Structural evolution of ammonium paratungstate during thermal decomposition in various atmospheres

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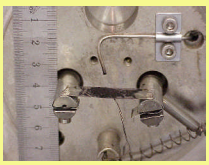
Introduction

• $Mo_{1-x}(V,W)_xO_{3-y}$ are employed as catalysts for the partial oxidation of light alkenes [1]. Ammonium heptamolybdate (AHM) and ammonium paratungstate (APT) are used as precursors for the production of MoO_3 and WO_3 [2, 3].

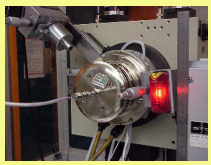
Motivation

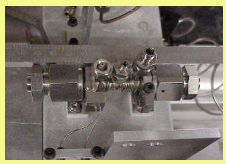
• Identify and quantify tungsten oxide phases and their formation during the decomposition of ammonium paratungstate (APT) under various atmospheres with in situ XRD and in situ XAS, TG/DSC.

Cu-Ka radiation
Bragg-Brentano geometry (secondary monochromator),
Stoe STADI-P diffractometer,
Bühler HDK combined with MS



In situ XRD





In situ XAS

HASYLAB (at DESY):
W L_3: 10.204 keV
Temperature range: RT-773 K
Cell volume: ~ 4 ml
Heating rate: 6 K/min
Pellets diameter: 5 mm
4 mg APT + 30 mg BN

TG/DSC

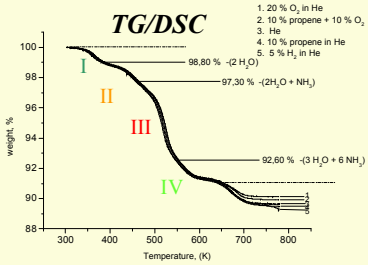


Figure 1 Weight loss during decomposition of APT in different atmospheres (temperature range from 300 to 800 K at 6 K/min)

$(NH_4)_{10}H_2W_{12}O_{42}*4H_2O \rightarrow 10H_2O+10NH_3+12WO_3$

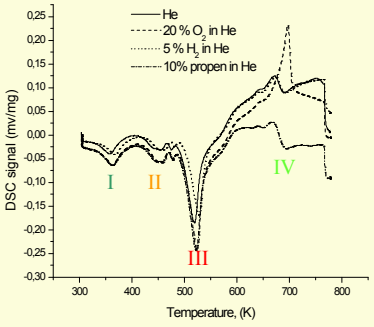


Figure 2 DSC signals during decomposition of APT in different atmospheres (temperature range from 300 to 800 K at 6 K/min)

XRD

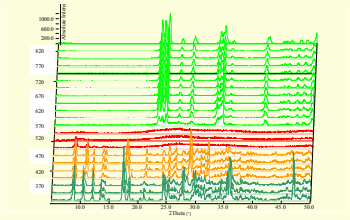
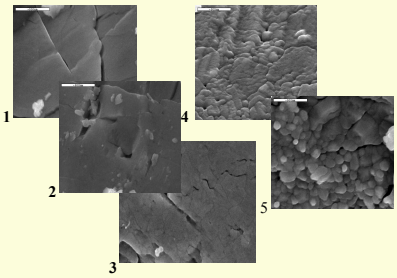


Figure 3 Evolution of X-ray diffraction patterns during decomposition of APT in static air (temperature range from 300 to 800 K, effective heating rate 0.1 K/min)



SEM images of the products of the decomposition of APT (1-in propene, 2-in helium, 3-in propene + oxygen (1:1), 4-in oxygen, 5-in static air)

	TG		XRD		XAS	
I	-($2H_2O$)	370 K	APT*$2H_2O$	380 K	APT*xH_2O	380 K
II	-($2H_2O$+NH_3)	470 K	$(NH_4)_xWO_3$	470 K	$(NH_4)_xWO_3$	460 K
III	-($3H_2O$+$6NH_3$)	550 K	$(NH_4)_xWO_3$/amorphous	620 K	$(NH_4)_xWO_3$	620 K
IV	-($3H_2O$+$3NH_3$)	770 K	WO_3 W_{met} (H_2)	770 K	WO_3 W_{met} (H_2)	770 K

XAS

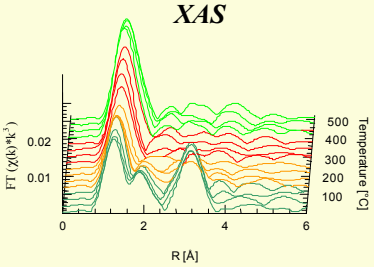


Figure 4 Fourier transformed W L_3 edge XAFS spectra of APT measured during decomposition in 20% oxygen in helium (temperature range from 300 to 800 K at 6 K/min, 2 min/spectrum)

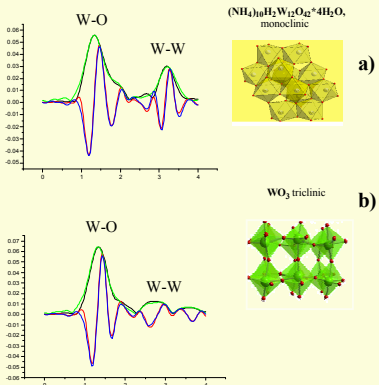
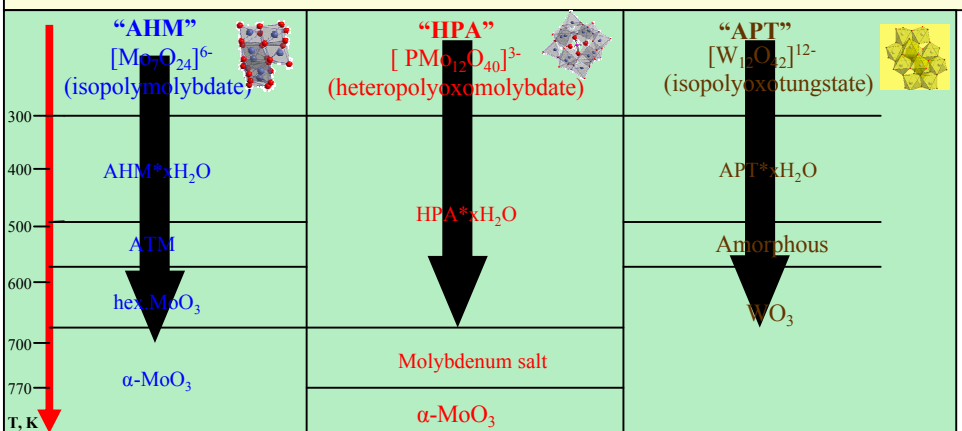


Figure 5 RDF and the fit results of the simulation with single crystal data of **a)** APT; **b)** the decomposition product of APT in oxygen



- **T~ 300 K - 650 K decomposition of APT independent of the gas phase composition.**
- **TG/DSC curves show four decomposition steps.**
- **Atmosphere affects the surface of the products. In oxygen and air (WO_3) the surface is rough, whereas in propene, helium, and propene + oxygen ($HxWO_3$) the surface is smooth with rifts.**
- **T~770K decomposition of $[W_{12}O_{42}]^{12-}$ and creation of new bonds in WO_3 takes place.**
- **Coprecipitation preferred for preparation of $Mo_{1-x}(V,W)_xO_{3-y}$ systems.**

[1] Grzybowska-Swierkosz, B., Topics in Catalysis 11/12, 23 (2000).
[2] Wienold, J., Jentoft, R.E., Ressler, T., Eur. J. Inorg.Chem. 6, 1058 (2003).
[3] Ressler, T., Jentoft, R.E., Wienold, J., Günter, M.M., Timpe, O., J. Phys.Chem. B 104, 6360 (2000).