# In situ investigations of the formation of a $(MoVW)_5O_{14}$ type mixed molybdenum oxide catalyst

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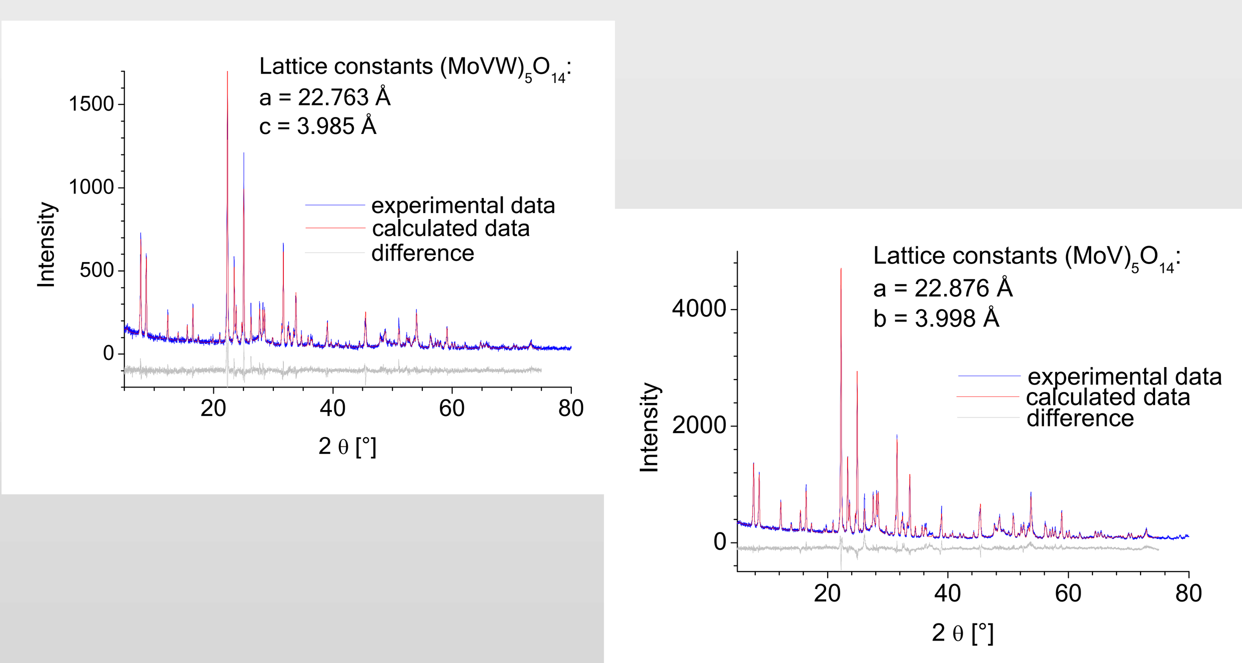
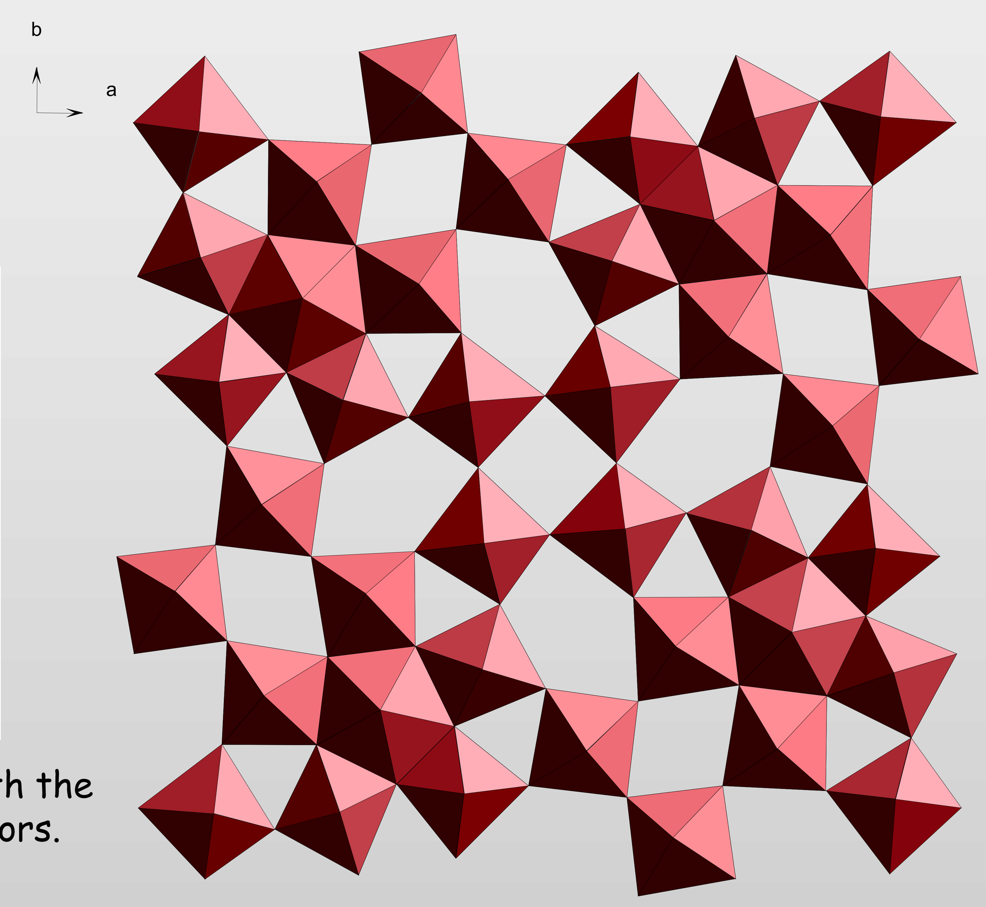
**Goals:**
- Development & characterization of model systems for catalysts industrially applied in the selective oxidation of propene
- Elucidation of the function of different metal centers for phase formation and stabilization

**Approach:**
- $Mo_5O_{14}$ type structure as model system for more complex mixed oxide catalysts
- Studies on the local structures of the metal centers during phase evolution of the $Mo_5O_{14}$ structure
- Investigations on the stability of the $Mo_5O_{14}$ phase

**Methods:**
- In situ XRD ($CuK_\alpha$) in Bragg-Brentano geometry, Bühler HDK combined with MS
- In situ XAS at HASYLAB, Hamburg. In situ XAS cell combined with online monitoring of gas phase composition by MS



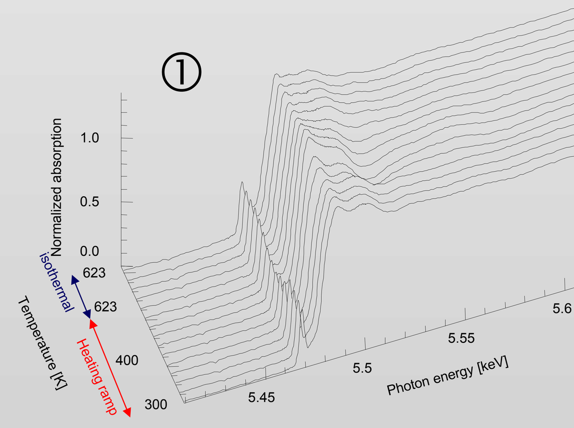
The long range ordered structure of the bulk is completely described with the $Mo_5O_{14}$ structure using refined lattice constants and site occupancy factors. The site occupancy factors indicate site preference for the different elements incorporated.

The metals contained in the catalyst under investigation have different characteristic coordination geometry and atomic radii. They may prefer one or the other coordination geometry of oxygen ligands and (de-)stabilize the short metal-metal distances at the pentagonal bipyramidal block units.

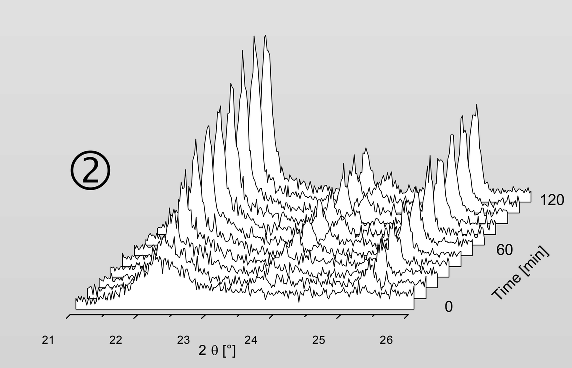
## Formation of (MoVW) mixed oxide

The precursor to the $(Mo_{0.68}V_{0.23}W_{0.09})_5O_{14}$ was prepared by spray-drying of aqueous solutions of ammonium heptamolybdate, ammonium metatungstate and vanadyl oxalate.

Heating in ① synthetic air to 623 K followed by ② heating in helium to 713 K.




The XANES at the V K edge. The pre-edge peak height goes through a minimum at 500 K. This is attributed to a minimum of the average valence of V in the precursor.



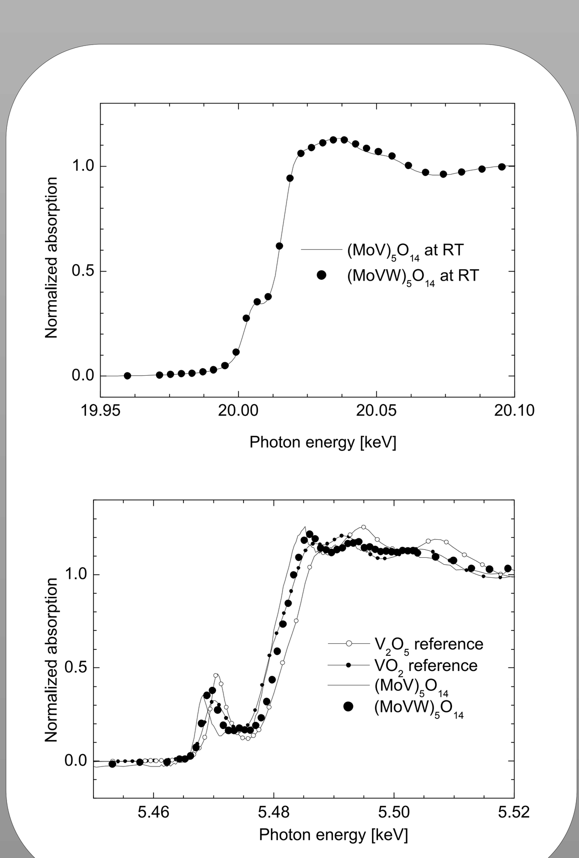

Increasing crystallinity of the (MoVW) oxide material at 773 K in helium.

## Isothermal redox experiment at 773 K

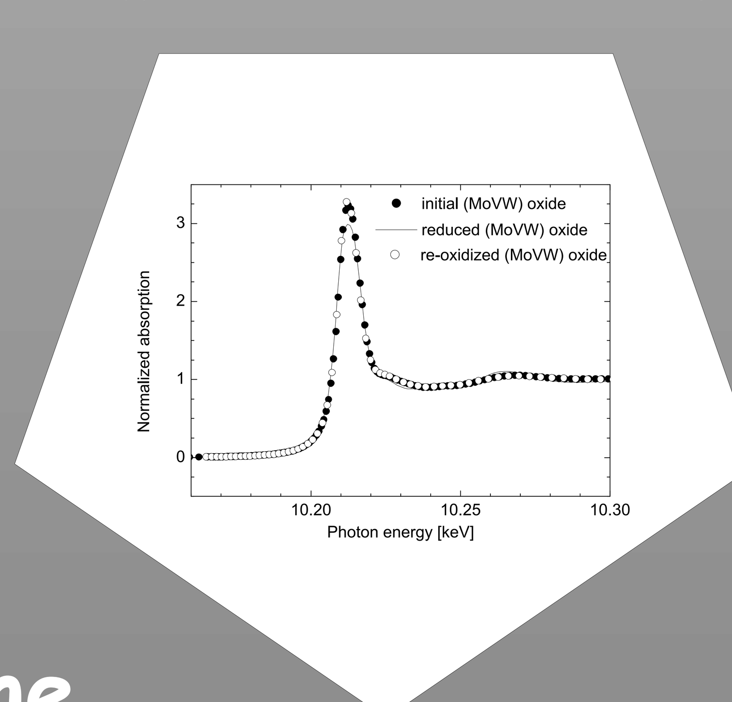
Heating of sample to 773 K in inert, at 773 K reduction in 10% propene followed by re-oxidation in 20% oxygen.

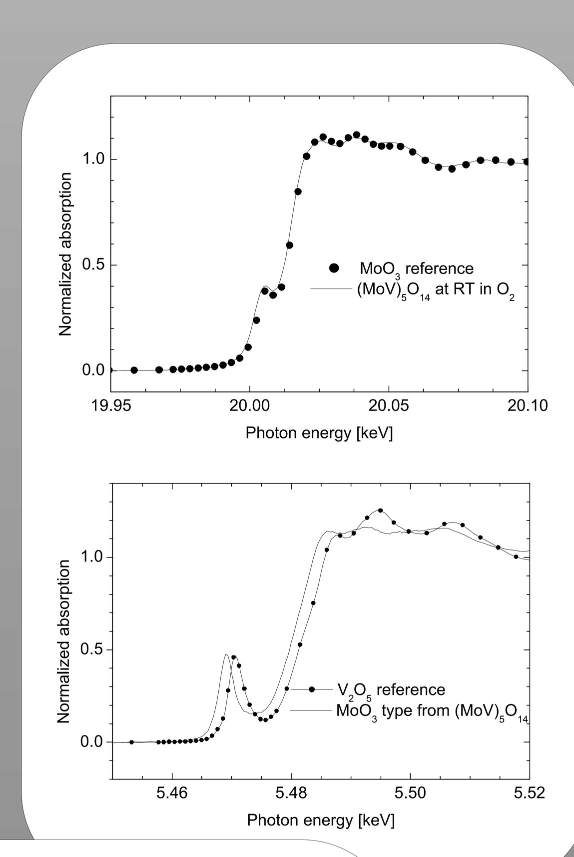
### In situ XAS

Helium

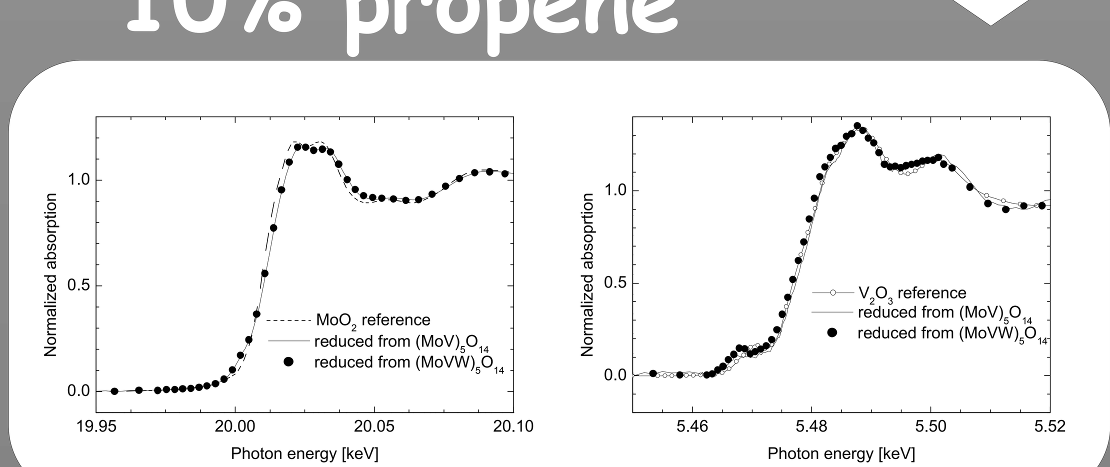



Isothermal redox experiments show reduction of $(MoV)_5O_{14}$ and $(MoVW)_5O_{14}$ into a $MoO_2$ type structure. Re-oxidation of (MoVW) oxide in 20% oxygen results in the initial $Mo_5O_{14}$ phase. In case of the reduced (MoV) oxide re-oxidation leads to a $MoO_3$ type structure with vanadium incorporated.

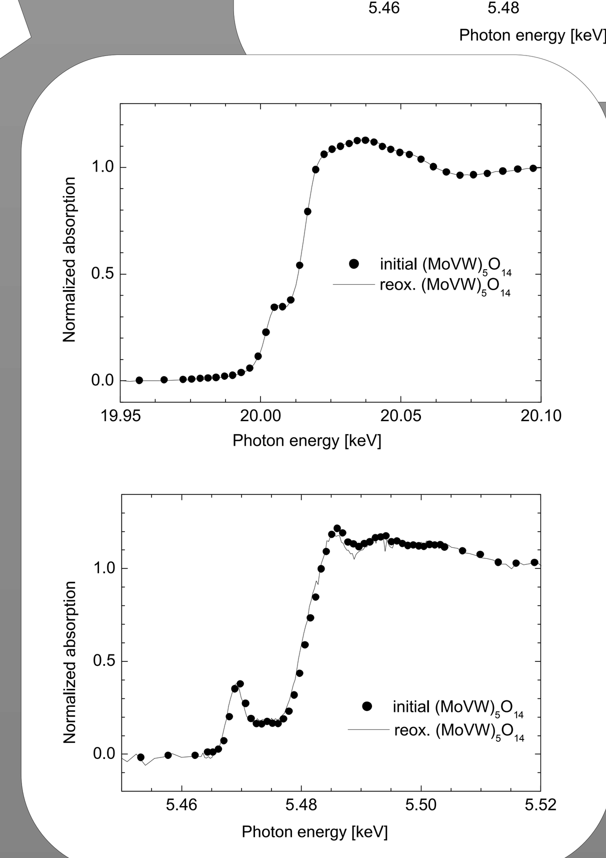


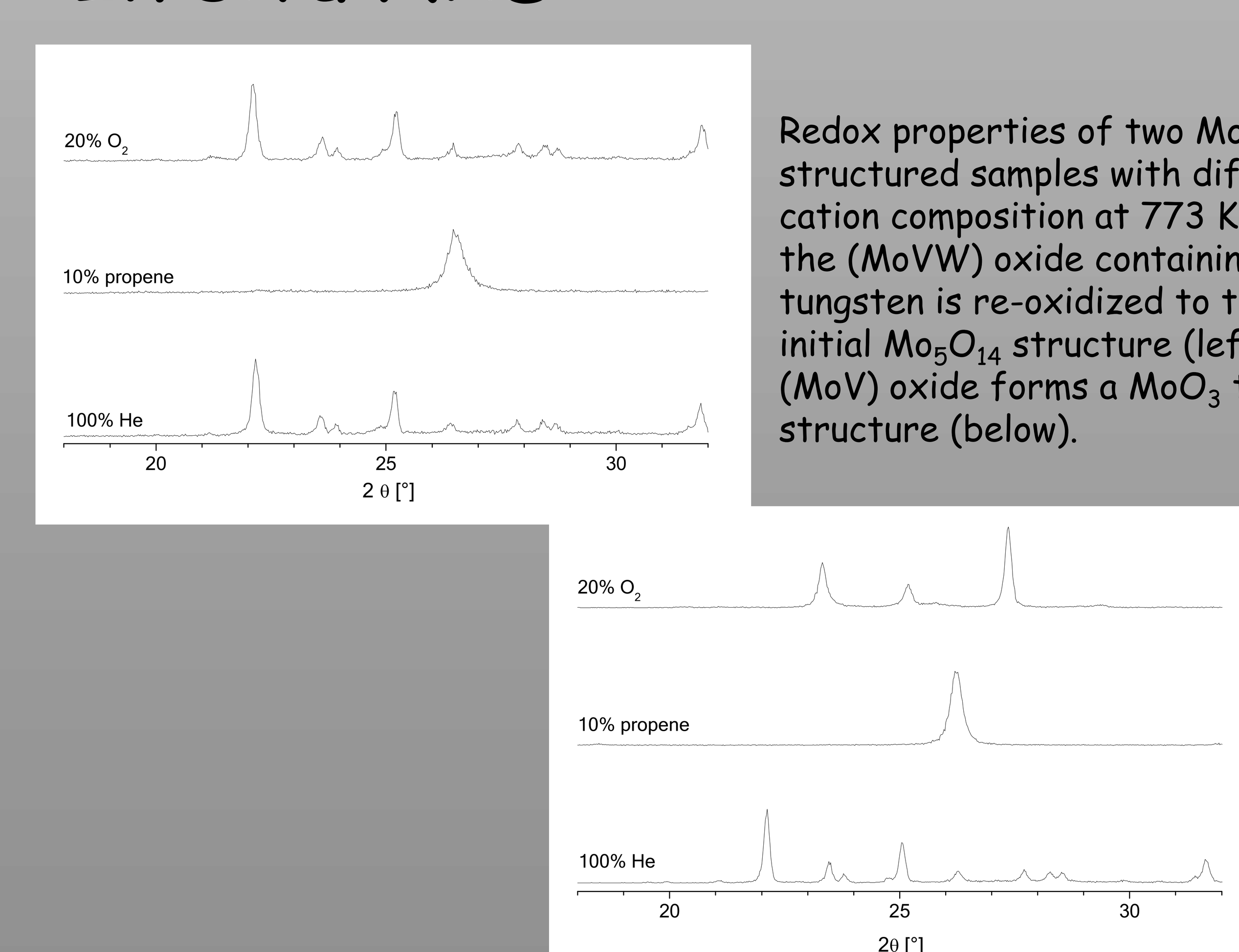

10% propene




20% oxygen




### In situ XRD




Redox properties of two $Mo_5O_{14}$ structured samples with different cation composition at 773 K. Only the (MoVW) oxide containing tungsten is re-oxidized to the initial $Mo_5O_{14}$ structure (left), the (MoV) oxide forms a $MoO_3$ type structure (below).

## Conclusions

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 $(MoVW)_5O_{14}$ exerts a structure-directing effect under oxidizing conditions resulting in the re-formation of the $Mo_5O_{14}$ type structure. Compared to the $MoO_2$ type material obtained from reduction of $(MoV)_5O_{14}$, the re-oxidation of tungsten containing metal dioxide to $(MoVW)_5O_{14}$ corroborates the redox-stabilizing effect of tungsten in molybdenum based catalysts under selective oxidation reaction conditions.

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