-}$	-	143.2	11.61
1464	0.4	AHM	-	63	5.11
1419	0.2	AHM	SiO_2 300	102.5	96.9

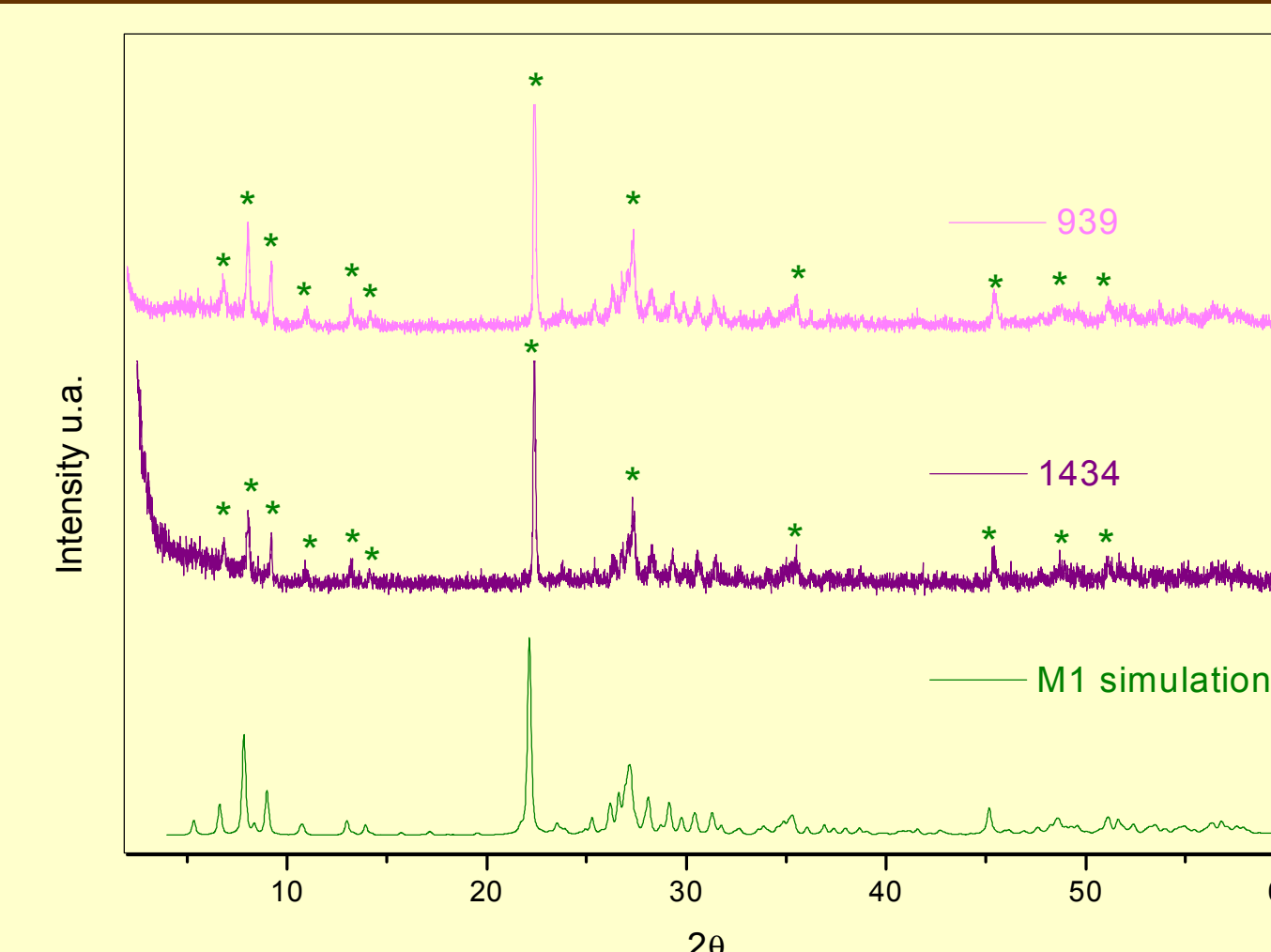


Fig.1 XRD patterns of the samples 939 and 1434
* M1 phase

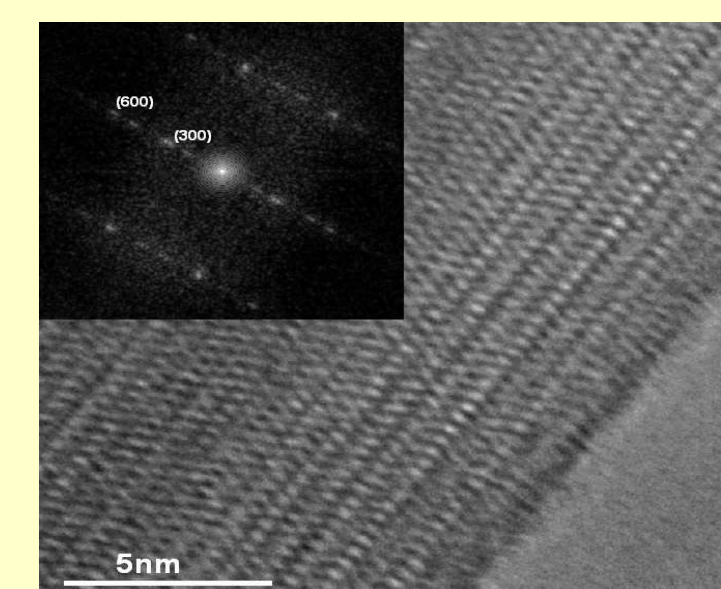


Fig. 2 HRTEM pattern of the sample 1434

The catalysts 939 and 1434, with identical precursor but activated at different temperatures, have the same pure orthorhombic structure (M1 phase). The XRD patterns of both samples show the typical peaks of the M1 phase (Fig.1). In the case of the sample 1434 this structure is also proved by the HRTEM pattern (Fig. 2).

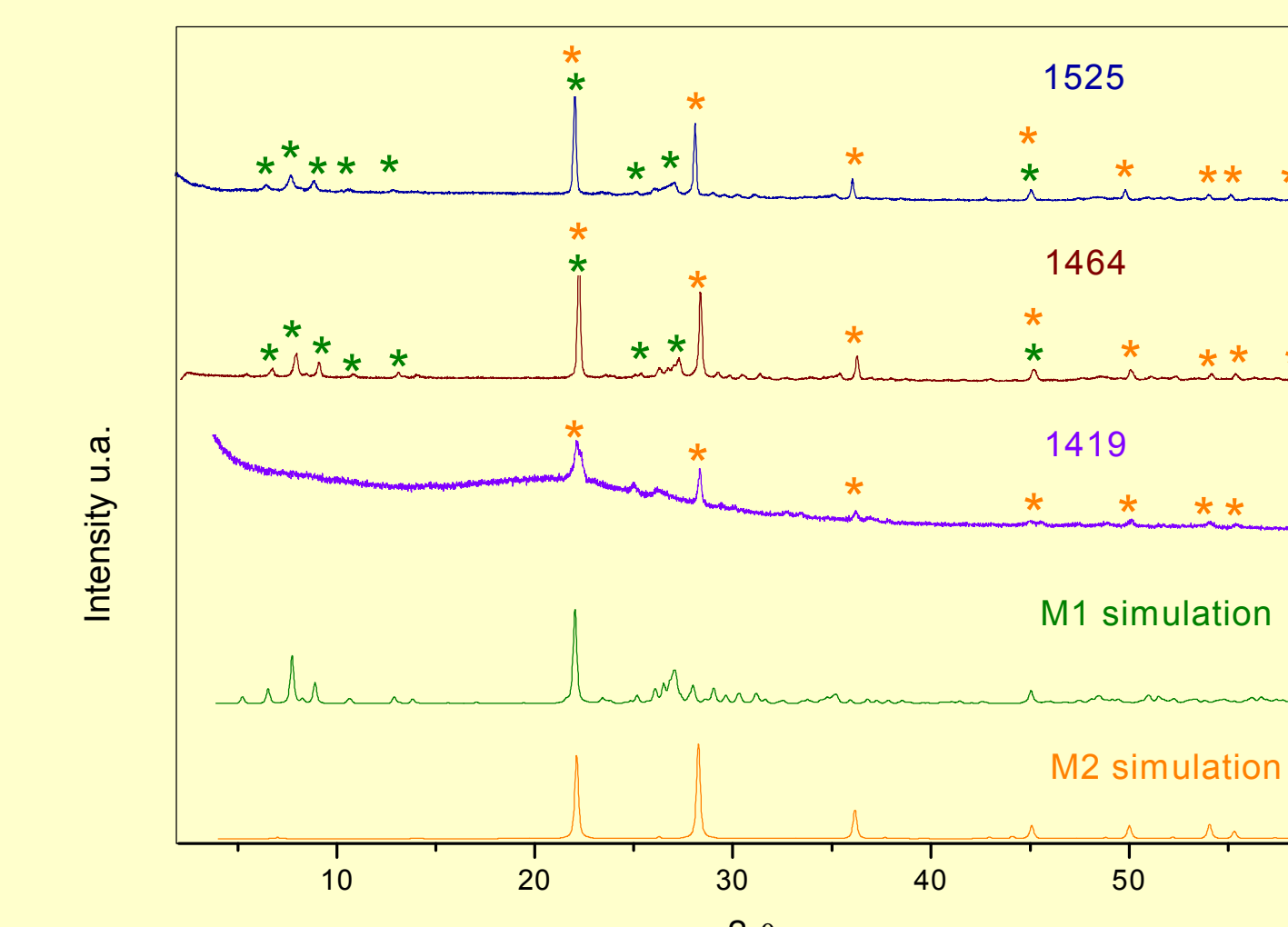


Fig.3 XRD patterns of the samples 1525, 1464 and 1419
* M1 phase, * M2 phase

M1: 62.94 %
M2: 37.06 %

M1: 57.99 %
M2: 42.01 %

M2 ~ 70 %
 $\sim \text{V}_{0.95}\text{Mo}_{0.97}\text{O}_5 \sim 30\%$

Table 3 catalytic test at 400°C and $\text{GHSV} = 1200\text{ h}^{-1}$.

code	$\text{C}_3:\text{O}_2:\text{N}_2:\text{steam}$ (% molar)	$X_{\text{C}_3\text{H}_8}$	S_{AA}	Y_{AA}
1525	0.85:1.9:15.2:12	56	10	6
1464	0.85:1.9:15.2:12	61	47	29
1419	0.85:1.9:15.2:12	11	55	6
939	0.85:1.9:15.2:12	38	73	28
1434	0.85:1.9:15.2:12	52	79	41

Conclusions

- Pure orthorhombic structure (M1 phase) has been formed in the case of the catalysts with stoichiometry $\text{Mo}_{0.1}\text{V}_{0.25}\text{Te}_{0.13}\text{Nb}_{0.124}$ independently of the different temperatures of the heat treatment (600 or 650°C).

- With different preparative parameters ($\text{Mo}_{36}\text{O}_{112}^{8-}$ as starting molybdenum-compound, higher metal concentrations, addition of a diluent) the BET surface area of the activated samples increases but a mixture of M1 and M2 phase (pseudo-hexagonal structure) is formed instead of the pure M1 phase.

- The heat treatment of the samples has a big influence on their catalytic activity. For catalysts identically synthesized (939, 1434), the one activated at higher temperature shows higher catalytic performance.

¹⁾ T. Ushikubo, K. Oshima, A. Kayou, M. Hatano, Stud. Surf. Sci. Catal. 112 (1997) 473.

²⁾ D. Vitry, Y. Morikawa, J. L. Dubois, W. Ueda, Applied Catalysis A: General 251 (2003) 411-424

³⁾ Robert K. Grasselli, Topics in Catalysis Vol.23 nos 1-4 2003