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## Microstructural and surface properties of phase-pure MoVTenb mixed oxide catalysts for selective oxidation of propane to acrylic acid

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**Abstract:** Crystalline MoVTenb mixed oxide catalysts composed of a single crystallographic phase have been prepared by hydrothermal synthesis and studied in the selective oxidation of propane to acrylic acid. The active surface can be regarded as a flexible arrangement of metal-oxygen polyhedra that differs chemically and structurally from the bulk phase structure.

**Keywords:** MoVTenbO<sub>x</sub> catalyst, M1, propane oxidation.

### 1. Introduction

Selective oxidation of light alkanes to aldehydes or acids requires catalysts exhibiting balanced redox and acid-base properties. Multi-metal oxides, such as MoVTenbO<sub>x</sub>, convert propane into acrylic acid with reasonably yields [1]. C-H activating and oxygen inserting abilities of the catalyst are attributed to a bronze-like phase called M1. To understand the active principle of this phase, the complex synthesis of MoVTenb mixed oxides has been investigated with the aim to develop reproducible preparation methods of phase-pure M1 as a basis for comprehensive microstructural and surface characterization in vacuum and under different reaction atmospheres, particularly in presence of steam.

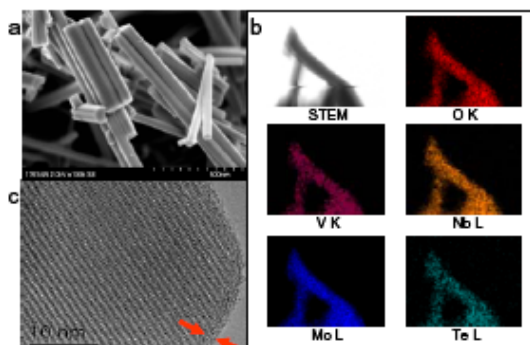
### 2. Experimental

Phase-pure M1 has been prepared by hydrothermal synthesis. The resulting catalysts were studied in the selective oxidation of propane to acrylic acid. A feed composed of C<sub>3</sub>H<sub>8</sub>/O<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O in a molar ratio of 0.85/1.9/15.2/12, at a GHSV of 1200 h<sup>-1</sup> and reaction temperatures between 623 and 693 K was applied. Transmission electron microscopy was carried out on a Philips CM 200 FEG TEM operated at 200kV. The microscope is equipped with a Gatan CCD camera for image acquisition and an EDAX Genesis EDX system. The near-surface region of phase-pure M1 (information depths between ca. 0.5 and ca. 1.5 nm) has been analyzed by X-ray photoelectron spectroscopy at a reaction temperature of 623 K in presence of the reactants (total pressure 0.3-0.5 mbar) at the synchrotron source BESSY (Berlin, Germany).

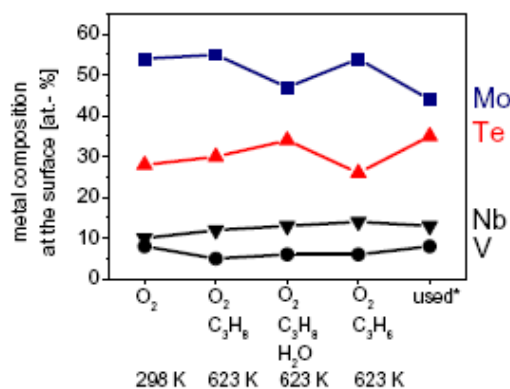
### 3. Results and discussion

Crystalline batches of phase-pure M1 have been prepared by hydrothermal synthesis applying different synthesis parameters and varying the procedures of thermal pre-treatment. Optimized synthesis conditions

with respect to temperature and time result in the formation of nano-crystalline M1 precursors possessing long-range order in the [001] direction. During subsequent heat treatment at 873-923 K in inert gas the typical needle-like crystal morphology of M1 is formed (Fig. 1a). The aspect ratio of the needles depends on the final temperature of the heat treatment. Evidently, a high degree of long-range order with respect to the metal components is necessary for the development of catalytic activity. Crystalline phase-pure M1 converts



**Figure 1.** SEM image of phase-pure M1 (a), elemental mapping of M1 needles measured by STEM/EDX (b), HRTEM image of a M1 needle viewed along the  $\langle 127 \rangle$  direction (c).



**Figure 2.** Surface composition of M1 (catalyst ID 1761) measured by in-situ XPS. \*catalyst tested in a fixed bed reactor

propane into acrylic acid with a selectivity of about 80%, whereas the propane conversion depends on the specific surface area. A substantial chemical flexibility of the M1 phase is reflected in a bulk metal content of the batches that varies in the range 51-58 at-% Mo, 12-15 at-% V, 10-15 at-% Te, and 17-23 at-% Nb. The individual needles are characterized by a very homogeneous spatial distribution of the metal components as shown by STEM/EDX (Fig. 1b). Independent of the crystal facet, the M1 surface is terminated by a structurally disordered surface layer [2] roughly 0.7 nm thick, as evidenced by HRTEM, taking into account beam damage effects by extrapolating the beam exposure time to  $t=0$  (Fig. 1c). In-situ X-ray photoelectron spectroscopic experiments reveal that the chemical composition of the near-surface region (Fig. 2) is incompatible with the M1 stoichiometry and changes in response to changes in the gas phase composition. The most pronounced effect is exerted by steam, an essential component of the feed mixture if acrylic acid is the target product of propane oxidation over MoVTenbO<sub>x</sub> catalysts.

#### 4. Conclusions

The function of MoVTenbO<sub>x</sub> catalysts in the complex transformation of propane to acrylic acid may be understood on the basis of the analysis of a single phase. Surface ensembles, which are chemically and structurally different from the bulk M1 phase are established under reaction conditions.

#### References

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