

Synthesis of single-phase M1 MoVTenbO_x catalysts – Optimization of hydrothermal reaction conditions

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Introduction

Acrylic acid is an essential intermediate in the production of various industrial and consumer products. Direct synthesis of acrylic acid by selective oxidation of propane has been intensively studied during the last decade with the objective to replace the current 2-step process starting from propene. MoVTenb oxide has been identified as the most promising catalyst for activation of propane in this reaction [1]. The mixed oxide mainly consists of two orthorhombic phases, Mo_{7.8}V_{1.2}NbTe_{0.937}O_{28.9} and Mo_{4.31}V_{1.36}Te_{1.81}Nb_{0.33}O_{19.81}, reported in the literature as M1 and M2, respectively [2]. The structural and chemical complexity of M1 seems to cope with the challenging task of propane activation, while M2 is regarded to be active and selective in oxidation of propene to acrylic acid. Correlations between phase composition and catalytic properties are discussed controversially [3-4]. A symbiosis of the two phases has been regarded to be responsible for high catalytic performance [5]. Due to the complexity of M1, preparation of phase-pure batches turned out to be not trivial. However, phase purity is an indispensable prerequisite to clarify the unique performance of M1 in propane activation by employment of surface sensitive methods and bulk characterization. In the present work, optimization of synthesis parameters for different types of autoclaves and batch sizes has been carried out assisted by microstructural, bulk and surface investigation of precursors and activated materials.

Experimental

Single-phase M1 mixed MoVTenb oxide catalysts were prepared by hydrothermal synthesis. Ammonium heptamolybdate, vanadyl sulfate, telluric acid and ammonium niobium oxalate were used as starting materials. The starting slurry was prepared by mixing the aqueous solutions of the chemicals with a Mo/V/Te/Nb atomic ratio of 1/0.25-0.33/0.15-0.23/0.124 and a molybdenum concentration of 0.26 M. Hydrothermal treatment was carried out in two different autoclaves (Table 1) at temperatures between 373 and 448 K and synthesis times between 48 and 144 h. The dark blue solid obtained was filtered, washed and dried for 16 hours at 353 K. Activation of precursor materials was carried out in N₂ at 873 or 923 K, either with or without previous calcination in air at 548 or 598 K.

Table 1: Characteristics of the autoclaves

Parameter	Autoclave 1 (A1)	Autoclave 2 (A2)
volume	200 ml	300 ml
wall material	hastelloy C276	teflon
stirring	250 rpm	no control
cooling	water cooling (1,6 K/min)	manually (6 K/min)

Results and discussion

Even though all preparative parameters (Mo/V/Te/Nb=1/0.25/0.23/0.124 and [Mo]=0.26 M) and hydrothermal conditions ($T=448$ K, $t_{\text{synthesis}}=48$ h) were maintained constant in the preparation of two catalysts by using the different autoclaves A1 and A2, the bulk structure of the Mo-V-T-Nb precursors obtained were quite different (Fig. 1a and 1b). Apparently, the nanostructure developed under hydrothermal conditions predetermines the final structure of the catalyst. After activation under inert gas at high temperatures, the precursor prepared in A1 crystallizes forming phase-pure M1 (Fig. 1c). By contrast, the precursor prepared in A2 crystallizes in a multi-phase structure (Fig. 1d). Consequently, the preparative parameters (metal stoichiometry, metal concentration) and the hydrothermal conditions (temperature, time) have been optimized in order to achieve the formation of M1 precursors by using A2. Relatively low temperature (403 K) and high synthesis time (96 h) compared to the standard hydrothermal conditions (448 K, 48 h) were acquired as the optimized parameters for M1 formation in A2. Deviating from these parameters results in reduced M1 content, which is accompanied by an increased fraction of M2 or other minority phases as shown exemplarily for different temperatures in Fig. 2. EDX analysis revealed that a significantly increased Nb content based on the metals in the precursor (20%) compared to the solution (8%) clearly indicates exclusive M1 formation.

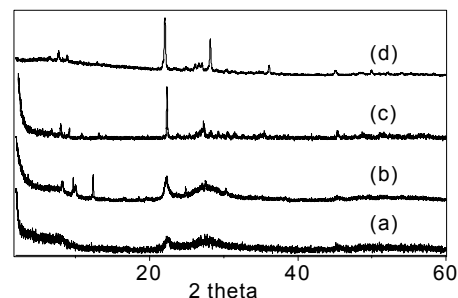


Fig.1. XRD patterns: (a) precursor of A1, (b) precursor of A2, (c) single-phase cat. (A1), (d) multi-phase cat. (A2).

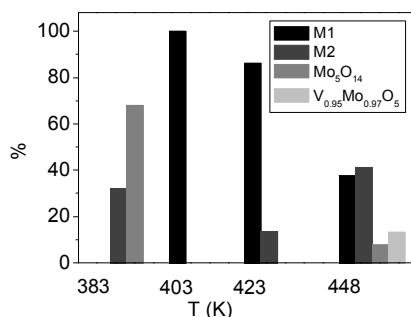


Fig. 2. M1 and M2 formation depending on temperature (96h) by using A2.

Such a high Nb content, reflected also in the activated catalysts, is twice as high as the Nb content in the reported structural analysis of the M1 phase (9%) [2], suggesting that niobium is not exclusively located in the pentagonal bipyramidal positions of the structural model. Further indication of phase purity is a high chemical homogeneity of the precursor as revealed by SEM/EDX. Irrespective of phase purity, the activated catalysts show significant inhomogeneities in chemical composition near the surface. A depth profile of the single-phase M1 material was analyzed by XPS applying different excitation energies, corresponding to a depth of 1 nm (surface) or 3 nm (bulk), respectively. The measurement was performed at room temperature under 0.3 mbar O_2 . Compared to the bulk composition in at.-% (Mo/V/Te/Nb=53/4/26/17), the upper fraction of the analyzed layer is considerably enriched in vanadium at the expense of niobium (Mo/V/Te/Nb=54/8/28/10). With respect to molybdenum and tellurium, no concentration gradients between surface and bulk were observed. The M1 structure, morphology and elemental composition was stable under the conditions of partial oxidation of propane to acrylic acid.

In summary, reproducible synthesis of single-phase M1 was achieved independent of the batch size and specific autoclave parameters, which is important for up-scaling the synthesis procedure in view of technical applications.

References

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