



Engineering the synthesis of MoVTeNb oxide catalysts with high stability in oxidation of propane

Annette Trunschke, Maricruz Sanchez Sanchez, Raoul Naumann d'Almoncourt, Frank Girgsdies, Robert Schlögl

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of Inorganic Chemistry, Faradayweg 4-6, 14195 Berlin, Germany, e-mail: trunschke@fhi-berlin.mpg.de

Introduction

The crystal structure M1 (Inorganic Crystal Structure Database entry 55097)¹ has been considered as essential constituent of MoVTeNb oxide catalysts for selective oxidation of C3 – C4 alkanes.^{2, 3} Chemical complexity, variability in valence state and differing site occupancy of the constituent metals account for multiple alternative surface terminations of the M1 crystals under reaction conditions, which causes insufficient reproducibility with respect to the functionality of M1 as catalyst. We have monitored the hydrothermal synthesis of the M1 phase from aqueous chemistry of precursor heteropoly anions in solution to the solid state by sampling and spectroscopic techniques (Raman and UV-vis) resulting in improved strategies to engineer a reproducible catalyst synthesis.

Experimental

MoVTeNb oxides were synthesized by hydrothermal reaction in the temperature range between 175°C and 220 °C, and reaction times between 1 h and 48 h. The starting solution contains the metals in a molar ratio of Mo/V/Te/Nb = 1/0.25/0.23/0.12. During reaction, samples of ca. 15 mL were extracted from the reactive mixture (260 mL). The suspensions obtained after hydrothermal synthesis were separated by centrifugation. The washed solid fractions were dried at 80 °C followed by a thermal treatment in Ar flow at 650 °C for 2 h. Precursors and final crystalline oxides were characterized by XRD, XRF, electron microscopy, and surface area analysis.

In-situ Raman measurements were done with a Kaiser Optics Spectrometer applying a fiber-optic probe head. In-situ DR-UV-vis spectra were measured using the spectrometer HR2000 (Oceanoptics) equipped with a fiber-optic probe R200-U-UV/Vis. The in-situ powder X-ray diffraction studies were performed in a STOE Theta/Theta diffractometer with reflection geometry (secondary graphite monochromator, Cu K α_{1+2} radiation ($\lambda = 1.5419 \text{ \AA}$), scintillation counter) equipped with an Anton Paar XRK 900 *in situ* XRD cell.

Catalytic tests were carried out in a 10-fold parallel reactor set-up designed by Integrated Lab Solutions (Berlin, Germany). Analysis of reactor effluent gas was done by on-line gas chromatography using an Agilent 7890 series GC equipped with a thermal conductivity detector and a flame ionization detector. The temperature was varied between 350°C and 390°C. A broad range of contact times (0.06 – 1.44 s g ml⁻¹) was applied. Propane feed concentration was varied between 1 and 3 %, steam content between 0 and 40 %, and O₂ feed concentration between 4.5 and 12 %.

Results and Discussion

Figure 1 shows the relative percentage of the phase M1 in the final product of hydrothermal synthesis of MoVTeNb oxides performed at different reaction times and temperatures. At short reaction times, a tetragonal phase of the M₂O₁₄-type (M=Mo,V,Nb)⁴ predominates in the product. In addition, minor amounts of the phases M2 (ICSD entry 55098)¹ and M1 are found. With increasing reaction times, the fractions of M₂O₁₄ and M2 decrease, while M1 becomes the main product. Temperatures above 190°C accelerate the transformation. Optimal hydrothermal conditions for the synthesis of phase-pure M1 in the autoclave applied in the present study are

temperatures in the range between 190°C and 210 °C and synthesis times between 6 and 20 hours. At temperatures higher than 210°C, thermodynamically more stable phases, such as VOMoO₄ are favoured.

In-situ Raman and UV-vis spectra taken during hydrothermal synthesis at synthesis temperature and autogeneous pressure revealed that mixing of reactants at 80°C leads to the precipitation of a salt of the anion [(TeO₃)₂Mo₁₂O₃₆]⁴⁻ (Raman bands at 775, 788, 809 and 968 cm⁻¹). Decomposition of this compound occurs already at 140°C, leading to intermediates in solution like [Te(Mo,V)₂O₂₄]⁷⁻ Anderson anions and the macroisopolyanion [Mo₃₆O₁₁₂]⁶⁻. As the temperature reaches 175°C, the most intense contribution in the Raman spectrum is centered at 835 cm⁻¹. This band is typically assigned to M-O-M vibrations in nanocrystalline M₂O₁₄.⁵ The appearance of shoulders at 800, 894, 880 and 325 cm⁻¹ with increasing reaction time is attributed to the formation of a nanocrystalline M1 precursor.⁶

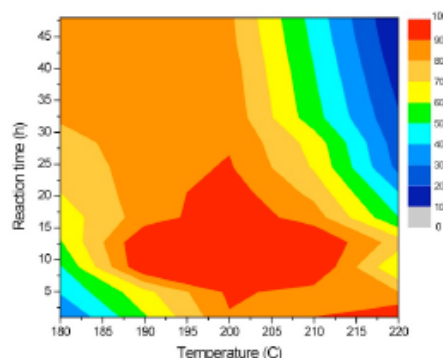


Figure 1. Fraction of the phase M1 (wt.-%) in the final reaction product of hydrothermal synthesis at various times and temperatures.

Within the determined window of hydrothermal reaction conditions for the synthesis of phase-pure M1, the chemical composition of the product varies, resulting in M1 catalysts with high V and Nb content and modified catalytic properties. Phase pure and crystalline M1 shows structural and catalytic stability over at least 1200 hours time on stream under a wide range of reaction conditions in selective oxidation of propane to acrylic acid as evidenced by a kinetic study and in-situ X-ray diffraction.

Conclusions

Systematic investigation of the hydrothermal synthesis of MoVTeNb oxide including the application of in-situ spectroscopic techniques provides insight into the formation mechanism of the M1 phase under hydrothermal conditions allowing better control of the catalytic properties of the resulting phase-pure mixed oxide.

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