



Synthesis of transition metal molybdates and tungstates and their reactivity in alkane and alkene oxidation

M. Jastak, R. Schlögl, A. Trunschke

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Introduction

Ni-Co molybdates have been reported to show high selectivities for propene in the oxidative dehydrogenation of propane [1, 2]. Other binary transition metal molybdates of the type $M\text{TeMoO}_6$ ($M = \text{Co}$) were reported to be active and selective in the partial oxidation of propene to acrolein and acrylic acid [3]. With the addition of Mn, sodium tungstate, which is structurally related to the corresponding molybdate, also showed considerable activity in the oxidative coupling of methane [4]. In this work, we have synthesized phase-pure $M\text{MoO}_4$ and $M\text{TeMoO}_6$ ($M = \text{Co}, \text{Mn}$) catalysts via a hydrothermal route and analysed their properties.

Experimental

Phase-pure $\alpha\text{-MnMoO}_4$ was prepared by hydrothermal synthesis at 190°C for 20 h (13 bar pressure). Initially two solutions were prepared containing $\text{Mn}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4 \times 2\text{H}_2\text{O}$. The latter solution had a Molybdenum concentration of 0.2 mol/l. Both solutions were mixed together at room temperature in the autoclave-vessel to form a white slurry (pH = 5.4). The suspension obtained after hydrothermal synthesis was filtered and washed with distilled water (150 ml). The solid fraction was dried at 100°C for 16 h.

Results

The $\alpha\text{-MnMoO}_4$ phase prepared by hydrothermal synthesis was analyzed by X-ray diffraction (XRD), X-ray fluorescence (XRF), nitrogen adsorption, thermal analysis, temperature-programmed reduction (TPR) and electron microscopy. Figure 1 shows the X-ray diffraction pattern of the prepared $\alpha\text{-MnMoO}_4$ sample after drying. It is clearly observable that the $\alpha\text{-MnMoO}_4$ -phase is the only crystalline phase that is obtained after hydrothermal synthesis. Also no traces of Na have been found by XRF-analysis of this sample. The as-prepared $\alpha\text{-MnMoO}_4$ -phase shows a high thermal stability for temperatures of 500 °C and a quite high specific surface area of around 87 m²/g. The TPR-profile of the synthesized $\alpha\text{-MnMoO}_4$ -phase (see Figure 2)

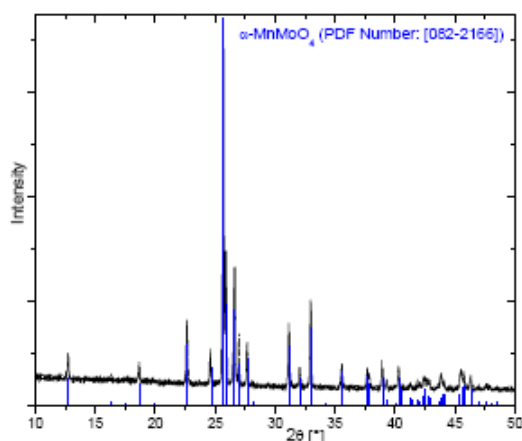


Figure 1: X-Ray powder diffractogram of phase-pure α -MnMoO₄ prepared by hydrothermal synthesis

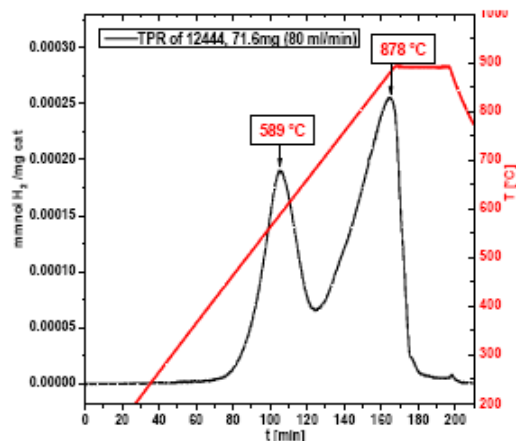


Figure 2: TPR-measurement of the synthesised α -MnMoO₄-phase (5.24% H₂ in Ar, 80ml/min)

shows an onset of H₂ consumption at about 410°C and two major peaks of H₂-consumption with their maximums at about 590 and 880°C respectively. The onset and temperatures of maximum H₂ consumption are substantially lower than those reported for catalysts synthesized by other preparation routes [5]. This could be due to a higher oxygen mobility of the samples synthesized by the relatively fast and mild hydrothermal route.

Conclusions

The here presented results show an example of a simple synthesis route to molybdate- and tungstate phases, which could potentially be used in selective oxidation reactions. The high thermal stability, the relatively high specific surface area, and increased oxygen mobility concluded from TPR-measurements of the synthesized sample suggest the applicability of hydrothermally synthesized molybdates and tungstates as catalysts in selective oxidation reactions of alkanes and alkenes.

References

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