



# In situ bulk structural investigations of molybdenum oxide catalysts under partial oxidation reaction conditions



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## Goal:

- Simple molybdenum oxides are 3D-model systems for industrial catalysts in the partial oxidation of propene to acrolein and acrylic acid.
- The reduced complexity of the catalyst allows insight into structure-activity relationships from in situ bulk structural investigations.

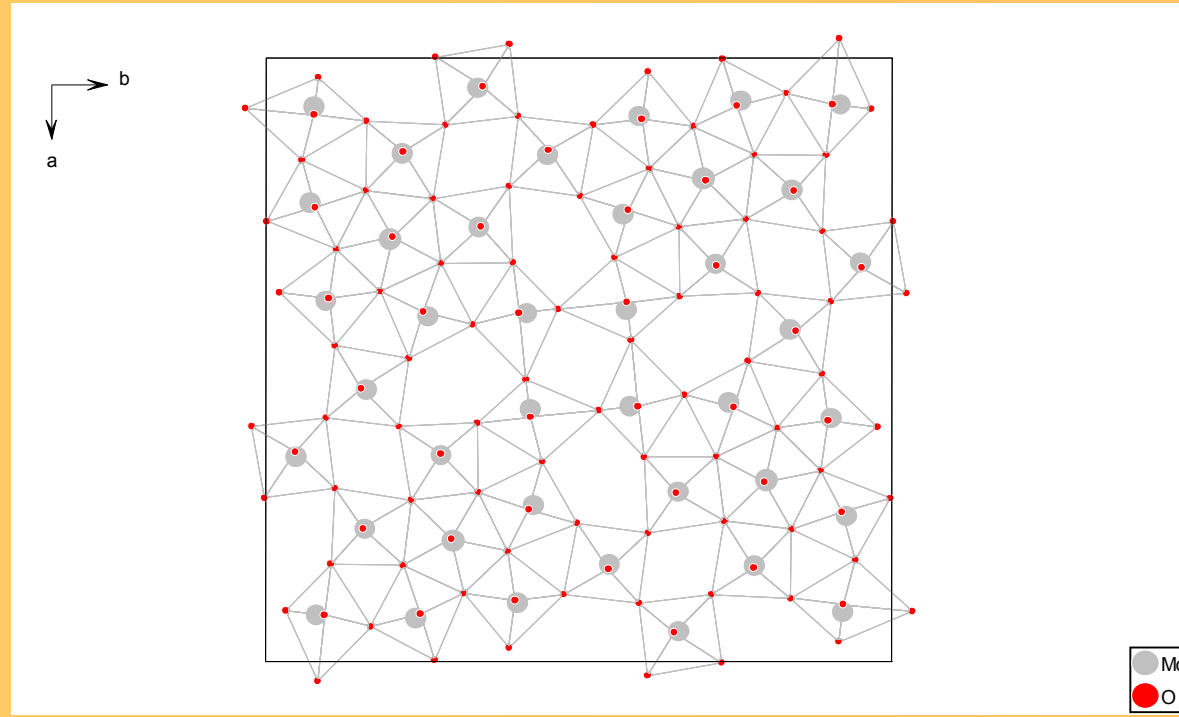
## Systems:

- Orthorhombic  $\text{MoO}_3$  is an active catalyst for the partial oxidation of propene in presence of gas phase dioxygen. The „hexagonal  $\text{MoO}_3$ “ undergoes a phase transformation into  $\alpha\text{-MoO}_3$  at elevated temperature ( $\sim 350^\circ\text{C}$ ).
- The  $\text{Mo}_5\text{O}_{14}$  type structure is a model system for more complex mixed oxide catalysts. An interesting structural feature is the coordination of the different cations present in the crystalline single phase material.

## Methods:

- In situ XRD ( $\text{CuK}\alpha$ ) in Bragg-Brentano geometry Bühler HDK combined with MS. Total gas flow 100 ml/min.
- In situ XAS at HASYLAB, Hamburg and ESRF, Grenoble. In situ XAS-cell (volume 4 ml), total gas flow 30 ml/min with online monitoring of products (MS).

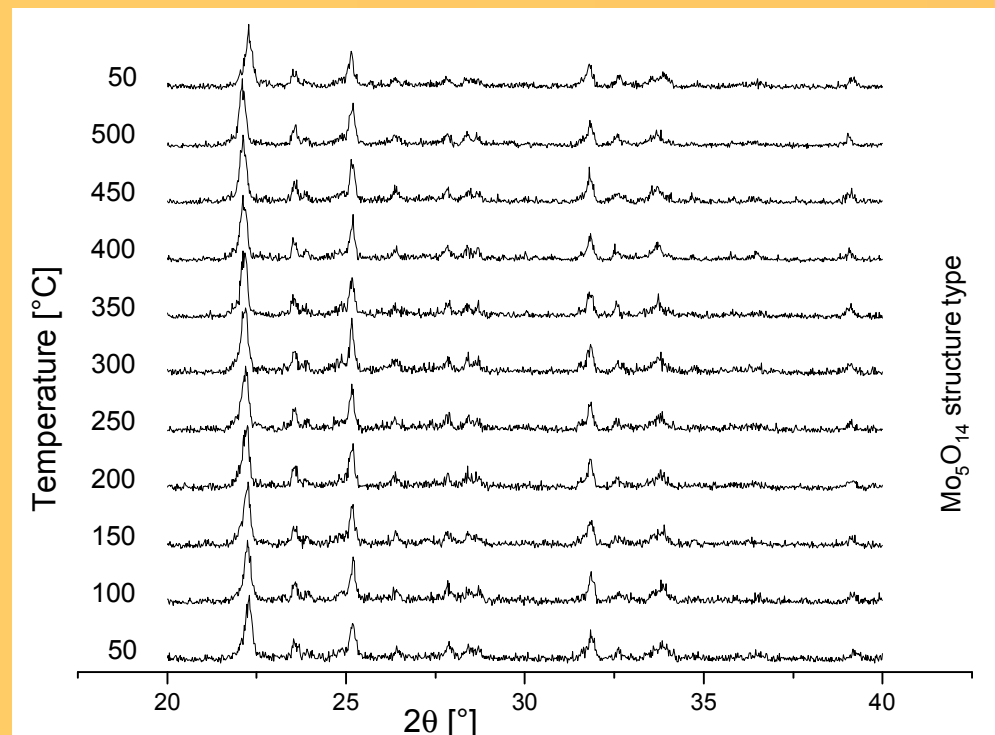
## $(\text{Mo}+\text{V}+\text{W})_5\text{O}_{14}$ mixed oxide catalyst



The structure of the catalyst is related to the  $\text{Mo}_5\text{O}_{14}$  structure published by Kihlborg (Ark. Kemi, 21, 40, 427 1963)

Composition of cations:  
68%Mo + 23%V + 9%W

## Catalytic conditions – mildly reducing atmosphere

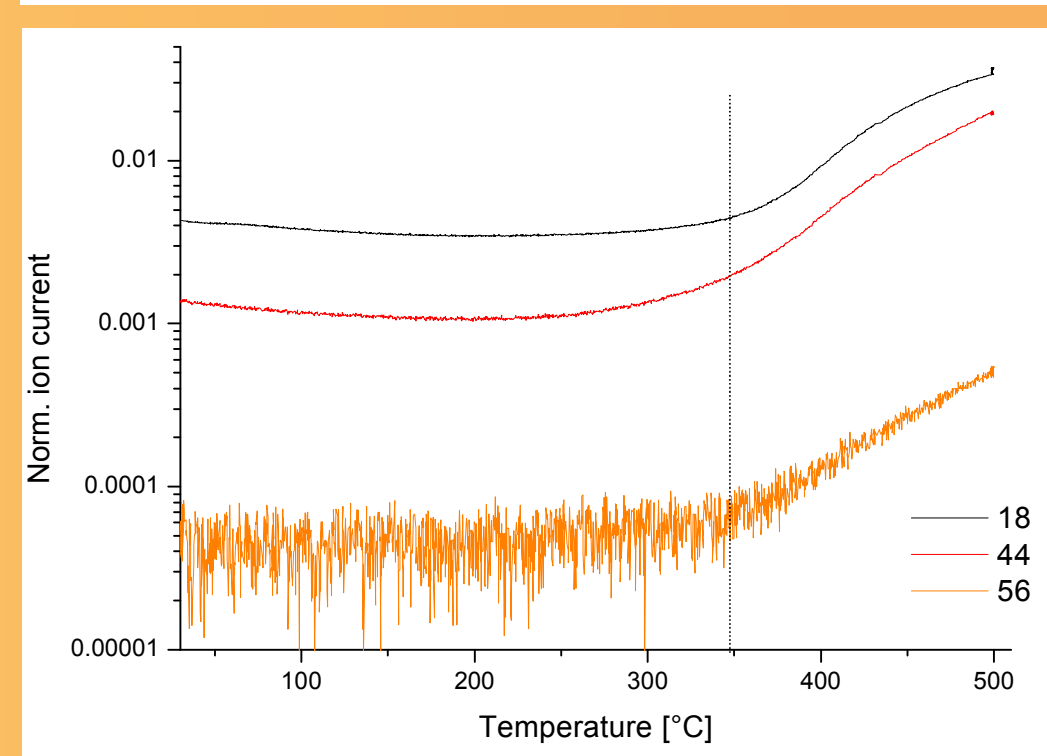
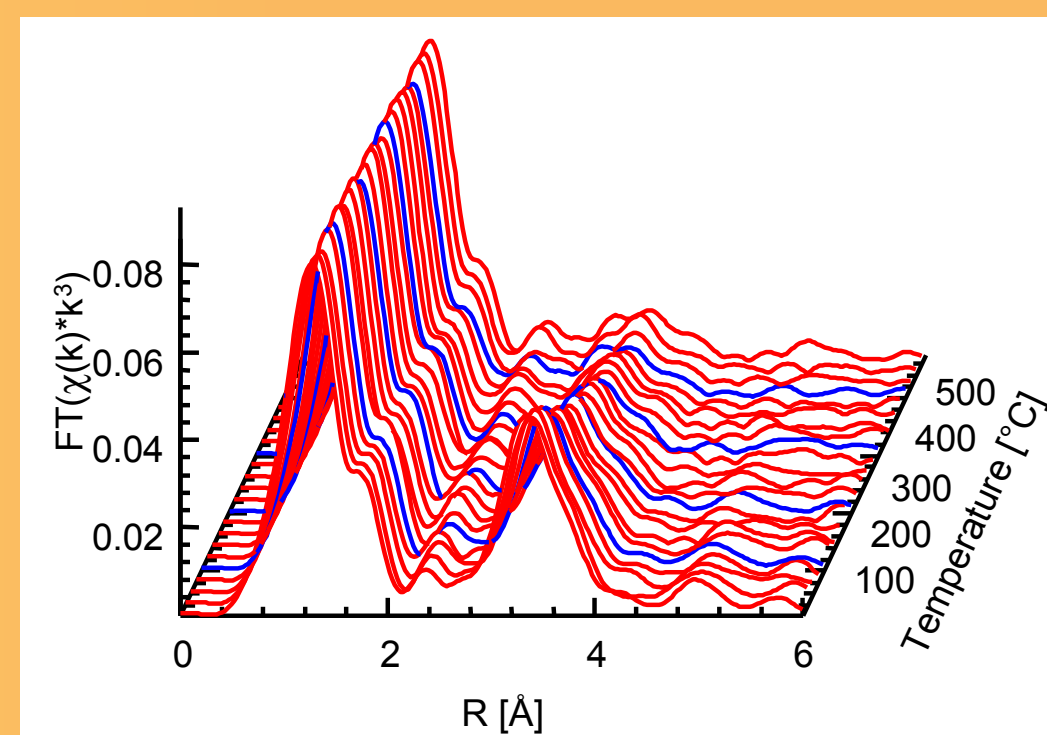


• left: XRD-pattern of catalyst in 10% propene + 10% oxygen

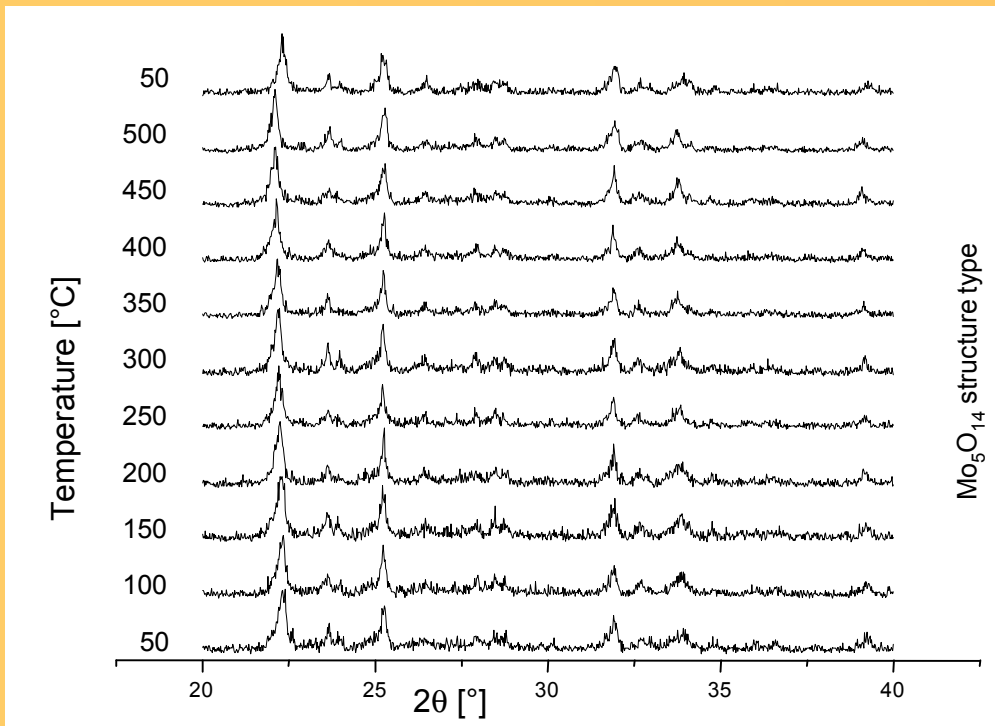
• right:  $\text{FT}(\chi(k)*k^3)$  of catalyst in 10% propene + 10% oxygen at Mo-K-edge

•  $\text{Mo}_5\text{O}_{14}$  structure is stable up to 500 °C in mildly reducing atmospheres

• Catalysis starts at 350 °C

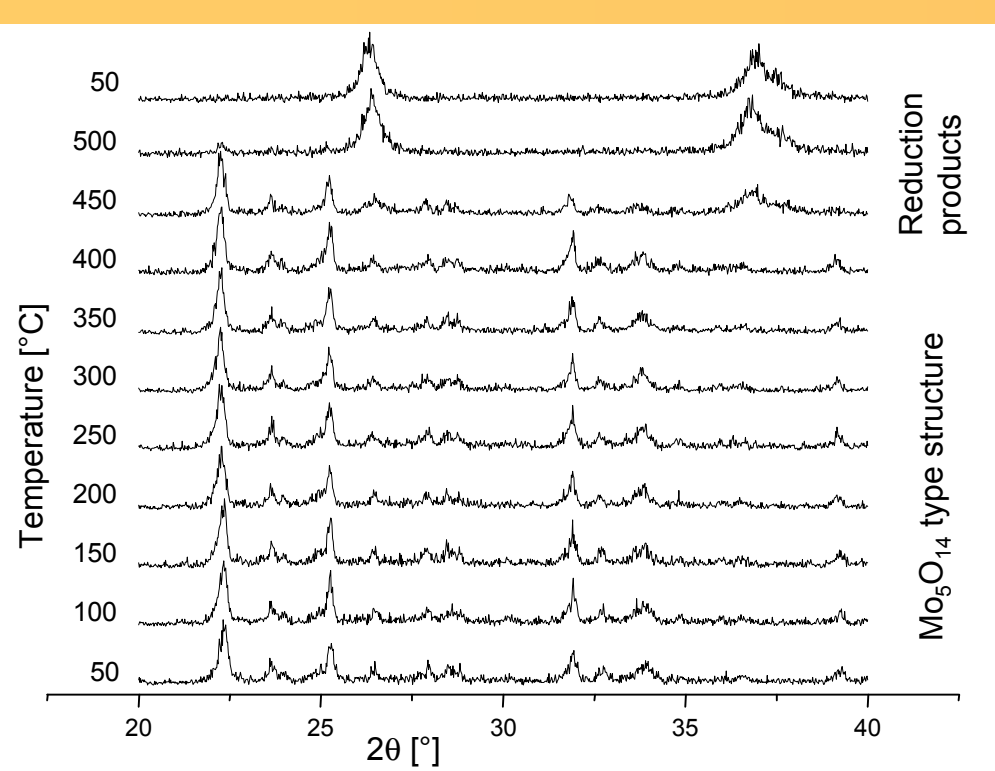


## Oxidizing conditions



Catalyst in 20% oxygen,  $\text{Mo}_5\text{O}_{14}$  structure is stable up to 500 °C in oxidizing atmosphere

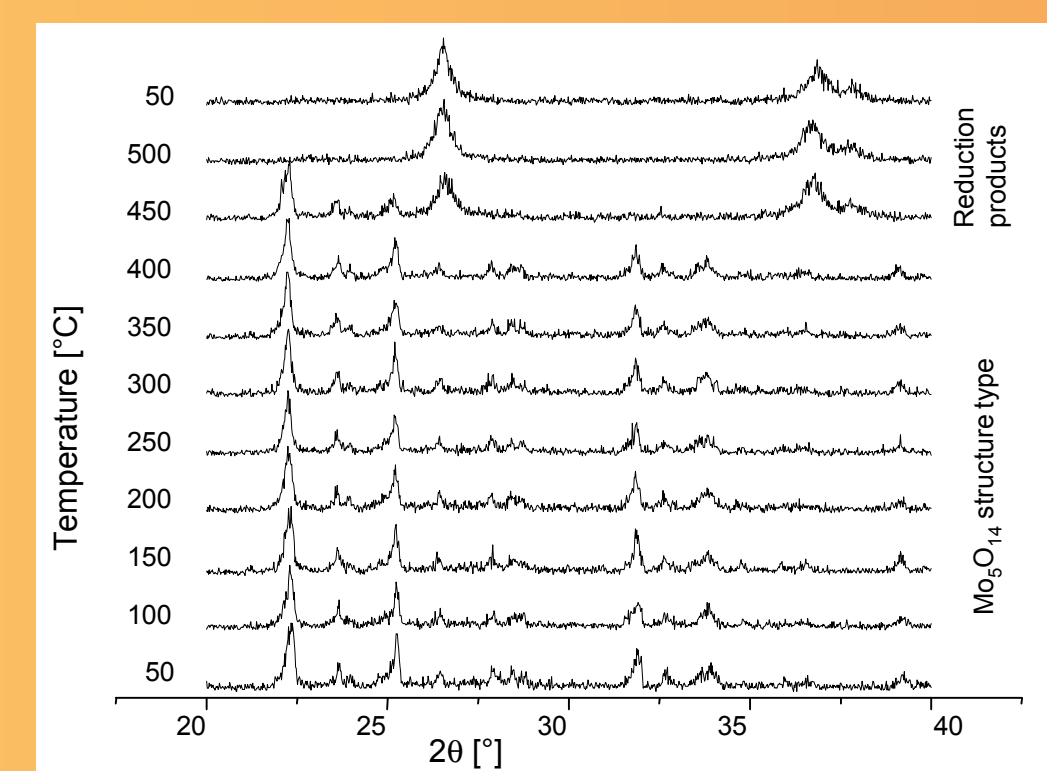
## Reducing conditions – strong reducing atmosphere



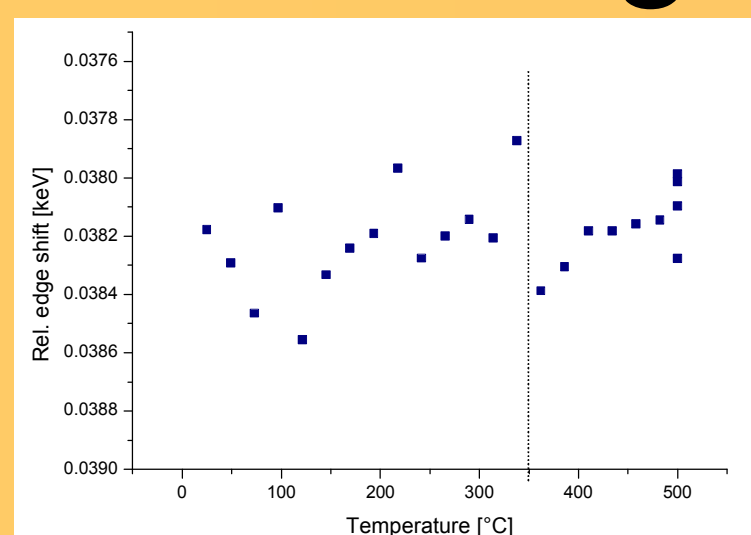
• left: 10% hydrogen in He

• right: 10% propene in He

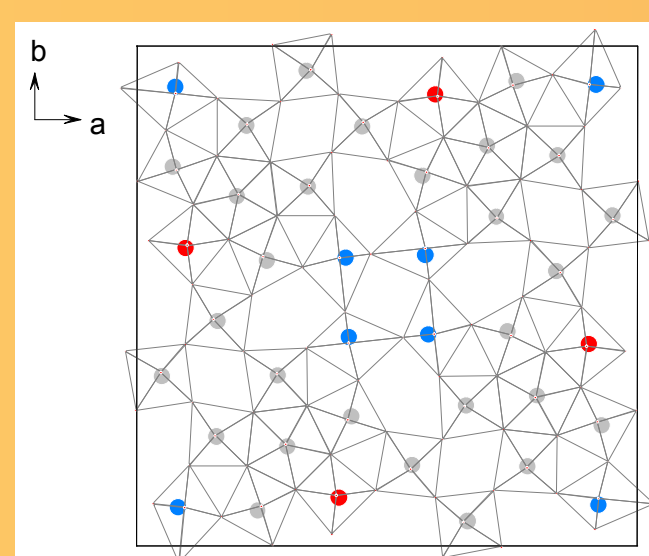
•  $\text{Mo}_5\text{O}_{14}$  mixed oxide is reduced at temperatures above 450 °C



## Mo K-edge

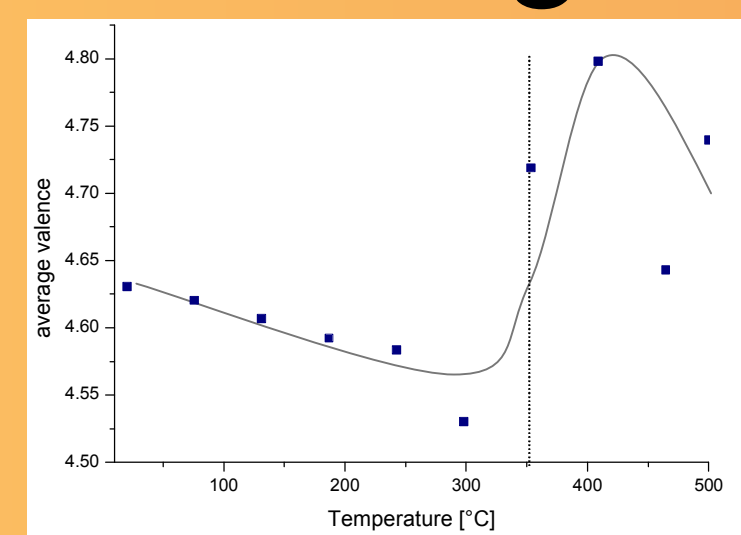


No significant change in average valence of Mo at onset of catalysis

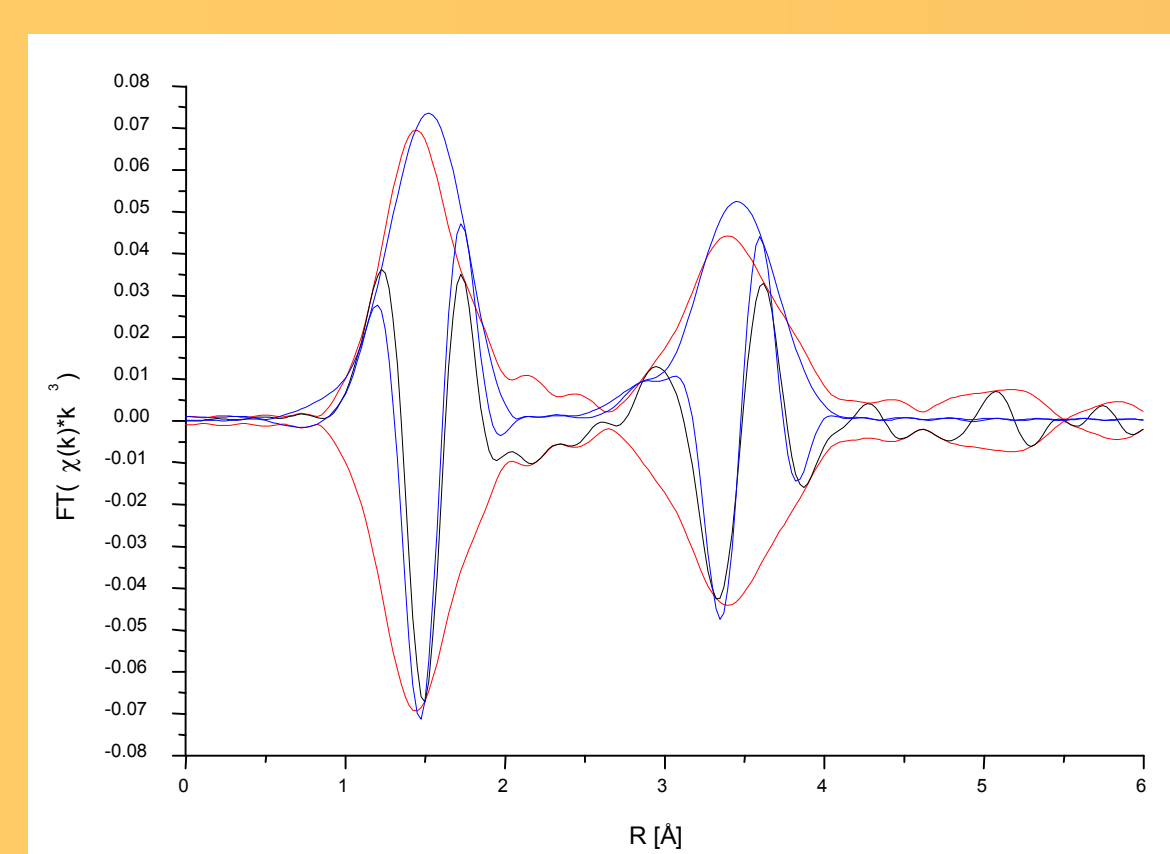


Positions of cations used in fit:  
Red: Mo positions  
Blue: V positions

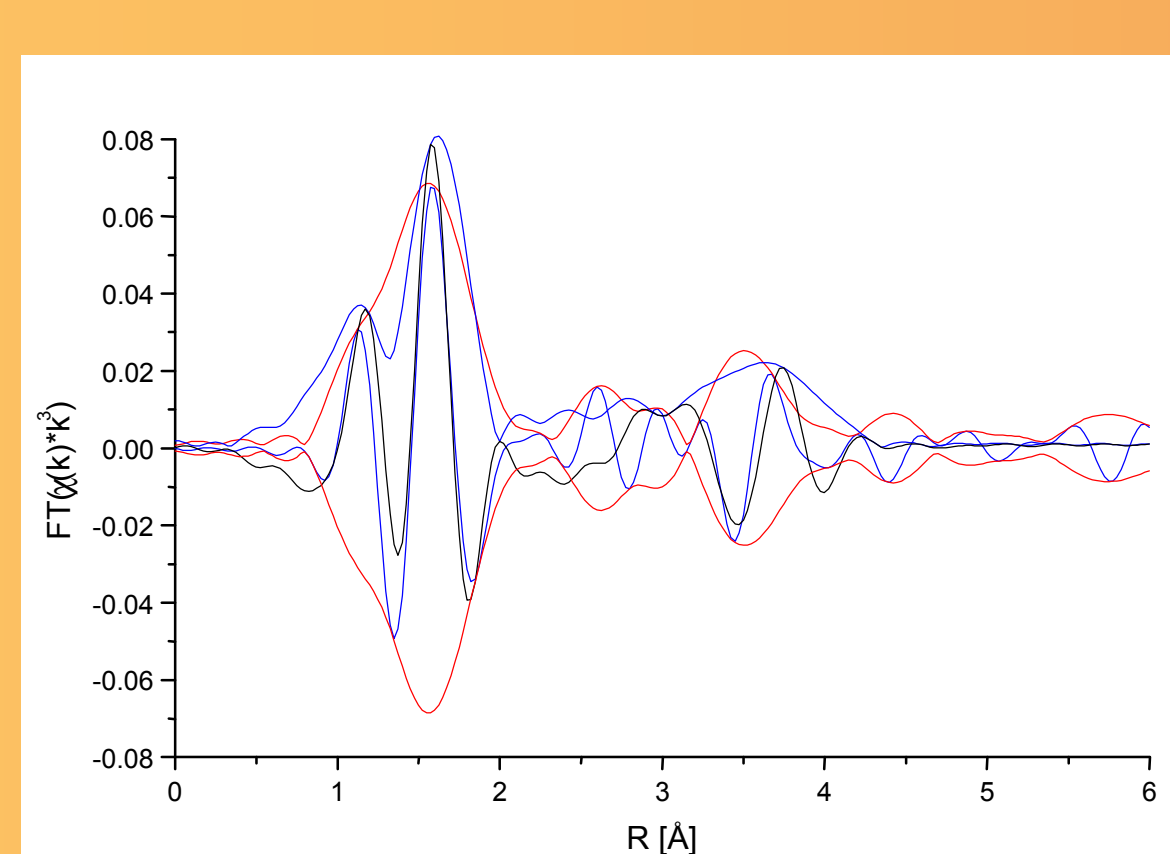
## V K-edge



Average valence of V changes at the onset of catalysis



EXAFS-data: Mo exhibits a distorted octahedral coordination by oxygen



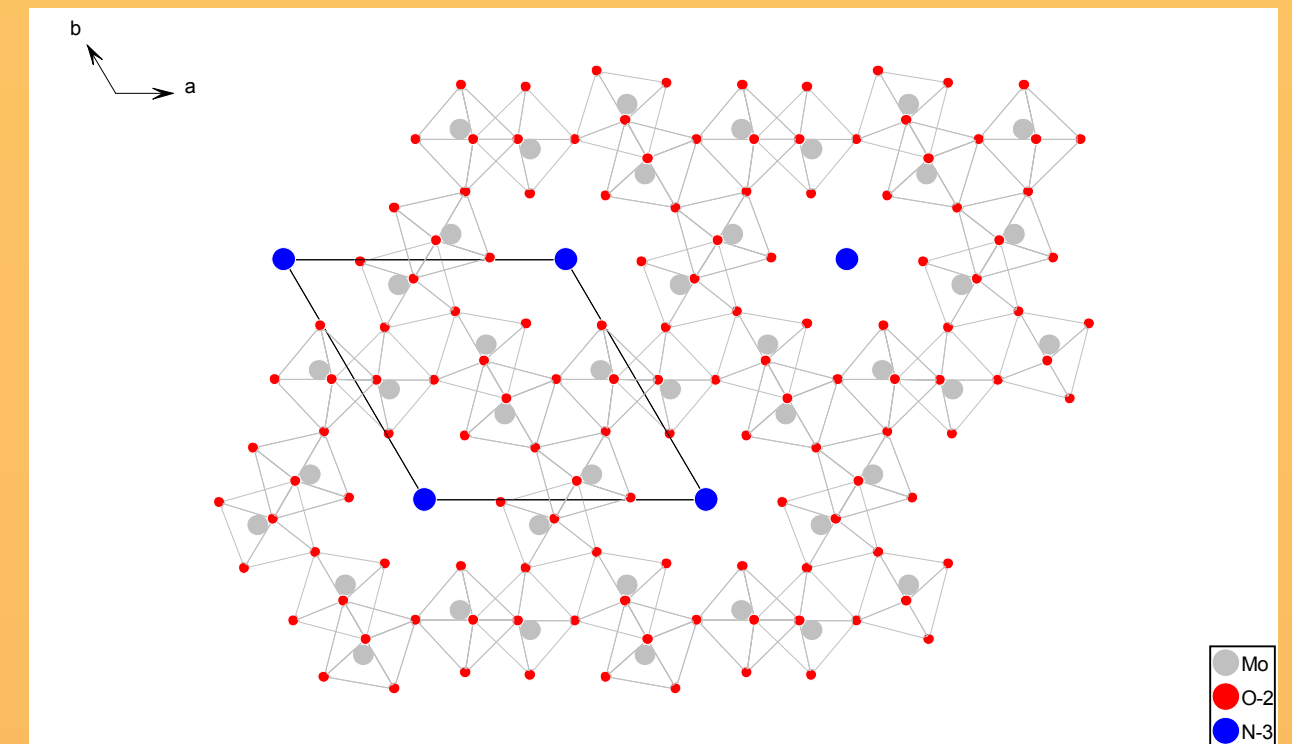
EXAFS-data: V exhibits a squared-pyramidal coordination by oxygen

## „Hexagonal $\text{MoO}_3$ “

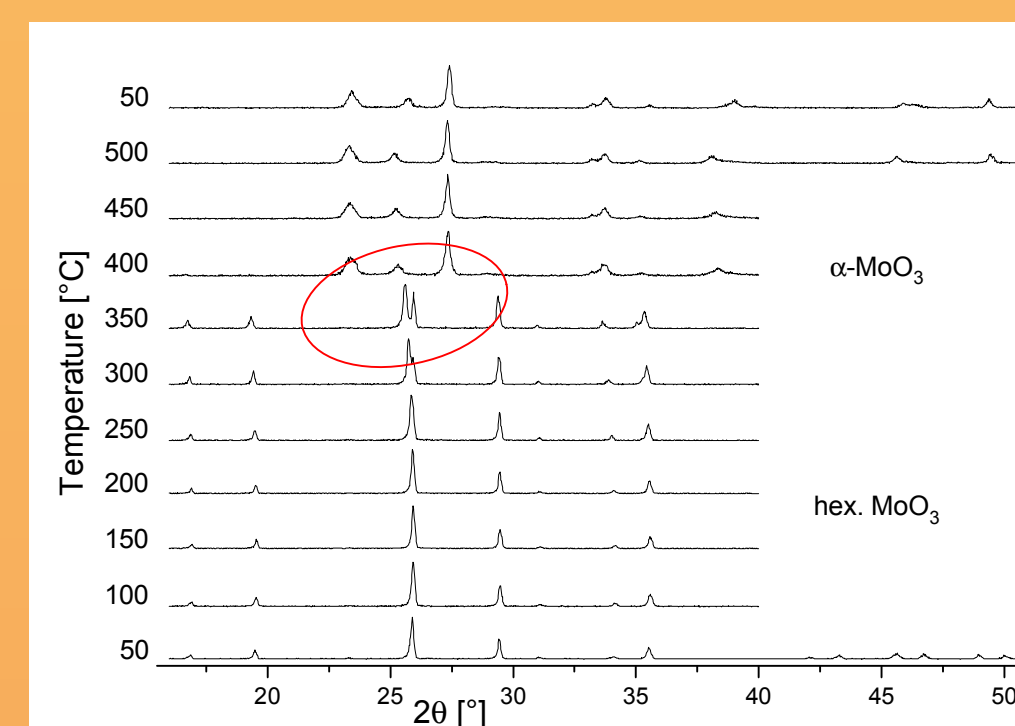
• Background: during thermal decomposition of ammonium heptamolybdate (AHM) several phases occur

• Hexagonal structure contains molybdenum and oxygen stabilized by cations, in this case  $\text{NH}_4^+$

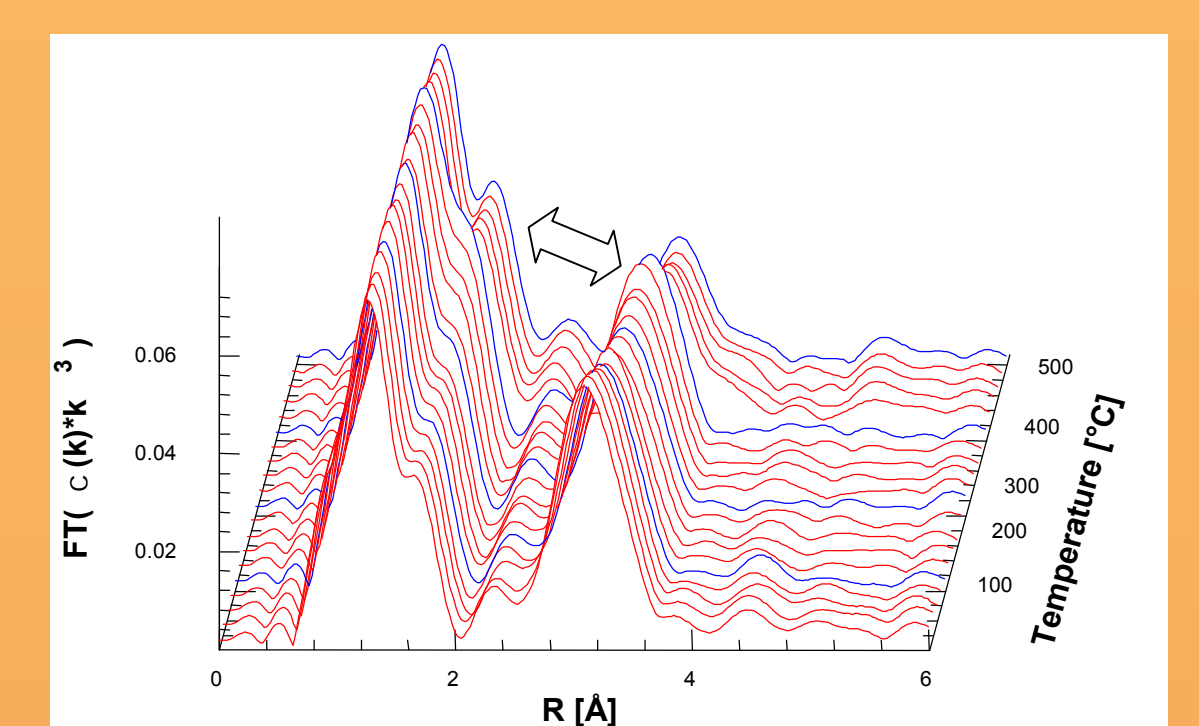
• Catalytic properties of hexagonal phase are not completely characterized



## Comparison XRD and XAS



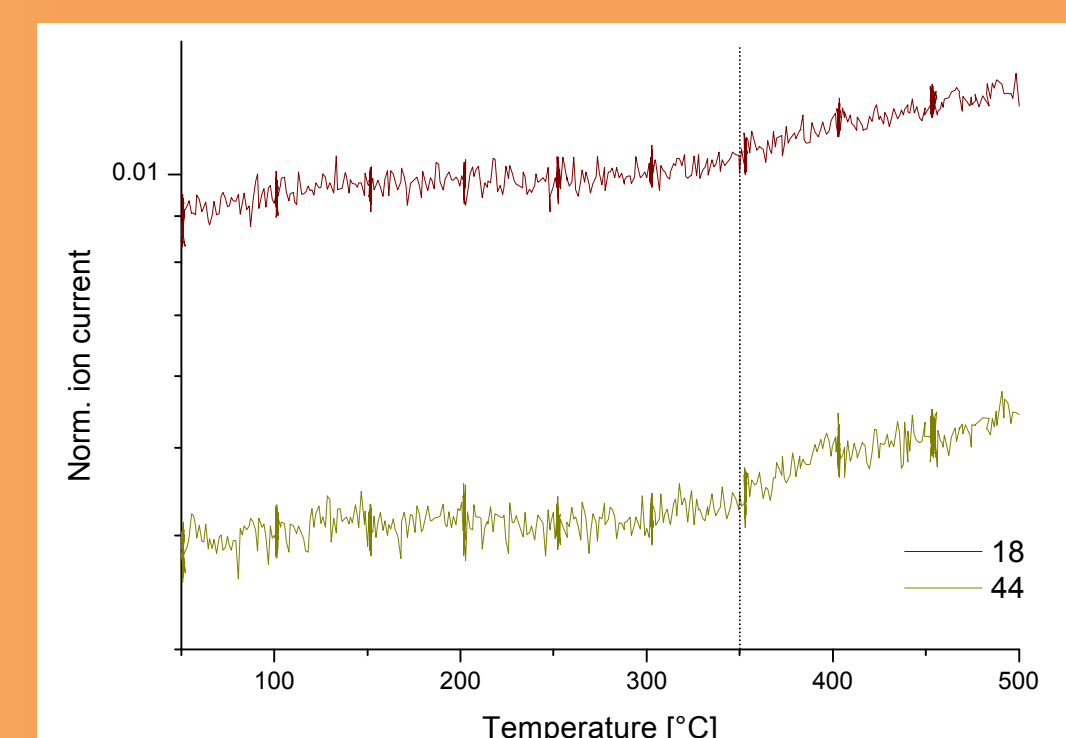
XRD-pattern: phase transition from hexagonal phase into  $\alpha\text{-MoO}_3$  between 350-400 °C (similar to AHM decomposition)



XAS-data: phase transition observable as slight changes of second shell between 350-400 °C

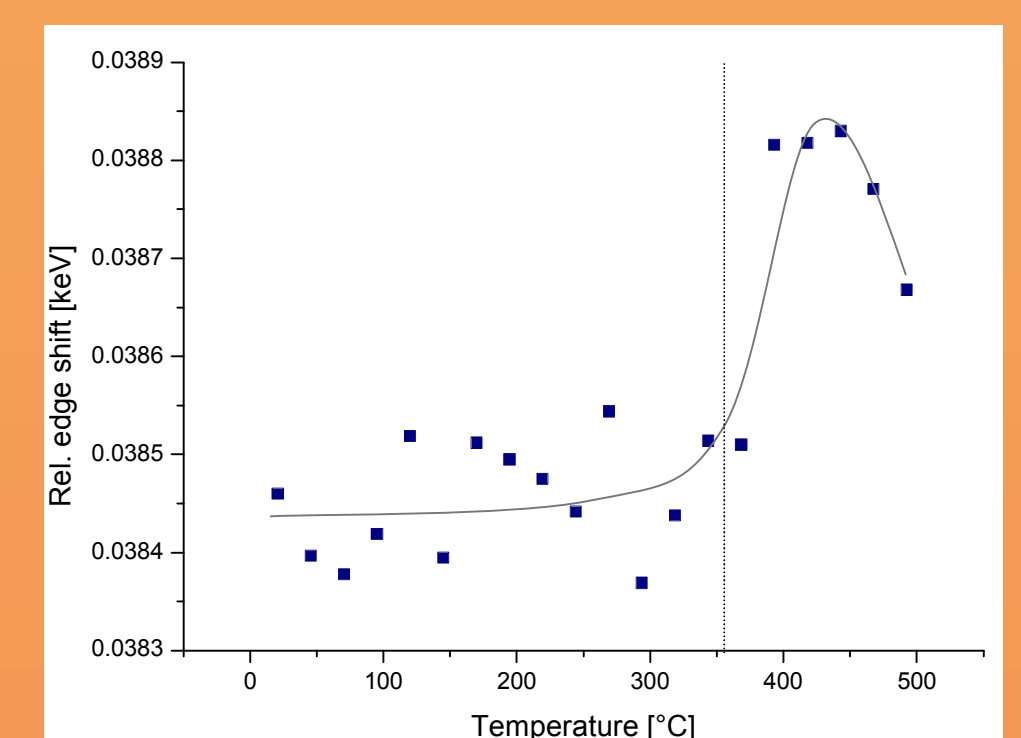
• Structural change during phase transition hardly modifies the distorted octahedral coordination of Mo by O (first shell)

• Rearrangement of the Mo-Mo and next nearest neighbor. Mo-O distances change second shell of  $\text{FT}(\chi(k)*k^3)$



• Catalysis starts at 350 °C - at this temperature peak splitting in XRD-pattern and increase of amplitude in  $\text{FT}(\chi(k)*k^3)$  second shell indicate rearrangement (see above)

• Data taken from XRD-experiment



• XANES: relative edge shift is correlated directly to the average oxidation state of Mo in the catalyst

• Average oxidation state of Mo in the sample increases at phase transition

• Conditions: 450 °C reduction in 1:1 atmosphere of propene and  $\text{O}_2$

## Conclusion

• „Hexagonal“  $\text{MoO}_3$  appears to exhibit no catalytic activity. Catalysis begins as soon as the hexagonal network structure is changed into the orthorhombic sheet structure of  $\alpha\text{-MoO}_3$ .

• Performance of Mo in  $\text{Mo}_5\text{O}_{14}$  mixed oxide seems to be similar to that in  $\alpha\text{-MoO}_3$ . Under catalytic conditions the long range order of the structure is retained, but the short range order changes.