

# The influence of calcination conditions on phase formation in MoVTeNbOx catalysts: A simultaneous in-situ-XRD/Raman study

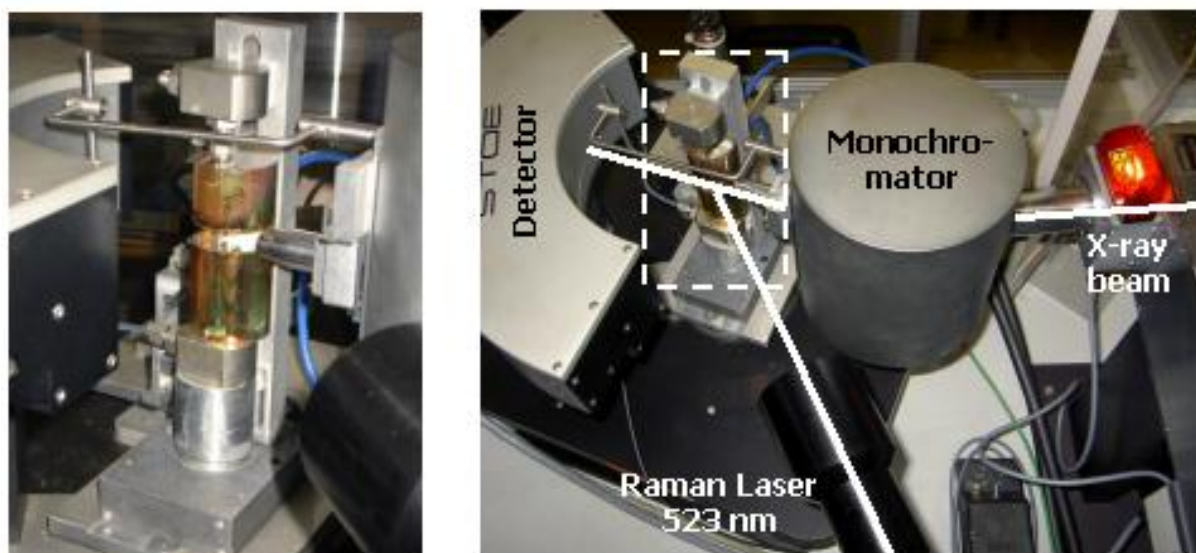
M. Schneider, S. Winkler, A. Brückner

Leibniz-Institut für Katalyse, D-12489 Berlin, Richard – Willstätter – Str. 12, Germany

## Motivation and Objectives

Mixed MoVNbTe oxides are versatile catalysts for the selective oxidation of lower alkanes and olefins. Their catalytic performance depends sensitively on the presence of target phases such as  $[\text{Mo}(\text{V},\text{Nb})]_5\text{O}_{14}$ , M1 and M2, while  $\text{MoO}_3$  and  $\text{MoO}_2$  are detrimental and have to be suppressed. Tailoring the calcination process to the preferential and reproducible formation of the target phases is highly desirable but difficult to realize since their crystallization is governed, apart from the synthesis of the precursor, by the calcination conditions, the influence of which is not sufficiently known so far.

Therefore, we have performed a systematic in-situ-XRD/Raman study to elucidate the influence of gas atmosphere, heating rate, final temperature and reactor geometry on the formation of different phases within the MoVNbTe oxide system. Special benefits derive from the simultaneous coupling of both techniques due to their different sensitivity, which is realized in a simple laboratory setup. Thus, Raman spectroscopy can detect nanocrystalline XRD-silent  $\text{MoO}_3$  while XRD visualizes the formation of reduced phases more sensitively than Raman.



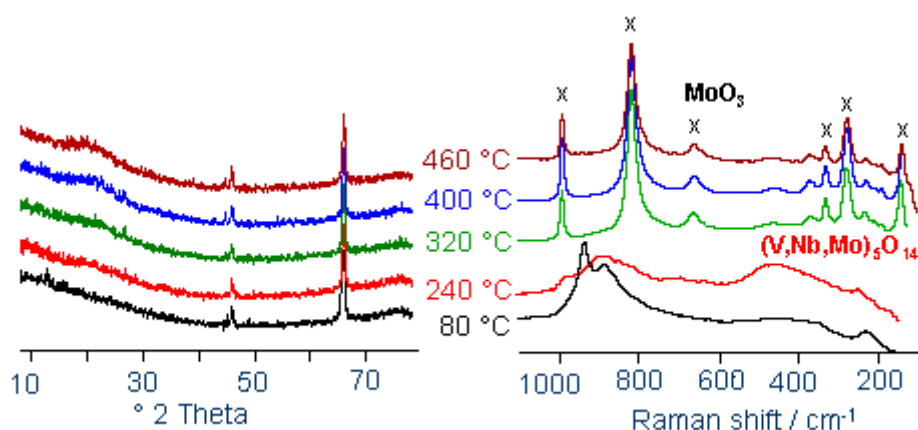
**Fig. 1.** Setup for simultaneous in-situ XRD/Raman-spectroscopy

## Results

Two MoVNbTe oxide precursors of similar composition but different preparation history (hydrothermal synthesis vs co-precipitation + spray drying) were analyzed in a capillary fixed-

bed reactor (Fig. 1) between 20 and 460 °C in flowing air or nitrogen using heating rates of 1, 5 and 10 K/min as well as isothermal hold intervals at different temperatures. For comparison, selected calcination runs were also performed in shallow bed geometry to test the influence of the reactor geometry.

Generally, calcination in air flow favours the formation of undesired MoO<sub>3</sub> in nanocrystalline XRD-silent form at all heating rates and already at temperatures as low as 320 °C (Fig. 2). Pronounced MoO<sub>3</sub> formation was also observed at low heating rate (1 K/min) in N<sub>2</sub> flow and in runs with several isothermal holds between 300 and 400 °C, which were necessary for recording the XRD patterns. In contrast, heating with 10 K/min in N<sub>2</sub> leads to crystalline MoO<sub>2</sub> when performed in the capillary reactor, while the target phases [Mo(V,Nb)]<sub>5</sub>O<sub>14</sub>, M1 and M2 are preferentially formed when the sample is calcined in a shallow bed. In this case, NH<sub>3</sub> which is liberated upon decomposition of the precursor can quickly leave the sample while in the capillary reactor, it is passed by the carrier gas through the whole catalyst bed. This causes deeper reduction. This result illustrates the crucial influence of the reactor cell when monitoring the calcination of such sensitive materials like MoVNbTe oxides. Further limitations of the capillary reactor relate to the low signal-to-noise ratio connected with measurements in transmission mode due to the thickness of the capillary. To overcome these problems, a simultaneous in-situ-XRD/Raman setup with shallow bed geometry for XRD measurements in reflection mode is currently under construction.



**Fig.2.** Simultaneous XRD/Raman-measurement during heating in air flow with 1 K/min.

## Conclusions

Comprehensive investigations of the influence of calcination conditions (temperature, heating rate, gas atmosphere, reactor geometry) on the formation of different phases in the MoVNbTe oxide system were performed. The target phases [Mo(V,Nb)]<sub>5</sub>O<sub>14</sub>, M1 and M2 are preferentially formed at moderate heating rates in inert gas and shallow bed geometry. Calcination in air favours MoO<sub>3</sub> crystallization already at rather low T while fast heating in a capillary tube reactor leads to deep reduction and MoO<sub>2</sub> formation. Special benefits derive from the simultaneous coupling of XRD and Raman due to their different sensitivity for various phases.