



Structure stabilizing effect of tungsten in mixed molybdenum oxides with Mo_5O_{14} -type structure

E. Rödel^a, O. Timpe^a, A. Trunschke^a, G.A. Zenkovets^b, G.N. Kryukova^b, R. Schlögl^a, T. Ressler^{c*}

^aFritz-Haber-Institut der MPG, Department of Inorganic Chemistry, Faradayweg 4-6, D-14195 Berlin, Germany

^bBoreskov Institute of Catalysis, Novosibirsk 630090, Russia

^cTechnische Universität Berlin, Institute of Chemistry, Sekr. C2, Strasse des 17. Juni 135, D-10623 Berlin, Germany

* Corresponding author: e-mail Thorsten.Ressler@TU-berlin.de, Tel.: +49 30 8413 3192; fax: +49 30 314 21106

Available online 16 May 2007.

Abstract

Bulk structural properties of single phase crystalline $(\text{Mo}_{0.91}\text{V}_{0.09})_5\text{O}_{14}$ and $(\text{Mo}_{0.68}\text{V}_{0.23}\text{W}_{0.09})_5\text{O}_{14}$ materials were investigated using in situ X-ray diffraction and in situ X-ray absorption spectroscopy at three metal edges. Temperature programmed experiments in reducing (propene) and oxidizing (oxygen) atmosphere and isothermal redox experiments at 773 K revealed differences in the bulk properties of the two phases studied. A structure stabilizing effect of tungsten in $(\text{MoVW})_5\text{O}_{14}$ under oxidizing conditions was found. Moreover, tungsten centers in a (MoVW) dioxide material exert a structure-directing effect towards re-oxidation to a Mo_5O_{14} -type structure.

Keywords: Mo_5O_{14} -type structure; X-ray diffraction; XAS; Redox properties

1. Introduction

Molybdenum containing metal oxide catalysts selectively oxidize propene to acrylic acid. The ability of molybdenum to occur in various coordination geometries gives rise to a high structural diversity of the mixed transition metal oxides. Catalytically active sites in these mixed oxides may be stabilized by characteristic structural motifs induced by the cationic composition [1,2]. Small amounts of V or W in Mo oxides may result in the formation of (MoV) oxides and (MoVW) oxides that crystallize in the tetragonal Mo_5O_{14} structure [3]. This structure has been suggested to represent the motif of the active phase for the selective oxidation of acrolein into acrylic acid [4,5]. The Mo_5O_{14} structure corresponds to a pentagonal column phase with a narrow phase width and an open structure with five- and six-fold channels parallel to the c-axis [6]. Several possible compositions with various cations stabilizing the Mo_5O_{14} structure have been described in the literature [7,8,9,10,11,12,13].

Here, $(\text{MoVW})_5\text{O}_{14}$ and $(\text{MoV})_5\text{O}_{14}$ have been prepared as crystalline single phase materials exhibiting catalytic activity in the selective oxidation of propene [14,23]. In situ X-ray diffraction (XRD) and in situ X-ray absorp-

tion spectroscopy (XAS) combined with online gas phase analysis are used to explore the structural evolution of these single phase Mo_5O_{14} -type materials under varying reactive atmospheres. XRD and XAS give access to both the long range order of the materials and the local structure around the metal centers in these mixed oxides.

2. Experimental

2.1. Preparation

The precursor of the $(\text{MoVW})_5\text{O}_{14}$ material was prepared as described previously [14]. Ammonium heptamolybdate (AHM) ($c = 0.963$ mol/L) and ammonium metatungstate (AMT) ($c = 0.27$ mol/L) were dissolved in bidistilled water at 353 K. V_2O_5 was dissolved in an aqueous solution of 1.93 mol/L oxalic acid at 353 K (vanadyl oxalate aqueous solution $c = 0.379$ mol/L). The solutions were mixed in a 2 L batch and heated to 353 K for 1 h. After spray-drying of the mixed solutions the resulting material was calcined for 2 h in synthetic air at 623 K and the heated for 2 h in helium at 713 K. The metal content in

the $(\text{MoVW})_5\text{O}_{14}$ phase amounted to 68 mol-% Mo, 23 mol-% V, and 9 mol-% W.

The $(\text{MoV})_5\text{O}_{14}$ material was prepared as follows. An aqueous solution of vanadyl oxalate was obtained by dissolving 7.7 mg V_2O_5 and 15.9 mg oxalic acid in 132 ml water. The resulting blue solution was mixed with a solution of 200 mg AHM in 500 ml water at 353 K. After stirring at this temperature for 1 h, the solution was spray-dried. The spray-dried powder was treated in helium at 773 K for 4 h followed by dissolution of impurities in 1 mol/L ammonia solution at 313 K for 5 min. Subsequently, the resulting material was heated in helium to 773 K for 4 h. The metal content in the $(\text{MoV})_5\text{O}_{14}$ phase amounted to 91 mol-% Mo and 9 mol-% V.

2.2. In situ X-ray diffraction

Combined in situ XRD/MS experiments were performed on a STOE Theta/Theta diffractometer (secondary Si (111) monochromator, Cu $\text{K}\alpha$ radiation). 30–80 mg of the powdered $(\text{MoVW})_5\text{O}_{14}$ or $(\text{MoV})_5\text{O}_{14}$ were used. The diffractometer was equipped with a XRK 900 high temperature cell from Anton Paar. All measurements were conducted under atmospheric pressure in flowing atmosphere at 100 ml/min. The gas phase composition at the cell outlet was analyzed on line with a mass spectrometer (Omnistar, QMS Pfeiffer). Ex situ XRD measurements were performed on a STOE STADI-P diffractometer with a Ge (111) primary monochromator and a position sensitive detector. Phase analysis was performed using the DIFFRAC PLUS evaluation software [15]. Structure refinement was conducted using the TOPAS 3 software package [16] and single crystal structure data from the inorganic crystal structure database (ICSD [17]).

2.3. In situ X-ray absorption spectroscopy

XAS measurements were performed in the transmission mode at the Mo K edge (19.999 keV), W L_{III} (10.204 keV) edge, and at the V K edge (5.465 keV) at beamline X1 and E4 at the Hamburger Synchrotronstrahlungslabor, HASYLAB, respectively. The experiments were conducted in a flow reactor of ~ 4 ml volume at atmospheric pressure in 30 ml/min flowing reactants. The gas phase composition at the cell outlet was analyzed on line with a mass spectrometer (Omnistar, QMS Pfeiffer). 30 mg BN were mixed with about 8 mg sample, ground, and pressed at a force of 1 ton into a pellet of 5 mm in diameter. The resulting edge jump amounted to $\Delta\mu \sim 1$ at the Mo K edge, $\Delta\mu \sim 0.2\text{--}0.3$ at the V K edge, and $\Delta\mu \sim 0.8$ at the W L_{III} edge. Data processing and analysis was performed with the software package WinXAS 3.1 [18]. The photon energy was calibrated to a spectrum

of the corresponding metal. First order polynomials were chosen for background subtraction. Third order (Mo K edge) or second order (V K edge, W L_{III} edge) polynomials were used for normalization. Average valences of vanadium were determined from the pre-edge peak height [19]. The average valence of molybdenum was obtained from analyzing the Mo K edge position according to a previously reported procedure [20].

2.4. Reduction and re-oxidation experiments

The structural evolution of $(\text{MoVW})_5\text{O}_{14}$ and $(\text{MoV})_5\text{O}_{14}$ was investigated during temperature-programmed and isothermal experiments. Temperature-programmed XAS and XRD measurements were conducted in reducing (10 % propene) and oxidizing (20 % oxygen) atmospheres in the temperature range from 300 K to 773 K. A heating rate of 3 K/min (XAS) or 0.4 K/min (XRD, average heating rate) was used. Prior to the isothermal redox experiments, $(\text{MoVW})_5\text{O}_{14}$ and $(\text{MoV})_5\text{O}_{14}$ were heated in helium to 773 K at a heating rate of 10 K/min. The structural stability of the materials in helium at 773 K was confirmed by XRD and XAS. Subsequently, the atmosphere was switched to 10 % propene or 10 % hydrogen at 773 K and XRD or XAS scans were measured until the sample was completely reduced. The resulting materials were re-oxidized in 20% oxygen at 773 K and XRD or XAS scans were measured until complete re-oxidation. In addition, XRD and XAS scans were measured at 300 K before and after the temperature-programmed and isothermal experiments.

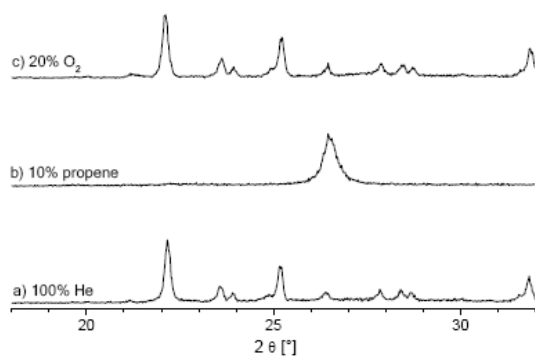
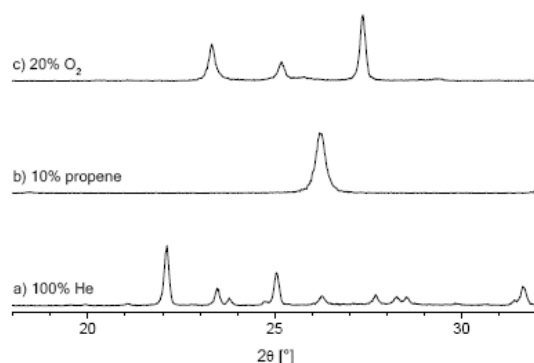
3. Results

3.1. Characterization of $(\text{MoVW})_5\text{O}_{14}$ and $(\text{MoV})_5\text{O}_{14}$

Phase purity of the $(\text{MoV})_5\text{O}_{14}$ and the $(\text{MoVW})_5\text{O}_{14}$ materials used was verified by XRD [21]. Lattice constants obtained from the refinement of the tetragonal Mo_5O_{14} structure (ICSD [27202]) to the experimental XRD pattern are given in Table 1. No detectable amounts of amorphous materials were found in a XRD analysis of a mixture of 50 % $(\text{MoVW})_5\text{O}_{14}$ and 50 % $\alpha\text{-Al}_2\text{O}_3$ as internal standard. The characteristic XRD pattern of the Mo_5O_{14} structure is given in Figure 1a. Transmission electron microscopy investigations showed only the Mo_5O_{14} -type structures in $(\text{MoVW})_5\text{O}_{14}$ and $(\text{MoV})_5\text{O}_{14}$.

Table 1: Lattice constants from XRD refinement of tetragonal $(\text{MoVW})_5\text{O}_{14}$ and $(\text{MoV})_5\text{O}_{14}$ based on ICSD [27202]

	$(\text{MoV})_5\text{O}_{14}$	$(\text{MoVW})_5\text{O}_{14}$
a [Å]	22.88	22.76
c [Å]	4.00	3.99

**Figure 1:** In situ XRD of sample $(\text{MoVW})_5\text{O}_{14}$ during redox experiment: heating in helium to 773 K, isothermal at 773 K reduction in 10% propene, re-oxidation in 20% oxygen.**Figure 2:** In situ XRD of $(\text{MoV})_5\text{O}_{14}$ during redox experiment: heating of sample in helium to 773 K, isothermal at 773 K reduction in 10% propene, re-oxidation in 20% oxygen.

3.2. Redox properties of $(\text{MoVW})_5\text{O}_{14}$ and $(\text{MoV})_5\text{O}_{14}$

In situ X-ray diffraction

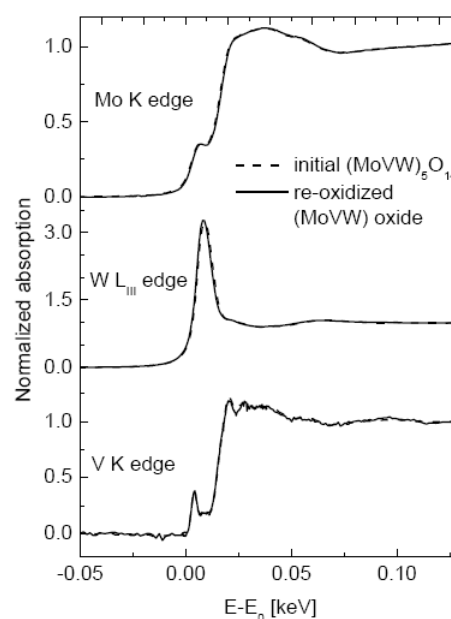
The Mo_5O_{14} -type structure of $(\text{MoVW})_5\text{O}_{14}$ and $(\text{MoV})_5\text{O}_{14}$ was stable during heating in helium to 773 K (Figure 1a and Figure 2a). Under reducing conditions in 10% propene at 773 K, the $(\text{MoV})_5\text{O}_{14}$ and $(\text{MoVW})_5\text{O}_{14}$ materials were completely transformed into monoclinic MoO_2 -type structures (Figure 1b and Figure 2b). Lattice constants obtained from a refinement of a MoO_2 model structure (ICSD [23722]) to the patterns of the MoO_2 -type phases are given in Table 2. Compared to the (MoVW) dioxide, the lattice constants of the (MoV) dioxide material

that contains less vanadium showed an expansion of the a-axis, shortening of the b- and c-axis, and an increased unit cell volume. Upon switching to 20% oxygen at 773 K, the (MoVW) dioxide was re-oxidized and the resulting oxide exhibited the Mo_5O_{14} -type structure of the initial $(\text{MoVW})_5\text{O}_{14}$ material (Figure 1c). Conversely, re-oxidation of the (MoV) dioxide in 20% oxygen at 773 K resulted in an orthorhombic MoO_3 -type structure (Figure 2c). No intermediate Mo oxide phases were detectable in the XRD patterns during reduction and re-oxidation.

Temperature-programmed XRD measurements in 10% propene yielded an onset of reduction of the $(\text{MoVW})_5\text{O}_{14}$ material to a monoclinic MoO_2 -type structure at 723 K. Conversely, reduction of $(\text{MoV})_5\text{O}_{14}$ to a monoclinic MoO_2 -type structure started already at 673 K. During temperature programmed thermal treatment of $(\text{MoVW})_5\text{O}_{14}$ in 20% oxygen, the Mo_5O_{14} -type structure was stable up to 773 K. No oxidation or decomposition was observed. Conversely, the Mo_5O_{14} -type structure of $(\text{MoV})_5\text{O}_{14}$ was stable during treatment in 20% oxygen only below 723 K. Above 723 K the Mo_5O_{14} -type structure of $(\text{MoV})_5\text{O}_{14}$ slowly decomposed and was oxidized into a MoO_3 -type structure.

In situ XAS

Very similar Mo K near-edge spectra of $(\text{MoVW})_5\text{O}_{14}$ and $(\text{MoV})_5\text{O}_{14}$ are indicative of molybdenum centers in a similar local structural coordination in both materials. The same holds for the local structure around the V centers in $(\text{MoVW})_5\text{O}_{14}$ and $(\text{MoV})_5\text{O}_{14}$ (Figure 4). Compared to the V K edge spectra of VO_2 and V_2O_5

**Figure 3:** XANES spectra measured at the Mo K edge, W L_{III} edge, and V K edge of initial $(\text{MoVW})_5\text{O}_{14}$ and re-oxidized (MoVW) oxide.

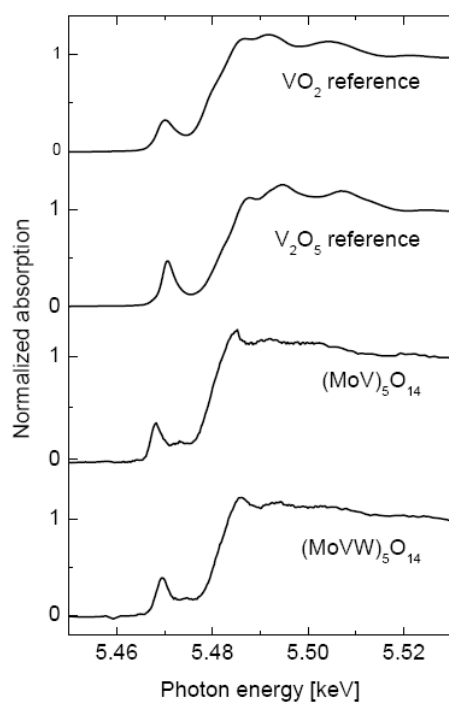


Figure 4: XANES spectra taken at V K edge of the initial (MoVW)₅O₁₄ and (MoV)₅O₁₄ compared to references VO₂ and V₂O₅.

references, the average valence of the V centers in (MoVW)₅O₁₄ and (MoV)₅O₁₄ amounts to about 4.5. Near-edge spectra at the Mo K, V K, and W L_{III} edges of the initial (MoVW)₅O₁₄ are shown in Figure 3. Moreover, Figure 3 depicts the near-edge spectra of the (MoVW)₅O₁₄ material obtained after a cycle of reduction in propene and re-oxidation at 773 K. Apparently, a similar local and electronic structure of all metal centers is found in the initial and the re-oxidized (MoVW)₅O₁₄ material. Conversely, the Mo K (Figure 5) and V K near-edge spectra of the initial (MoV)₅O₁₄ and the re-oxidized material indicate a different local structure around the molybdenum and vanadium centers. Moreover, compared to the spectrum of a MoO₃ reference (Figure 5), the Mo centers in the MoO₃-type structure of the re-oxidized (MoV) oxide exhibit a slightly reduced average valence (~ 5.8) and a different local structure. The latter maybe due to the incorporation of vanadium centers in the MoO₃-type structure. Furthermore, XRD analysis of the material obtained from re-oxidizing the (MoV) dioxide yielded a minor amount of a mixed Mo_xV_{2-x}O₅ phase (e.g. 0.5 % Mo_{0.56}V_{1.44}O₅ ICSD [24338]).

Mo centers in the as-prepared (MoVW)₅O₁₄ and (MoV)₅O₁₄ materials exhibited an average valence of less than 6 (~ 5.8). A similarly reduced average valence was observed for the Mo centers in the Mo₅O₁₄-type structure obtained from re-oxidizing the (MoVW) dioxide. Conversely, the Mo centers in the MoO₃-type structure obtained from re-oxidizing the (MoV) dioxide exhibit an average valence of about 6 (Figure 5). The local structure and the average valence of the Mo centers in the (MoVW)

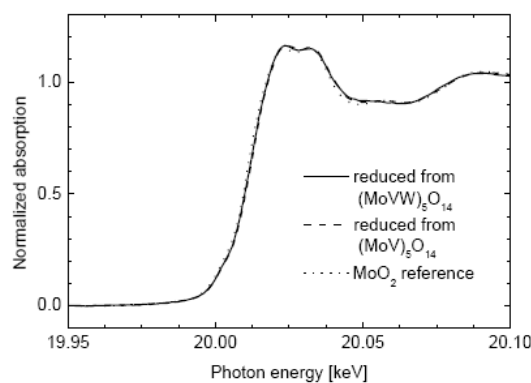


Figure 5: XANES spectra taken at the Mo K edge of re-oxidized (MoV) oxide after reduction in 10% propene compared to a MoO₃ reference.

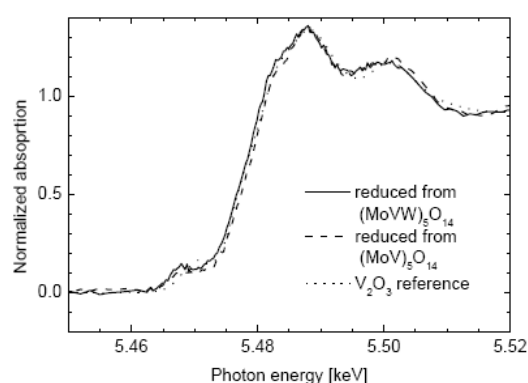


Figure 6: XANES spectra of (MoVW) oxide and (MoV) oxide at the Mo K edge after reduction in 10% propene compared to a MoO₂ reference.

dioxide and the (MoV) dioxide were similar to those of the Mo centers in MoO₂ (Figure 6). Slight differences are indicative of the incorporation of V and W in the corresponding MoO₂-type structures. The V K near-edge spectra of the dioxides obtained from reducing the corresponding Mo₅O₁₄-type oxides in propene at 773 K are depicted in Figure 7. Apparently, the average valence and the local structure of the V centers in the dioxide materials is similar to those of the V centers in V₂O₃.

Mo K near-edge spectra measured during temperature programmed treatment of (MoVW)₅O₁₄ and (MoV)₅O₁₄ in 10 % propene showed an onset of transformation into a MoO₂-type structure at a temperature of ~ 685 K. Conversely, V K and W L_{III} near-edge spectra measured during treatment of (MoVW)₅O₁₄ and (MoV)₅O₁₄ in 10 % propene exhibited an onset of structural changes at ~ 650 K. In particular, a decrease in the characteristic V K pre-edge peak height at ~ 650 K was observed. This is indicative of an onset of reduction of the V centers in the Mo₅O₁₄-type structures prior to a detectable reduction of the Mo centers. The detailed EXAFS analysis of the structural changes occurring during thermal treatment of the Mo₅O₁₄-type materials is underway.

4. Discussion

4.1. Influence of vanadium on electronic and geometric structure

Partially reduced vanadium centers in selective oxidation catalysts are assumed to enhance the hydrogen abstraction from hydrocarbon reactants. Accordingly, in the Mo_5O_{14} -type metal oxides investigated, the V centers exhibit an average valence of less than 5 (Figure 4). During thermal treatment under reducing conditions, the V centers are reduced prior to the Mo or W centers. This may be in agreement with a participation of the V centers in the active site of Mo_5O_{14} -type catalysts for selective oxidation. Conversely, the W centers in the mixed oxide catalysts may rather play a structural role than being involved in the catalytic cycle. The (MoVW) dioxide and (MoV) dioxide obtained from reduction of the Mo_5O_{14} -type materials exhibit a reduced average valence of the V centers (Figure 7) compared the Mo centers (Figure 6). This is in agreement with previous reports on the average valence of V centers in vanadium oxides doped with up to 10 % molybdenum [22]. There, the authors did not detect changes in the Mo average valence but reduction of vanadium to preserve electro neutrality of the materials.

The long-range structural data presented indicate an influence of the V centers on the geometric structure of the Mo_5O_{14} -type materials studied. (MoVW) $_5\text{O}_{14}$ and (MoV) $_5\text{O}_{14}$ were prepared with different amounts of vanadium (i.e. 23 % and 9 %). Accordingly, a decrease in the lattice constants (Table 1) and the volume of the unit cell was found with an increasing V content. Moreover, the distortion of the dioxide phases obtained from reduction of the Mo_5O_{14} -type materials from the nearly rutile type MoO_2 also increases with increasing V content (Table 2). In agreement with Vegard's law, the smaller size of the vanadium centers compared to Mo and W results in a reduced unit cell volume of the mixed oxides. Hence, (MoVW) dioxide possesses a smaller unit cell volume than (MoV) dioxide.

4.2. Stabilizing effect of tungsten in Mo_5O_{14} -type structures

(MoV) $_5\text{O}_{14}$ and (MoVW) $_5\text{O}_{14}$ were transformed into a monoclinic MoO_2 -type phase (Figure 1 and Figure 2) during thermal treatment under reducing conditions (10 % propene) at about 670 K and 720 K, respectively. During treatment under oxidizing conditions (20 % oxygen), the Mo_5O_{14} -type structure of (MoVW) $_5\text{O}_{14}$ was stable at 773 K. Conversely, the (MoV) $_5\text{O}_{14}$ material slowly undergoes a phase transformation into MoO_3 -type material starting at 723 K. Apparently, the (MoVW) $_5\text{O}_{14}$ material exhibited a higher stability under reducing and oxidizing conditions compared to the tungsten-free (MoV) $_5\text{O}_{14}$ material. The onset temperature of the transformation of (MoV) $_5\text{O}_{14}$ in oxygen into the MoO_3 -type structure is close to the onset

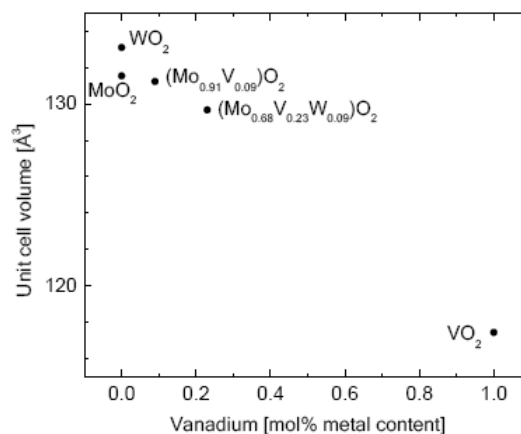


Figure 7: XANES spectra of (MoVW) oxide and (MoV) oxide at the V K edge after reduction in 10% propene compared to a V_2O_5 reference.

Table 2: Lattice constants from XRD refinement of monoclinic (MoVW) dioxide and (MoV) dioxide based on ICSD [23722]

	(MoV) dioxide	(MoVW) dioxide
a [Å]	5.69	5.63
b [Å]	4.79	4.84
c [Å]	5.56	5.61
β [°]	121.17	121.00

temperature of the reduction of (MoV) $_5\text{O}_{14}$ in propene. On the one hand, the oxygen mobility in the oxide materials is a prerequisite for both, reduction to the MoO_2 -type phase and oxidation to the MoO_3 -type phase. On the other hand, tungsten in the (MoVW) $_5\text{O}_{14}$ material stabilizes the Mo_5O_{14} -type structure and prevents complete oxidation, even under conditions of sufficient oxygen mobility and a high oxidation potential of the gas phase.

The stabilizing and structure directing effect of tungsten in the (MoVW) oxide is particularly apparent in the re-oxidation behavior of the corresponding (MoVW) dioxide. The tungsten centers in the MoO_2 -type material obtained from reducing (MoVW) $_5\text{O}_{14}$ exert a strong structure-directing effect under oxidizing conditions. Eventually, re-oxidation of the (MoVW) dioxide leads to the reformation of the Mo_5O_{14} structure. It has been frequently reported, that the Mo_5O_{14} -type structure can be obtained from thermal treatment of suitable molecular mixed metal precursors [14]. The corresponding reaction proceeds through a series of polycondensation steps resulting in the three-dimensional Mo_5O_{14} structure. Here we have shown for the first time that it is possible to transform the tetragonal (MoVW) $_5\text{O}_{14}$ material into a monoclinic MoO_2 -type structure, and to then re-oxidize the (MoVW) dioxide into the Mo_5O_{14} -type structure. This striking ability is most likely due to the single cation position in the monoclinic structure which does not provide a driving force for further cation rearrangement. Further structural studies on the un-

derlying mechanism of this solid-gas reaction are under way.

Similar to our (MoVW)₅O₁₄ material, the reduction and re-oxidation properties of a (MoVNb)₅O₁₄ system as a suitable model catalyst have been recently discussed [23]. The (MoVW)₅O₁₄ material studied here combines suitable redox properties with a sufficient catalytic performance [24]. Therefore, it can be used as a model system for the redox behavior of the more complex MoVTeNb oxides applied in the selective oxidation of propane.

5. Summary

Bulk structural properties and stabilities of crystalline single phase (Mo_{0.91}V_{0.09})₅O₁₄ and (Mo_{0.68}V_{0.23}W_{0.09})₅O₁₄ phases were investigated under reducing and oxidizing reaction conditions. A stabilizing effect of tungsten in the (MoVW)₅O₁₄ sample under oxidizing conditions was found. Additionally, tungsten centers in

a (MoVW) dioxide material obtained from reducing (MoVW)₅O₁₄ exert a pronounced structure-directing effect under re-oxidation conditions. The effect of tungsten centers on the particular bulk structural properties of (MoVW)₅O₁₄ may account for the structural promoting effect of tungsten in selective oxidation.

Acknowledgement

HASYLAB/Hamburg is acknowledged for providing beamtime for this work.

References

1. G. Mestl, Ch. Linsmeier, R. Gottschall, M. Dieterle, J. Find, D. Herein, J. Jäger, Y. Uchida, R. Schlögl, *Journal of Molecular Catalysis A: Chemical* 162, (2000) 463
2. M. Dieterle, G. Mestl, J. Jäger, Y. Uchida, H. Hibst, R. Schlögl, *Journal of Molecular Catalysis A: Chemical* 174 (2001) 169
3. S. Breiter, M. Estenfelder, H.-G. Lintz, A. Tenten, H. Hibst, *Applied Catalysis A* 134 (1996) 81
4. 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
5. V. M. Bondareva, T. V. Andrushkevich, G. I. Aleshina, L. M. Plyasova, L. S. Dovlitova, O. B. Lapina, D. F. Khabibulin, A. A. Vlasov, *React. Kinet. Catal. Lett.* 87, 2 (2006) 377
6. Peter De Santo, Douglas J. Buttrey, Robert K. Graselli, Claus G. Lugmair, Anthony, F. Volpe, Brian H. Toby, Thomas Vogt, *Topics in Catalysis* Vol. 23, 1-4 (2003)
7. L. Kihlberg, *Arkiv Kemi* 21, 40 (1963) 427
8. N. Yamazoe, L. Kihlberg, *Acta Cryst. B* 31 (1975) 1666
9. T. Ekström, M. Nygren, *Acta Chem. Scand.* 26 (1972) 1827
10. T. Ekström, *Acta Chem. Scand.* 26 (1972) 1843
11. T. Ekström, *Materials Research Bulletin* 7 (1972) 19
12. T. Ekström, M. Nygren, *Acta Chemica Scandinavica* 26, 5 (1972) 1836
13. L. Kihlberg, *Acta Chem. Scand.* 23 (1969) 1834
14. S. Knobl, G. A. Zenkovets, G. N. Kryukova, O. Ovsitser, D. Niemeyer, R. Schlögl, G. Mestl, *Journal of Catalysis* 215 (2003) 177
15. DIFFRAC plus Evaluation Package release (2003)
16. TOPAS Version 2.1 Bruker AXS
17. Inorganic Crystal Structure Database, Fachinformationszentrum (FIZ) Karlsruhe, Germany
18. T. Ressler, *J. Synchrotron Rad.* 5 (1998) 118
19. J. Wong, F. W. Lytle, R. P. Messmer, D. H. Maylotte, *Phys. Rev. B* 30, 10 (1984) 5596
20. T. Ressler, J. Wienold, R.E. Jentoft, T. Neisius, *Journal of Catalysis* 210 (2002) 67
21. E. Rödel, R. Schlögl, T. Ressler, in preparation.
22. F. Haaß, A. H. Adams, T. Buhrmester, G. Schimanke, M. Martin, H. Fuess, *PCCP* 5 (2003) 4317
23. M. Roussel, M. Bouchard, E. Bordes-Richard, K. Karim, S. Al-Sayari, *Cat. Today* 99, 1-2 (2005) 77
24. E. Rödel, S. Knobl, R. Schlögl, T. Ressler; in preparation