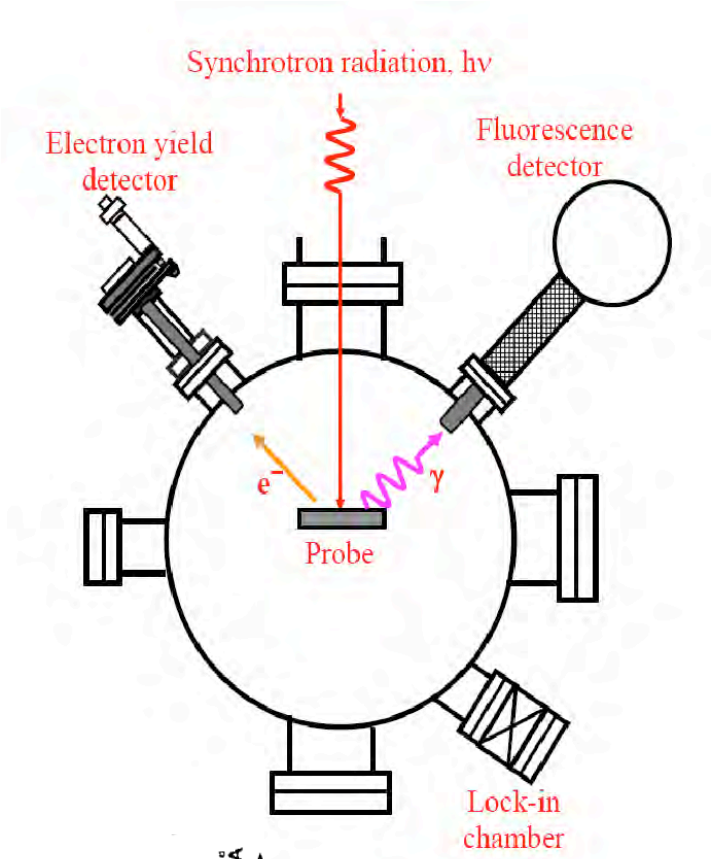
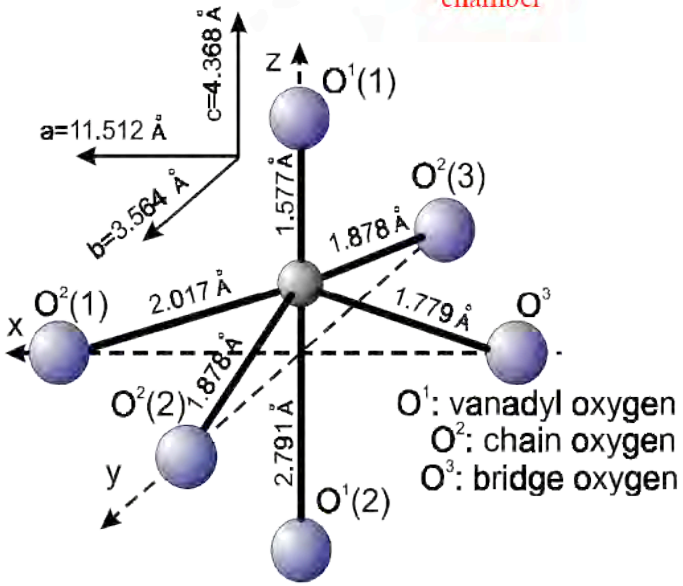
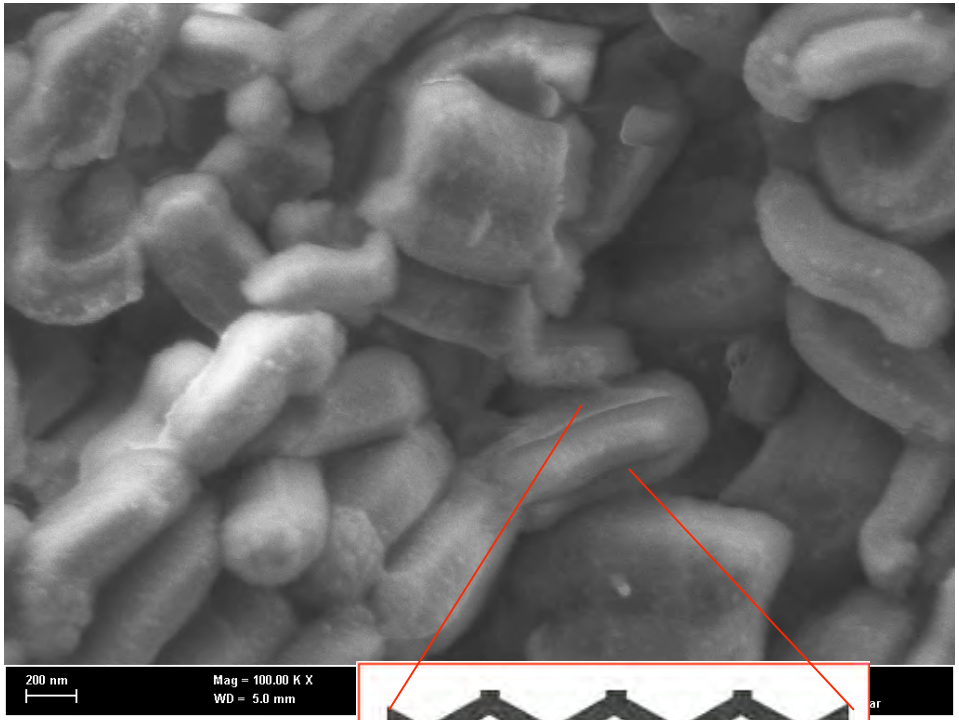
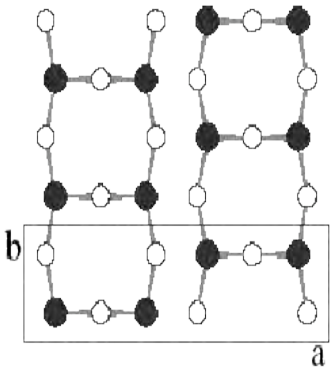
Effects of catalysis on the structure of vanadia in SBA-15

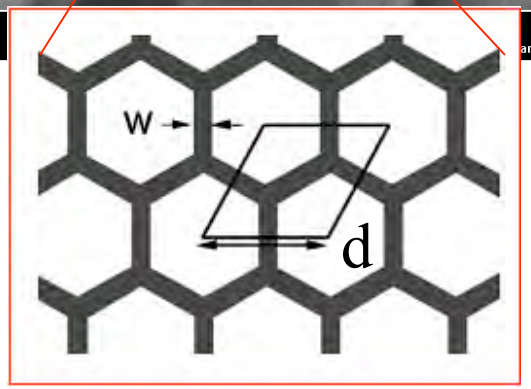
- R. Mitdank, H. Winter HUB (C11)
  (NEXAFS ; RBS)
- A. Berthold, H. Schubert TUB (B 7)
  (Preparation ; SEM ; XRD ; Organisation)
- S. Arndt TUB
  (ODP)
- T. Wolfram FHI (B 2)
  (Synthesis SBA-15 / V_xO_y)

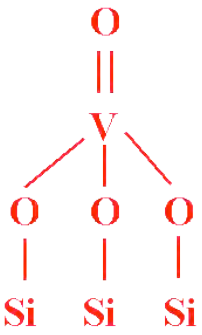

Synchrotron radiation, hν
Electron yield detector
Fluorescence detector
e⁻
γ
Probe
Lock-in chamber

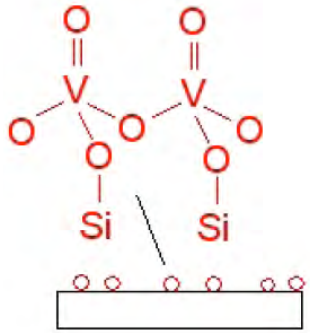

z
O¹(1)
c=4.368 Å
a=11.512 Å
b=3.564 Å
1.577Å
O²(3)
1.878 Å
O²(1)
2.017 Å
1.779 Å
O³
x
1.878Å
O²(2)
y
2.791 Å
O¹(2)
O¹: vanadyl oxygen
O²: chain oxygen
O³: bridge oxygen


200 nm
Mag = 100.00 K X
WD = 5.0 mm


b
a

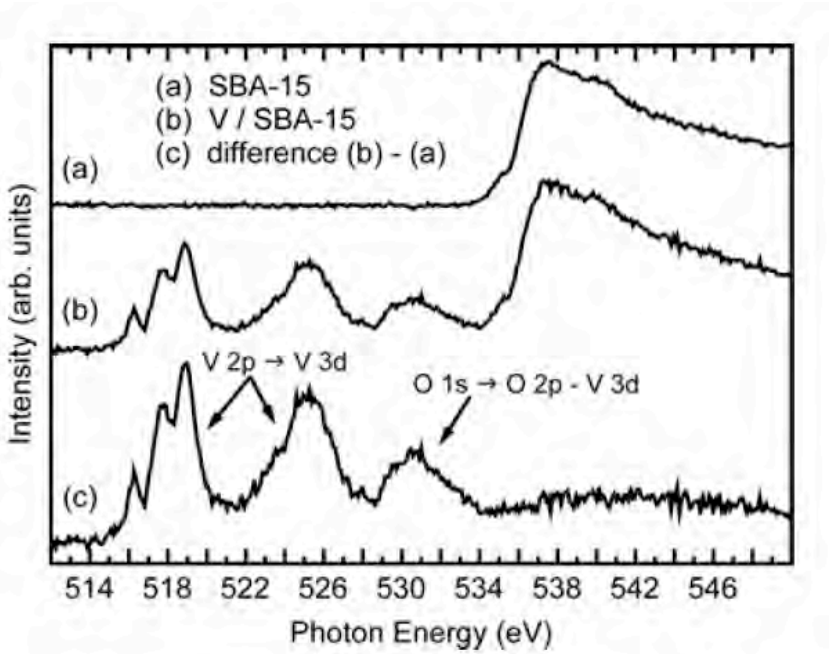

W
d


O
V
O
O
O
Si
Si
Si

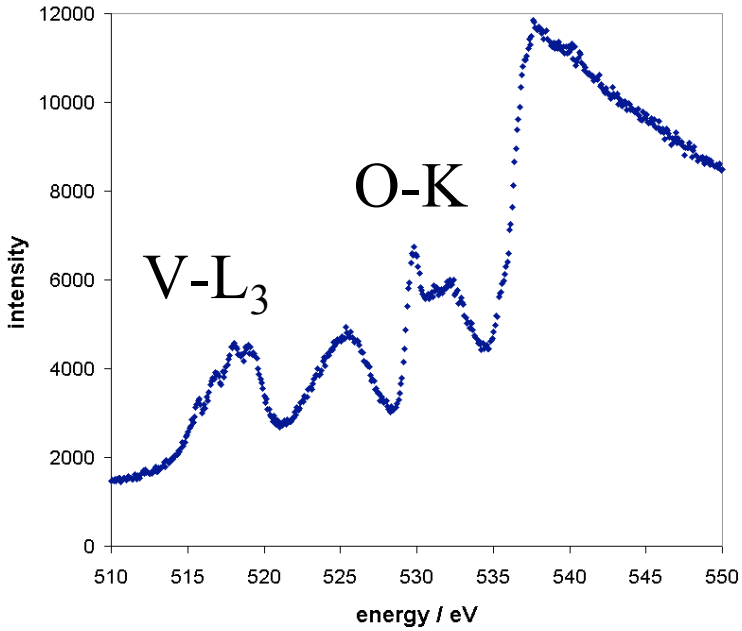

O
V
O
O
O
O
V
O
O
O
Si
Si

Comparision of absorption spectra

Electron yield



Fluorescence yield



/1/ M. Cavalleri, K. Herrmann, A. Knop-Gericke, M. Hävecker, R. Herbert, C. Hess, A. Oesterreich, J. Döbler. R. Schlögl
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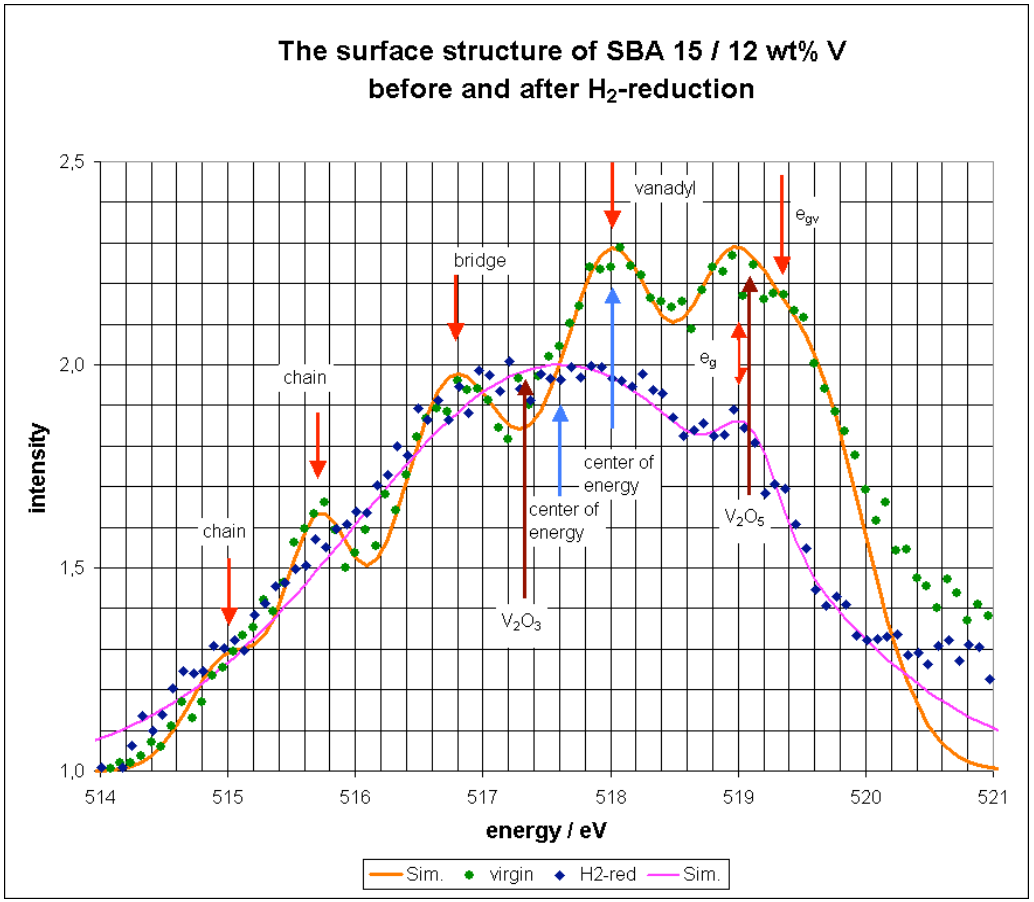
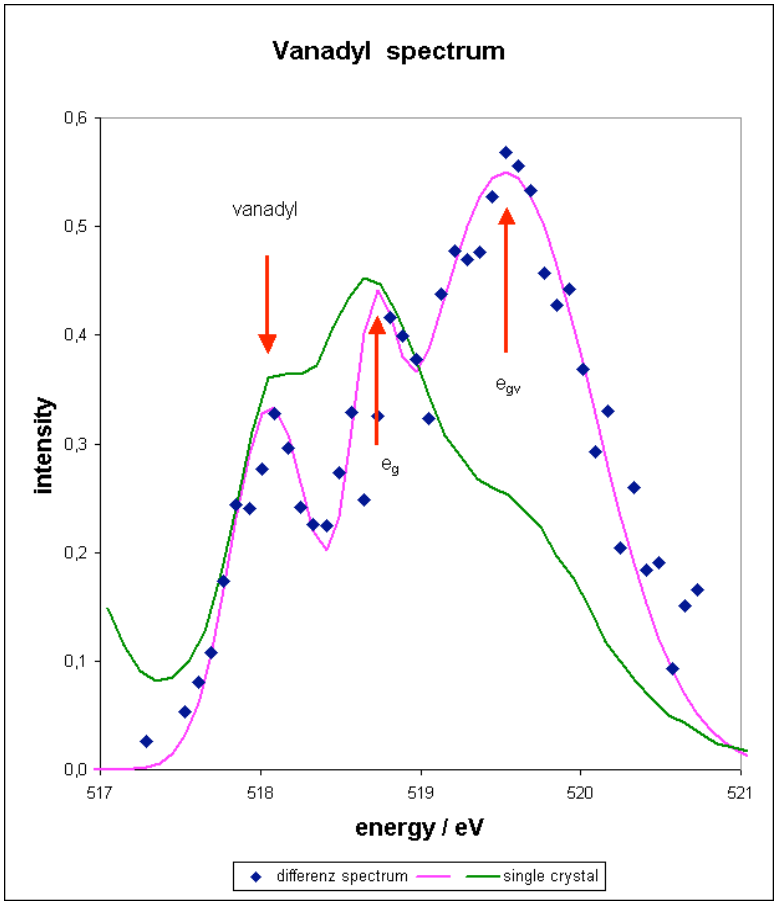
SBA-15 / vanadia ; 12 wt% V

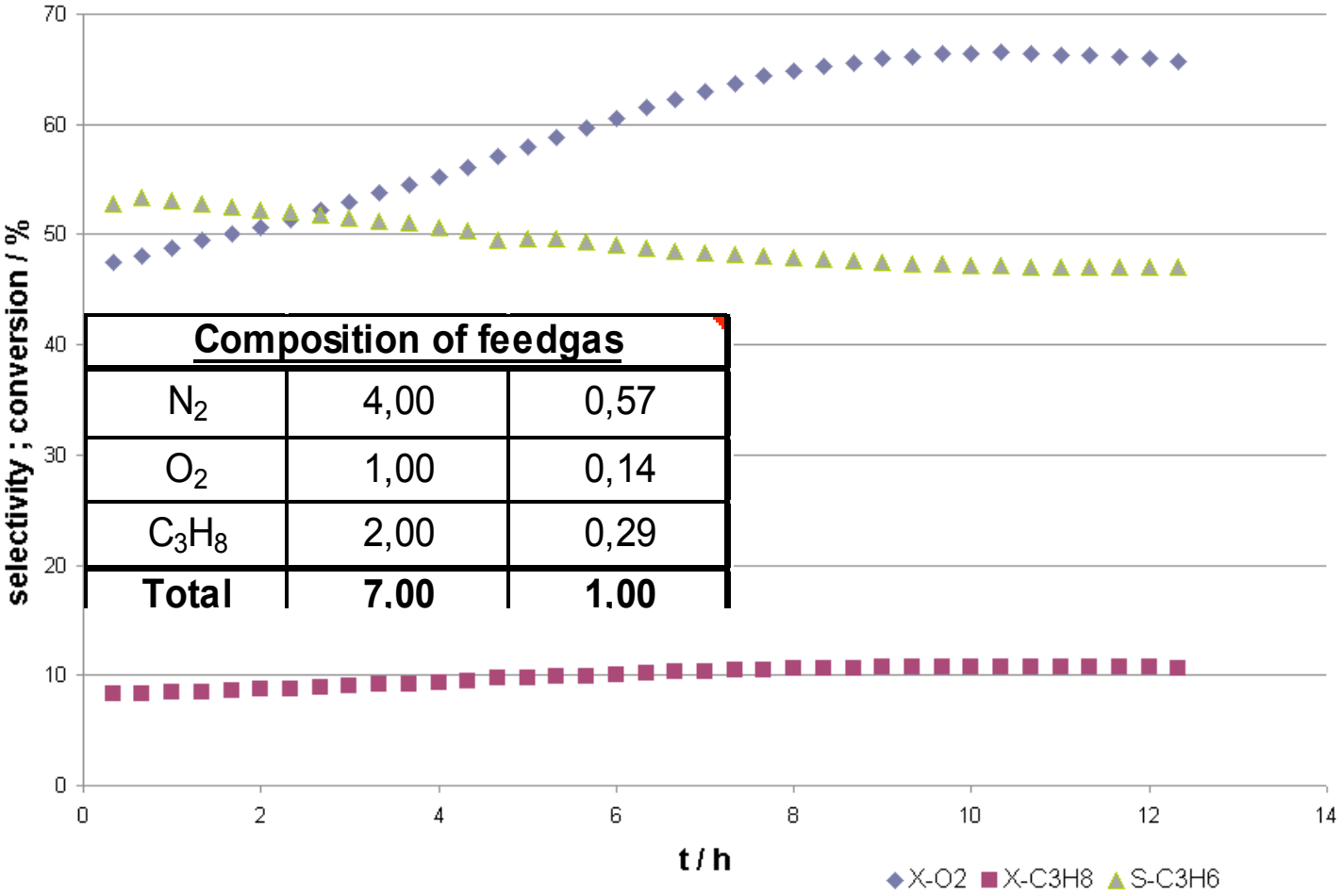
L_3 spectrum of virgin material - The effect of H_2 reduction





- In virgin material, we find a pseudooctahedric coordination of oxygen
- H_2 reduction (absence of O_2) eliminates vanadyl oxygen; formation of V_2O_3

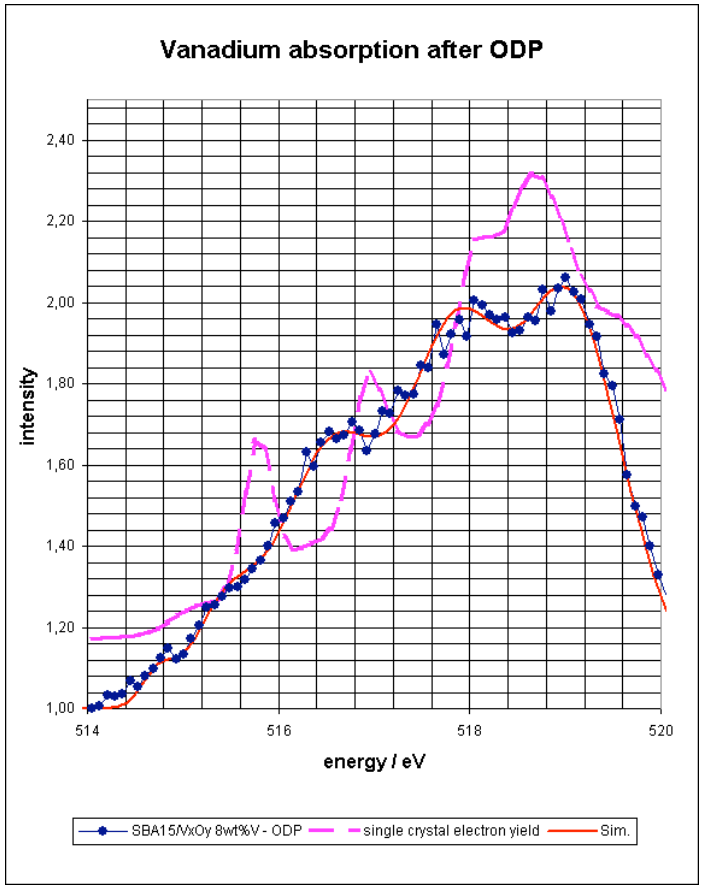
Oxidative Dehydrogenation of Propane

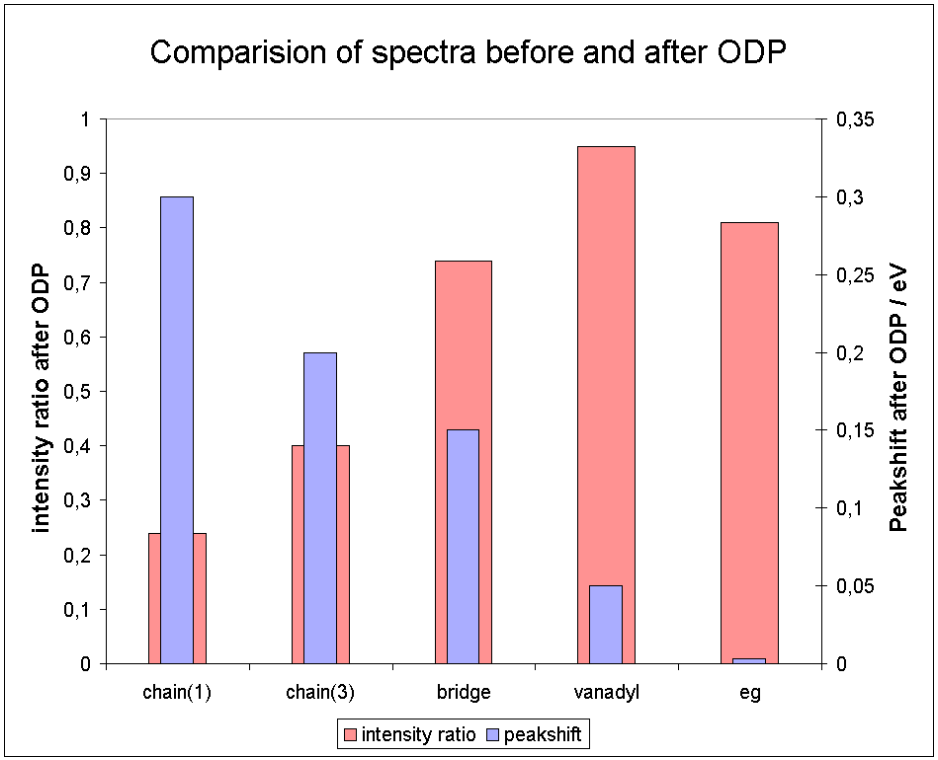


Composition of feedgas		
N_2	4,00	0,57
O_2	1,00	0,14
C_3H_8	2,00	0,29
Total	**7.00**	**1.00**

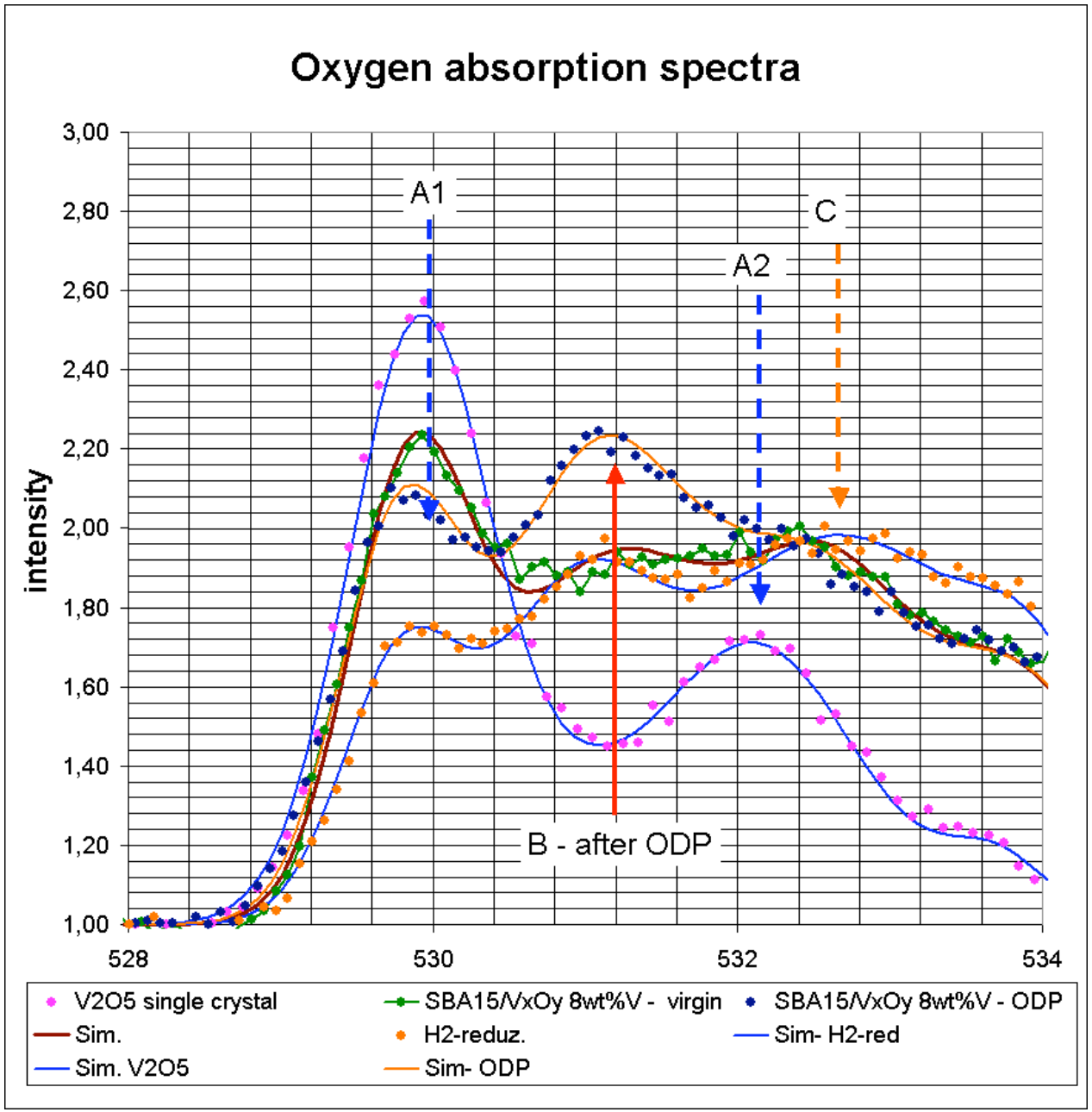
Reaktion
2 C3H8 + λ O2 _ a C3H8 + b O2 + c C3H6 + d CO + e CO2 + f H2O + g C2H6 + h C2H4 + i CH4

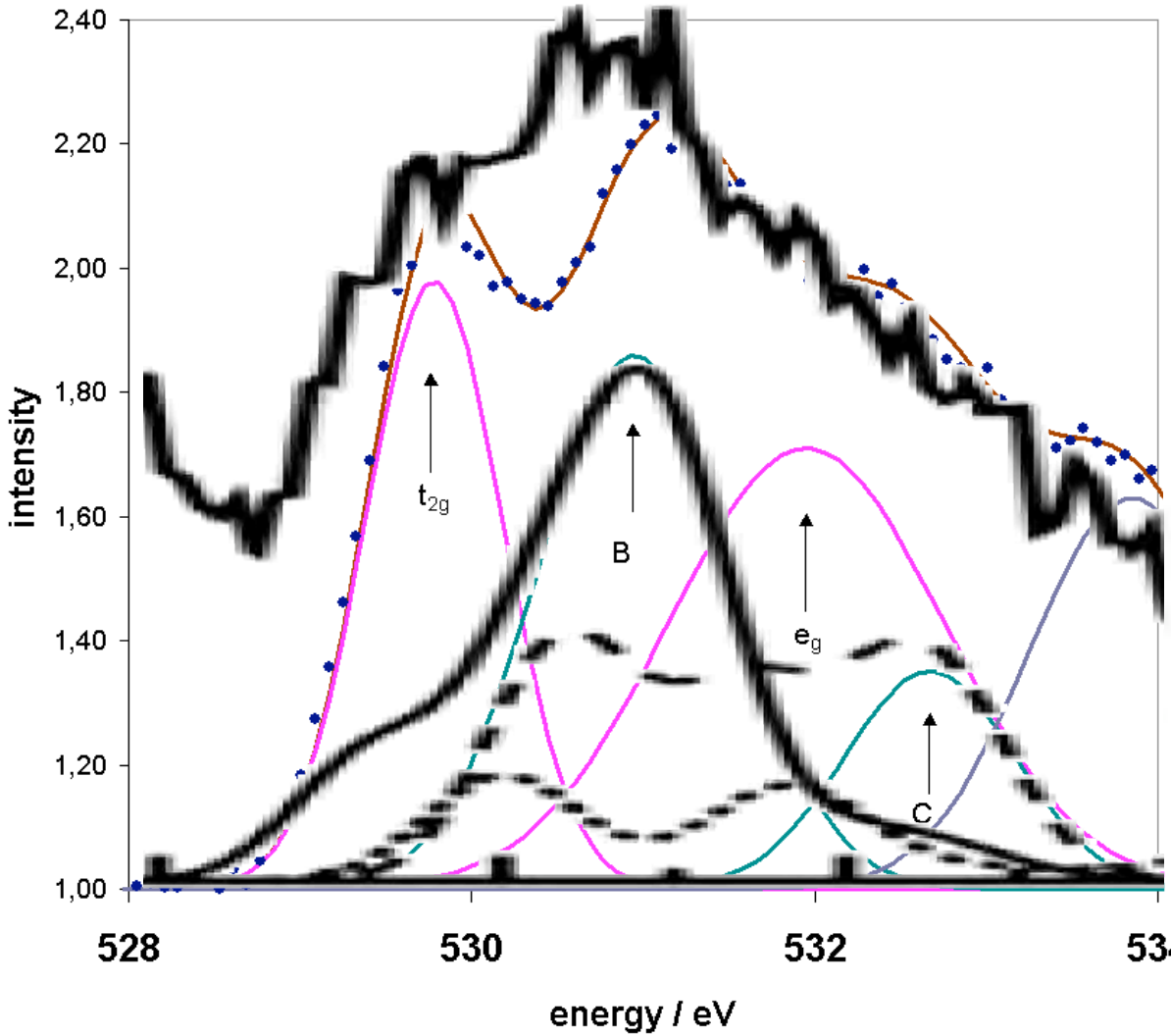
Effect of ODP on the structure of vanadia



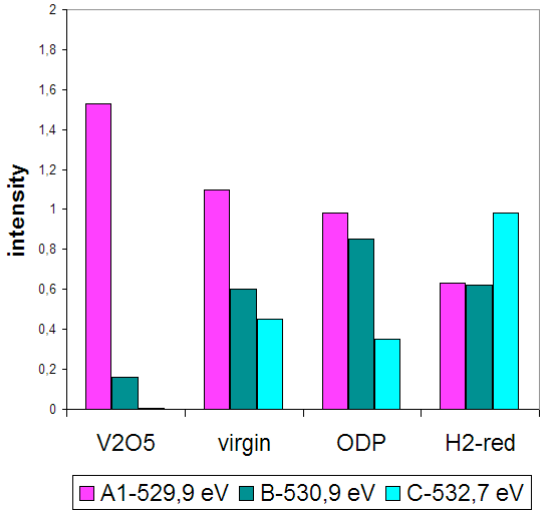


- The distortion of the octahedron increases
- The bond length and concentration of vanadyl groups is unchanged
- The bond length for bridging oxygen increases
- Chains are cutted – dispersion of vanadia is observed


Oxygen absorption spectra
intensity
3,00
2,80
2,60
2,40
2,20
2,00
1,80
1,60
1,40
1,20
1,00
528
530
532
534
A1
A2
C
B - after ODP
V2O5 single crystal
SBA15/VxOy 8wt%V - virgin
SBA15/VxOy 8wt%V - ODP
Sim.
H2-reduz.
Sim- H2-red
Sim. V2O5
Sim- ODP



Effect of catalysis on dispersion and oxidation



—— V=O(1)

- - - V-O(2)-V

..... V-O(2)-Si

Effects of ODP - Summary

results for V-L3 – edge

- octahedron distortion ↑
- dominant vanadyl –and bridging bondings
- no change of bond length and concentration of vanadyl groups
- bond length of bridging oxygen ↑
- chains are cutted, dispersion of vanadia observed
- oxidation state after ODP is conserved

results for O-K – edge

- superposition of 3 components:
  octahedral coordinated V_2O_5 (A)
  highly dispersed material (B)
  reduced components (C)
- The short range order of vanadia is octahedral coordinated
- vanadyl and bridging oxygen may contribute to the dispersed vanadia according /1/ (monomers and dimers)
- oxidation status of V increases after ODP