



In situ investigation of tungsten as structure-directing agent during formation of Mo_5O_{14} type partial oxidation catalysts

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Introduction

Crystalline, single phase $(\text{MoVW})_5\text{O}_{14}$ and $(\text{MoV})_5\text{O}_{14}$ constitute three-dimensional model systems for the more complex technical catalysts for the partial oxidation of propene to acrolein and acrylic acid [1]. In the mixed oxide systems little is known about the cooperation of the different metal centers and their role for the stabilization of the active phase [2,3,4]. Here we report in situ X-ray absorption spectroscopy (XAS) and in situ X-ray diffraction (XRD) studies on the bulk structural evolution of $(\text{MoVW})_5\text{O}_{14}$ and $(\text{MoV})_5\text{O}_{14}$ under reducing, oxidizing, and catalytic conditions. At temperatures above ~ 600 K the molybdenum oxide material obtained is active for the selective oxidation of propene in presence of gas phase oxygen.

Experimental

Combined in situ XRD/MS experiments were performed on a STOE Theta/theta diffractometer equipped with a XRK900 high temperature cell and a mass spectrometer for on-line gas analysis. Combined transmission XAS/MS experiments were performed at the Mo K and W L_{III} edge at beamline X1 at HASYLAB in a flow-through reactor at atmospheric pressure with total flow of 30 ml/min.

The thermal stability of $(\text{MoVW})_5\text{O}_{14}$ and $(\text{MoV})_5\text{O}_{14}$ was studied by XRD and XAS in heating experiments from RT to 773 K in different atmospheres. For isothermal redox experiments $(\text{MoVW})_5\text{O}_{14}$ and $(\text{MoV})_5\text{O}_{14}$ were heated in helium to 773 K. At 773 K the atmosphere was isothermally switched to 10% propene and XRD or XAS scans were measured until complete reduction of the sample. The resulting materials were re-oxidized in 20% oxygen and XRD or XAS scans were collected until no reduced phase was detectable.

Results and Discussion

In situ XRD experiments of $(\text{MoVW})_5\text{O}_{14}$ and $(\text{MoV})_5\text{O}_{14}$ in 5% propene and 10% oxygen showed the stability of the Mo_5O_{14} type structure under catalytic conditions up to 773 K. This result is confirmed by in situ XAS measurements at the Mo K edge.

EXAFS refinement of the model structure to the RDF showed decreasing amplitudes with increasing temperature due to a higher thermal disorder. Metal-metal distances increase with higher temperature as a result of lattice expansion.

Long range order evolution (XRD) during heating experiments in 10% propene revealed reduction of $(\text{MoV})_5\text{O}_{14}$ and $(\text{MoVW})_5\text{O}_{14}$ into a monoclinic MoO_2 type phase starting at ~ 673 K. For the short range order the same result is obtained with XAS.

In situ XRD showed that the $(\text{MoVW})_5\text{O}_{14}$ structure is stable in 20% oxygen up to 773 K. Conversely, the $(\text{MoV})_5\text{O}_{14}$ catalyst slowly undergoes a phase transformation into MoO_3 type material starting at 723 K.

Isothermal redox experiments also showed reduction of $(\text{MoV})_5\text{O}_{14}$ and $(\text{MoVW})_5\text{O}_{14}$ into the MoO_2 type structure. Moreover, re-oxidation in 20% oxygen results in the initial Mo_5O_{14} phase. In case of the reduced MoV oxide re-oxidation leads to a MoO_3 type structure with vanadium incorporated.

$(\text{MoV})_5\text{O}_{14}$ material exhibits a lower stability against gas phase oxygen compared to tungsten containing $(\text{MoVW})_5\text{O}_{14}$. The onset temperature of the phase transformation of $(\text{MoV})_5\text{O}_{14}$ in oxygen into the MoO_3 type structure is close to the onset temperature of the reduction of $(\text{MoV})_5\text{O}_{14}$ in 10% propene. Hence, oxygen mobility in the oxide systems is a prerequisite for both reduction to MoO_2 type materials and decomposition and oxidation to MoO_3 . Apparently, the presence of tungsten in the oxide systems stabilizes the Mo_5O_{14} type structure and prevents complete oxidation even under conditions of sufficient oxygen mobility and high oxidation potential of the gas phase. Furthermore, tungsten in the MoO_2 type material obtained from the reduction of $(\text{MoVW})_5\text{O}_{14}$ exerts a structure-directing effect under oxidizing conditions resulting in the re-formation of the Mo_5O_{14} type structure. In contrast to the MoO_2 type material obtained from reduction of $(\text{MoV})_5\text{O}_{14}$, re-oxidation of tungsten containing MoO_2 to $(\text{MoVW})_5\text{O}_{14}$ corroborates the redox-stabilizing effect of tungsten in molybdenum based catalysts under partial oxidation reaction conditions.

References

- [1] S. Knobl, G. A. Zenkovets, G. N. Kryukova, O. Ovsitser, D. Niemeyer, R. Schlögl, G. Mestl, *Journal of Catalysis* 215 (2003) 177.
- [2] O. Ovsitser, Y. Uchida, G. Mestl, G. Weinberg, A. Blume, J. Jäger, M. Dieterle, H. Hibst, R. Schlögl, *Journal of Molecular Catalysis A* 185 (2002) 291.
- [3] Y. Uchida, G. Mestl, O. Ovsitser, J. Jäger, A. Blume, R. Schlögl, *Journal of Molecular Catalysis A: Chemical* 187 (2002) 247.



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[4] R.K. Grasselli, Catalysis Today 49 (1999) 141.