



MAX-PLANCK-GESELLSCHAFT

Preparation and characterisation of single phase $(\text{MoVW})_5\text{O}_{14}$ -type catalyst material

S. Knobl^a, A. Blume^a, G.A. Zenkovets^b, G. Kryukova^b,
P. Beato, G. Mestl^a, O. Ovsitser^a, D. Niemeyer^a and R. Schlögl^a

^aDepartment of Inorganic Chemistry, Fritz-Haber-Institute of the MPG, Faradayweg 4-6, DE-14195 Berlin

^bBoreskov Institute of Catalysis, Pr. Akad. Lavrentieva, 5, Novosibirsk.



Introduction

MoVW based materials are highly effective catalysts for partial oxidation reactions such as conversion of acrolein to acrylic acid. They offer a high selectivity, high yields and a good long term stability. Preceding work has identified the catalytically active phase of the MoVW catalyst and characterised it by Raman spectroscopy. The current work has been carried out to synthesise and characterise this active $(\text{MoVW})_5\text{O}_{14}$ type structure

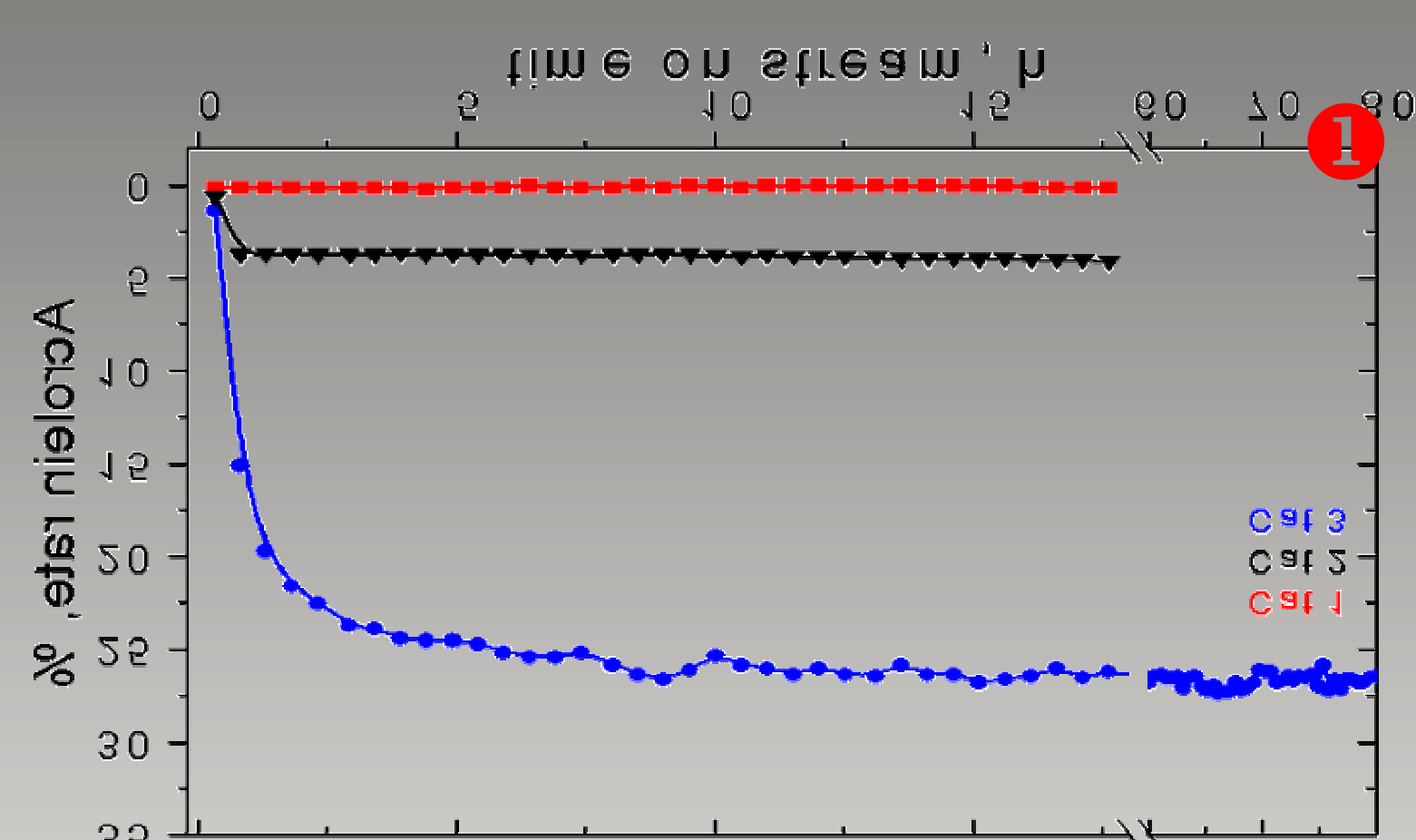
Experimental

Appropriate amounts of ammonium heptamolybdate (AHM) and ammonium metavanadate (AMT) were dissolved in dest. water. The vanadyl oxalate solution was prepared by dissolving an aqueous vanadium(V)-oxide suspension in oxalic acid. Quantitative analysis of the metal cations was carried out by AAS. The combined solutions were spray dried. A black powder was obtained, which was calcined at 623 K in air for two hours and subsequently at 713K in He for another two hours.

Catalysis: Structure - Reactivity relationship

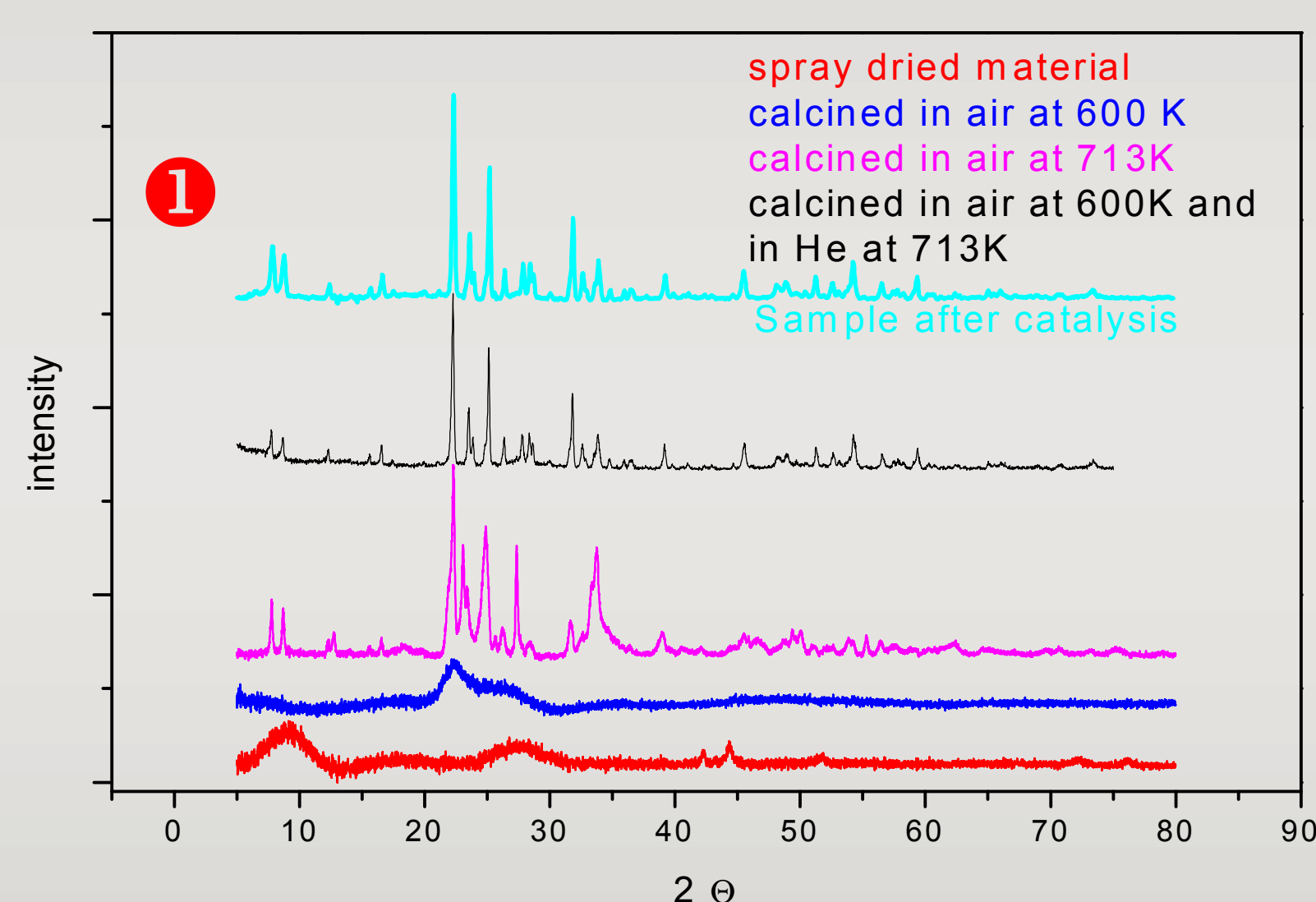
Catalysis

Cat 1: Spray dried
Cat 2: Calc. at 623 K (air), 2h + 713 K (He), 2h
Cat 3: Calc. At 623 K (air), 2h (s. Ref. 5)



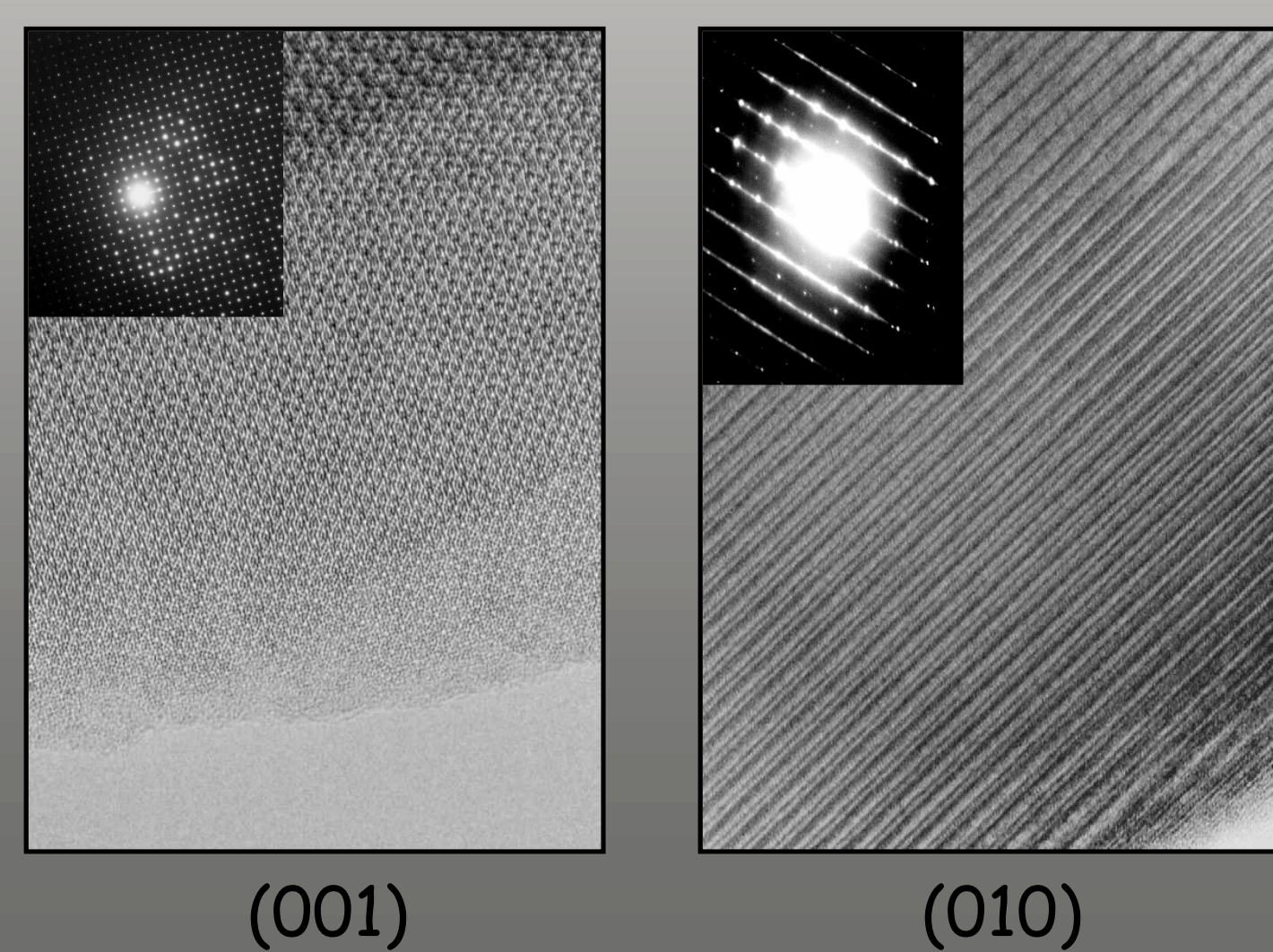
XRD

Spray dried: nanocryst. Mo_5O_{14} -type structure (s. Ref. 2, 3).
Calc. air 720 K: crystalline + additional phases
Calc. air 623 K and He 713 K: Mo_5O_{14} single phase
After catalytic reaction: Mo_5O_{14} structure (s. Ref. 5)



TEM

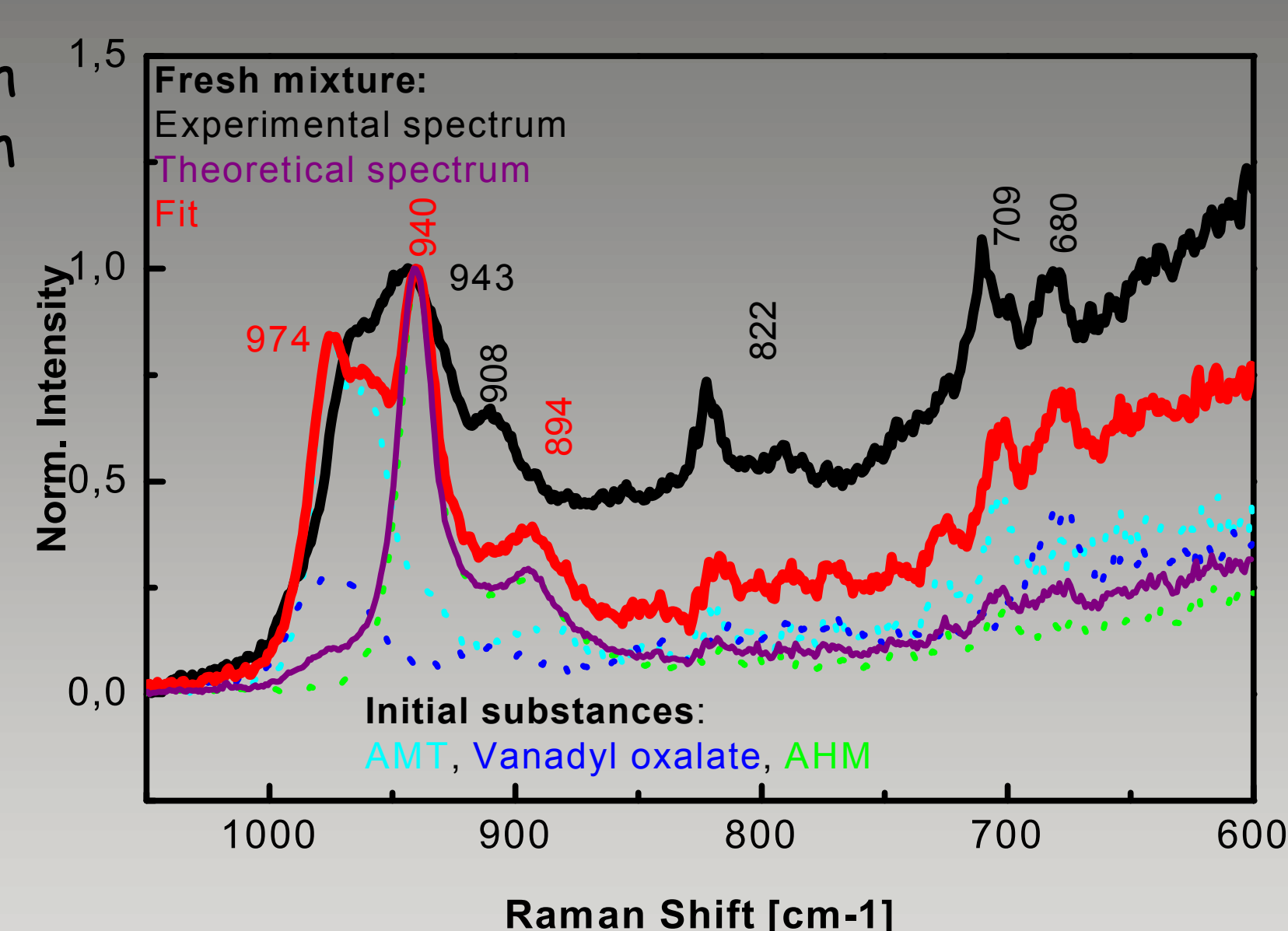
Well ordered Mo_5O_{14} structure in basal plane (001). Open channels in basal plane
Pseudo lamellar in (010) direction (s. Ref. 3+5).



From aqueous solution to solid

Raman spectra of the solutions

The experimental spectrum does not match the theoretical spectrum (in which just a mixture of the initial compounds was assumed)



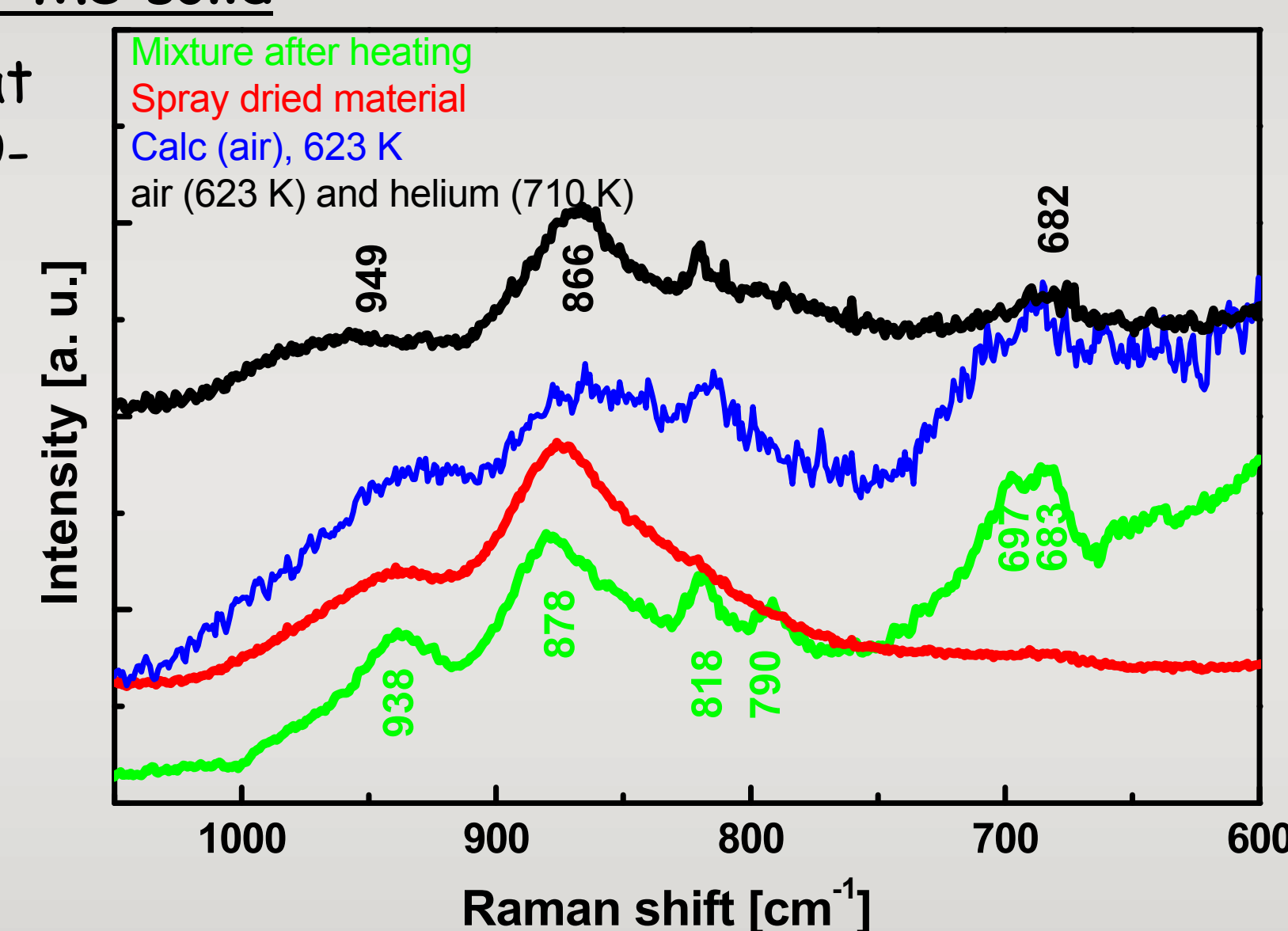
New polyoxometal compound (s. Ref. 4)

Raman spectroscopy of the solid

After drying: New band at 878 cm^{-1} caused by Me-O-Me modes.

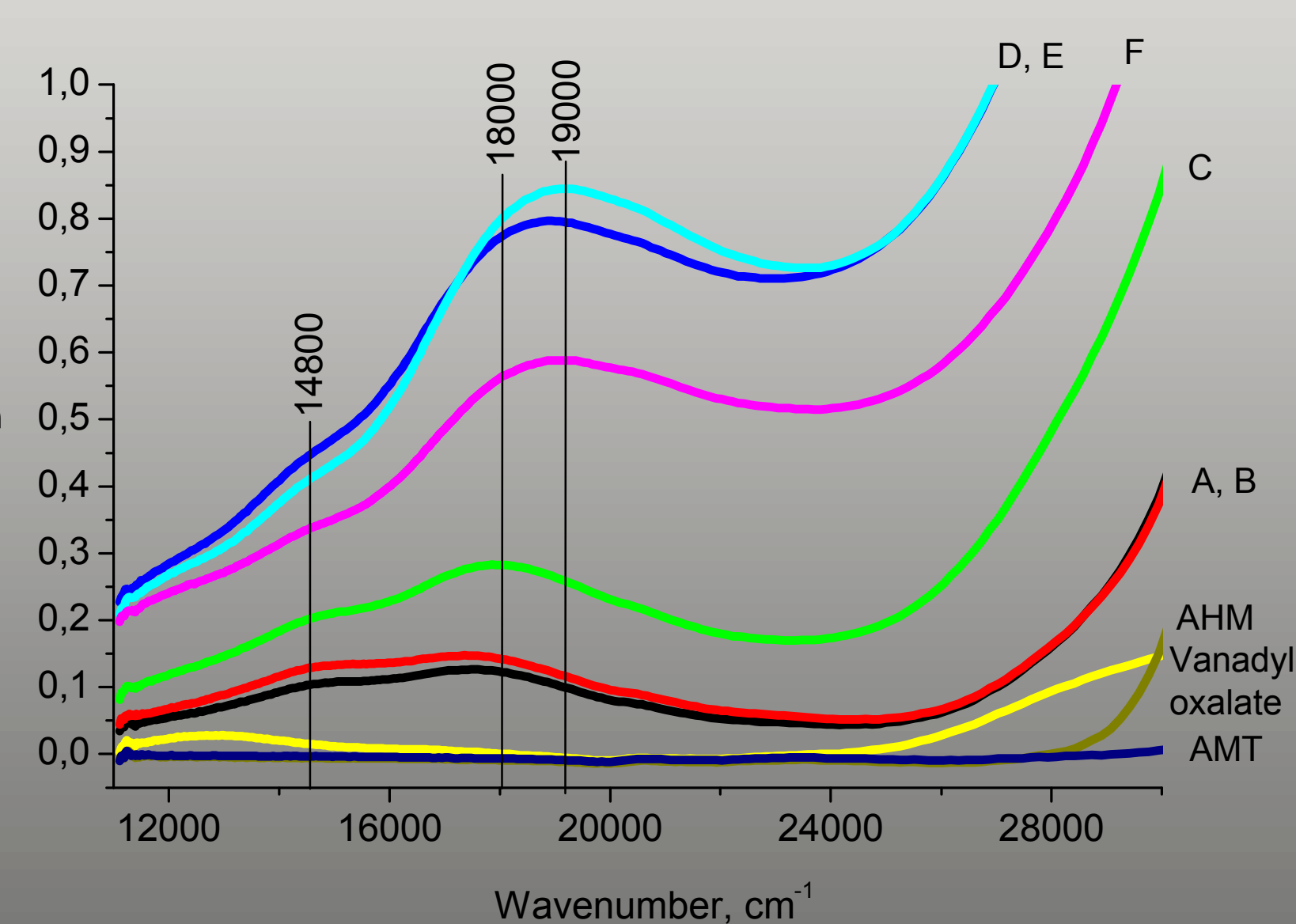
Polymeric precursor of $(\text{MoVW})_5\text{O}_{14}$ structure.

After calcination: Development of Mo_5O_{14} structure.



UV/vis spectroscopy of the solution

Mixture shows different bands than each of the single compounds. Whilst the band at 14800 cm^{-1} is characteristic for vanadyl species, the band at 19000 cm^{-1} points to Mo-O-V intervalence charge transfer transitions.



UV/Vis investigation on solution; metal-ligand charge transfer region, 0.001 mm cuvette. A: 20 % Vanadyl oxalate; B: 40 %, C: 60 %, D: 80 %, E: 100 %, F 100 % and AMT

Conclusions:

The Mo_5O_{14} structure is catalytically active and selective; the catalytic activity depends on the degree of crystallisation of the solid. Additional work is currently underway to identify the precursor states in solution and solid

References:

- Hibst, H., Unverricht, S. (BASF), DE 19815281 A 1.
- Mestl, G., Linsmeier, C., Gottschall, R., Dieterle, M., Find, J., Herein, D., Jäger, J., Uchida, Y., Schlögl, R., J. Mol. Catal. A 162 (2000) 455-484.
- Dieterle, M., Mestl, G., Jäger, J., Hibst, H., Schlögl, R., J. Mol. Catal. A 174 (2001) 169-185.
- Mestl, G., Srinivasan, T. K. K., Catal. Rev.-Sci. Eng., 40(4), 451-570 (1998)
- Ovsitser, O., Uchida, Y., Mestl, G., Weinberg, G., Blume, A., Dieterle, M., Hibst, H., and Schlögl, R., J. Mol. Catal. A, in print.