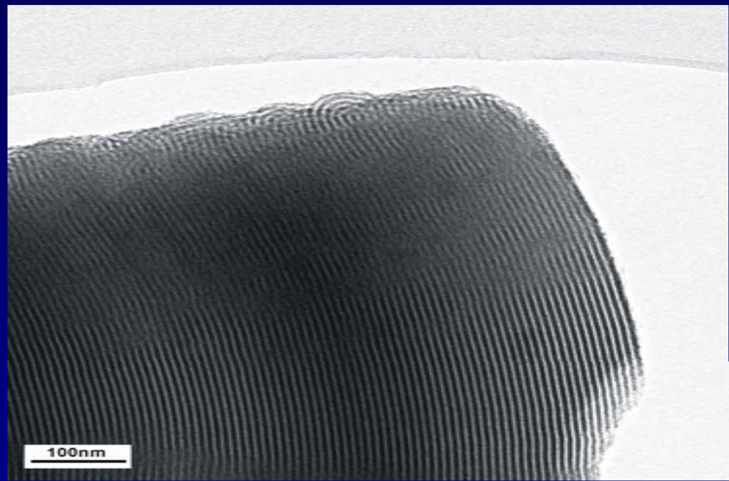
Nanostructured vanadia model catalysts for partial oxidation reactions

Christian Hess

Dept. Inorganic Chemistry, Fritz Haber Institute



Emmy Noether-Programm
Deutsche Forschungsgemeinschaft
DFG

SBA-15 (TEM, 200 kV)

- **Model catalysts based on nanostructured materials**
- **Spectroscopic characterization**
  - **- Synthesis**
  - **- Catalyst surface structure and dispersion**
- **Selective oxidation over highly dispersed vanadia**

- Model catalysts based on nanostructured materials
- Spectroscopic characterization
  - Synthesis
  - Catalyst surface structure and dispersion
- Selective oxidation over highly dispersed vanadia

Why use nanostructured materials as support ?

- High(er) specific surface area of nanostructured materials
  - → increased activity
  - → formation of isolated, catalytic sites

…an estimate based on a material with spherical particles

using (1) $A = 4 \Pi r^2 / m$

(2) $m = 4/3 \rho \Pi r^3$

⇨ **$A = 3/\rho r$**

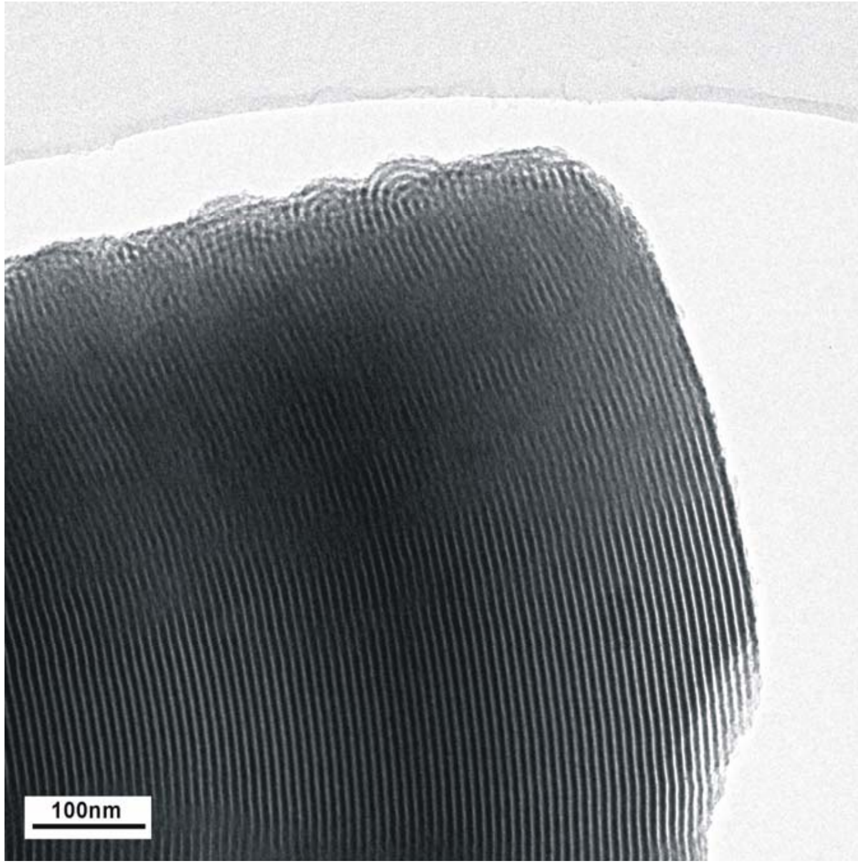
with $\rho \sim 3$ g/cm^3 (typ. oxide value)

shows that for
r = 1 cm ⇨ A = 10^{-2} m^2/g
r = 1 μm ⇨ A = 1 m^2/g
r = 1 nm ⇨ A = 1000 m^2/g

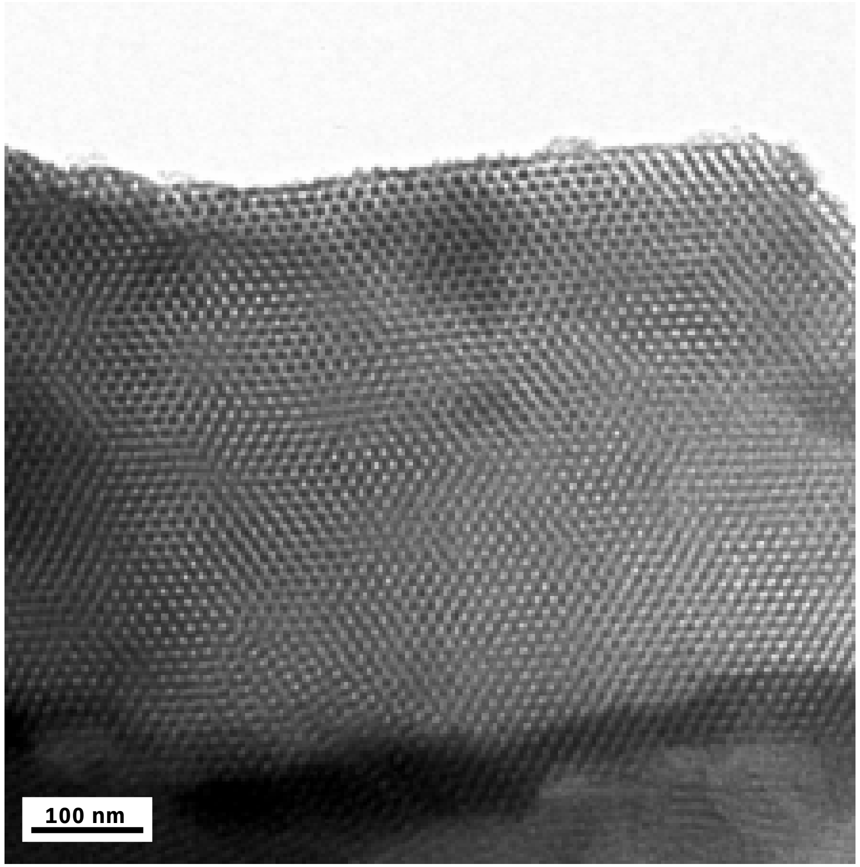
⇨ Creation of high surface requires nanoscale structuring

Characterization of mesoporous silica SBA-15

TEM characterization



along a longitudinal section



in a section of hexagonal pores

⇨ Silica SBA-15 is a very ordered large-pore (6 nm) material

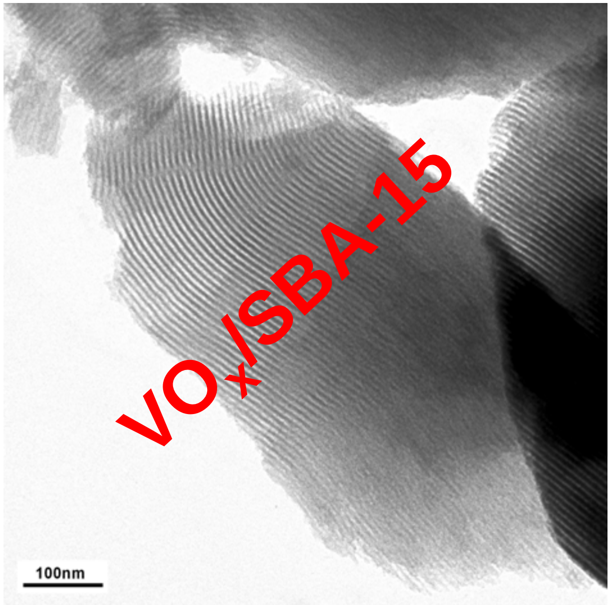
Model catalysts based on nanostructured SBA-15

• Support properties are well defined (structural homogeneity)
and tunable (pore diameter)

➞ control over support properties

➞ well-structured silica platform for vanadia catalysts

⇨ *3-D model catalyst with full catalytic function*



as shown below

• *well-known preparation*

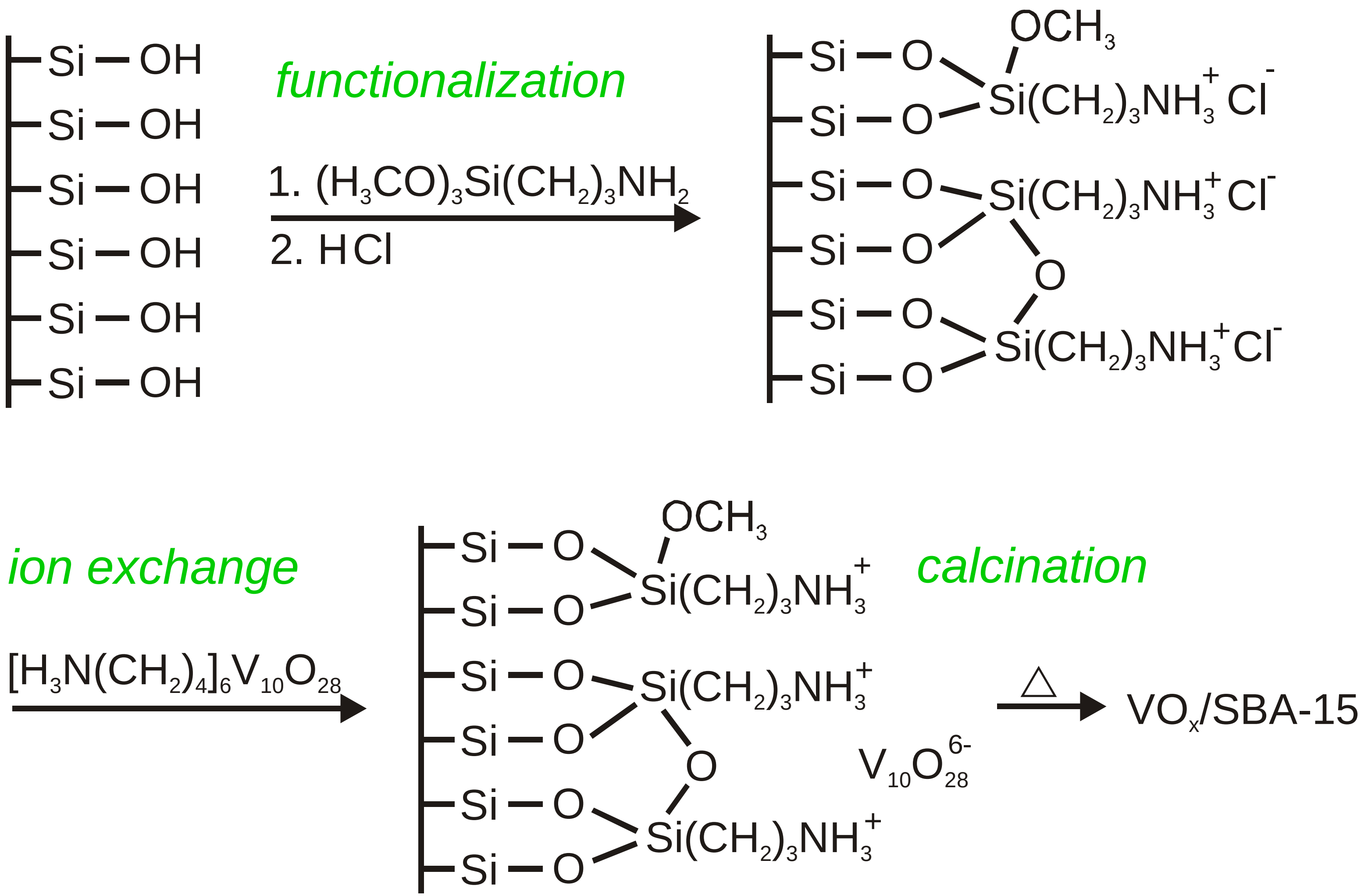
• *high density uniform sites*

• *allows to mimic active sites*

C. Hess, Surf. Sci. 600 (2006) 3695

- Model catalysts based on nanostructured materials
- Spectroscopic characterization
  - Synthesis
  - Catalyst surface structure and dispersion
- Selective oxidation over highly dispersed vanadia

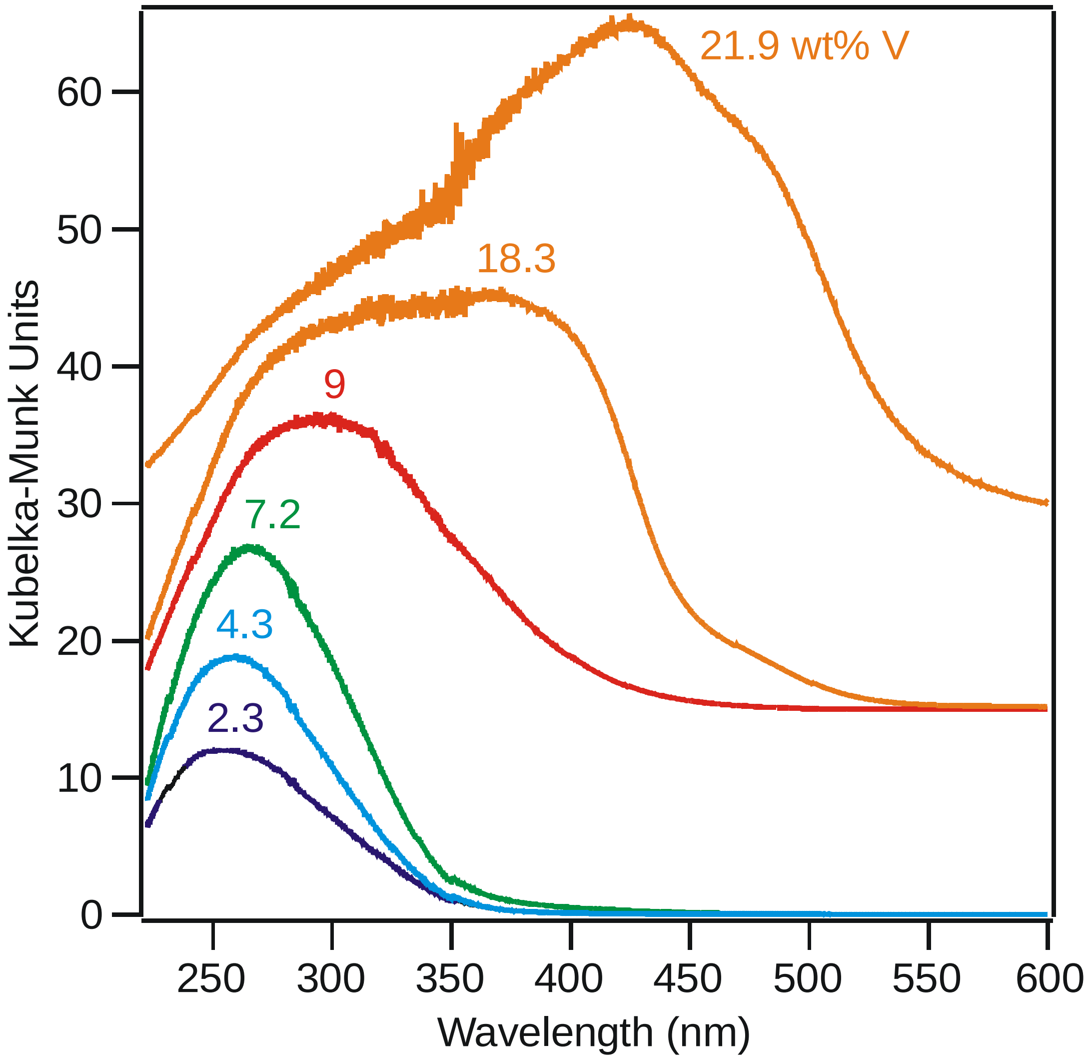
Synthesis of vanadia supported on silica SBA-15



⇨ Novel method to anchor TM oxides on mesoporous supports

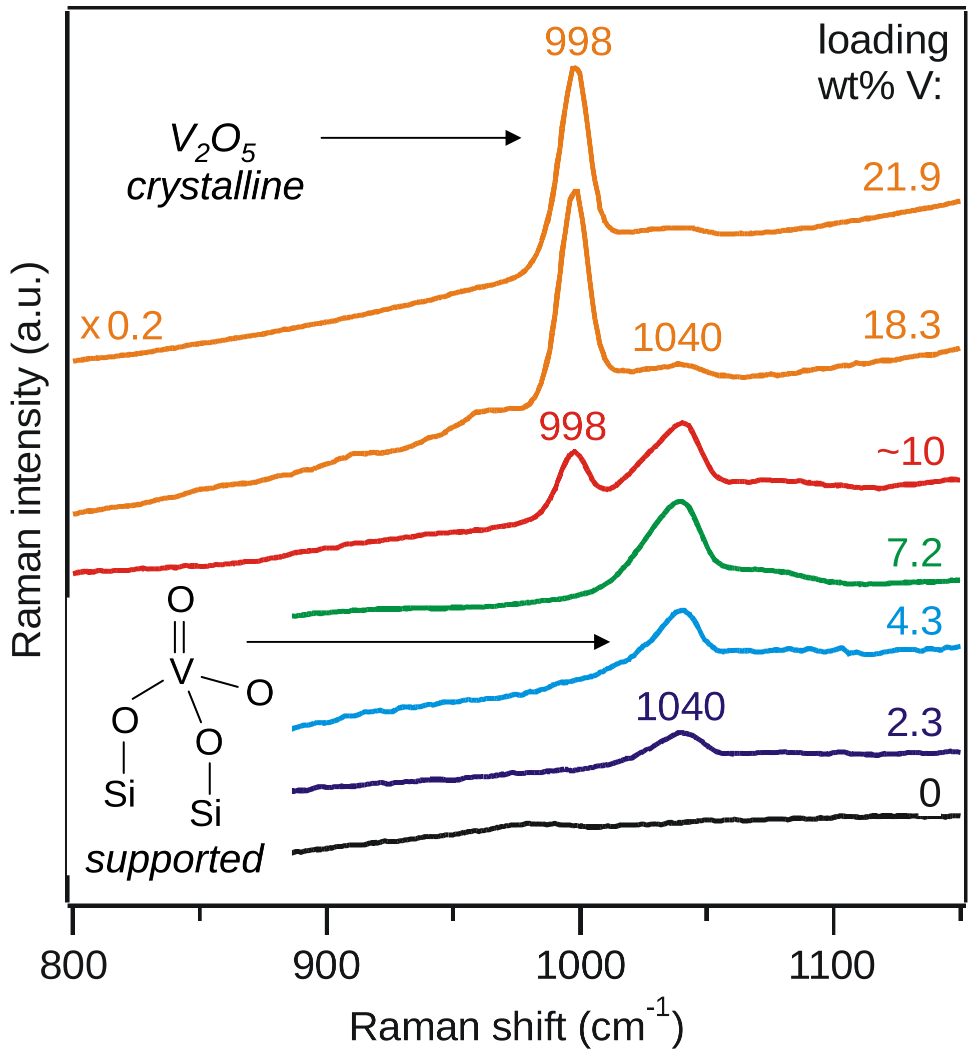
C. Hess, J.D. Hoefelmeyer, T.D. Tilley, JPCB 108 (2004) 9703

DR UV-VIS characterization of VO_x/SBA-15



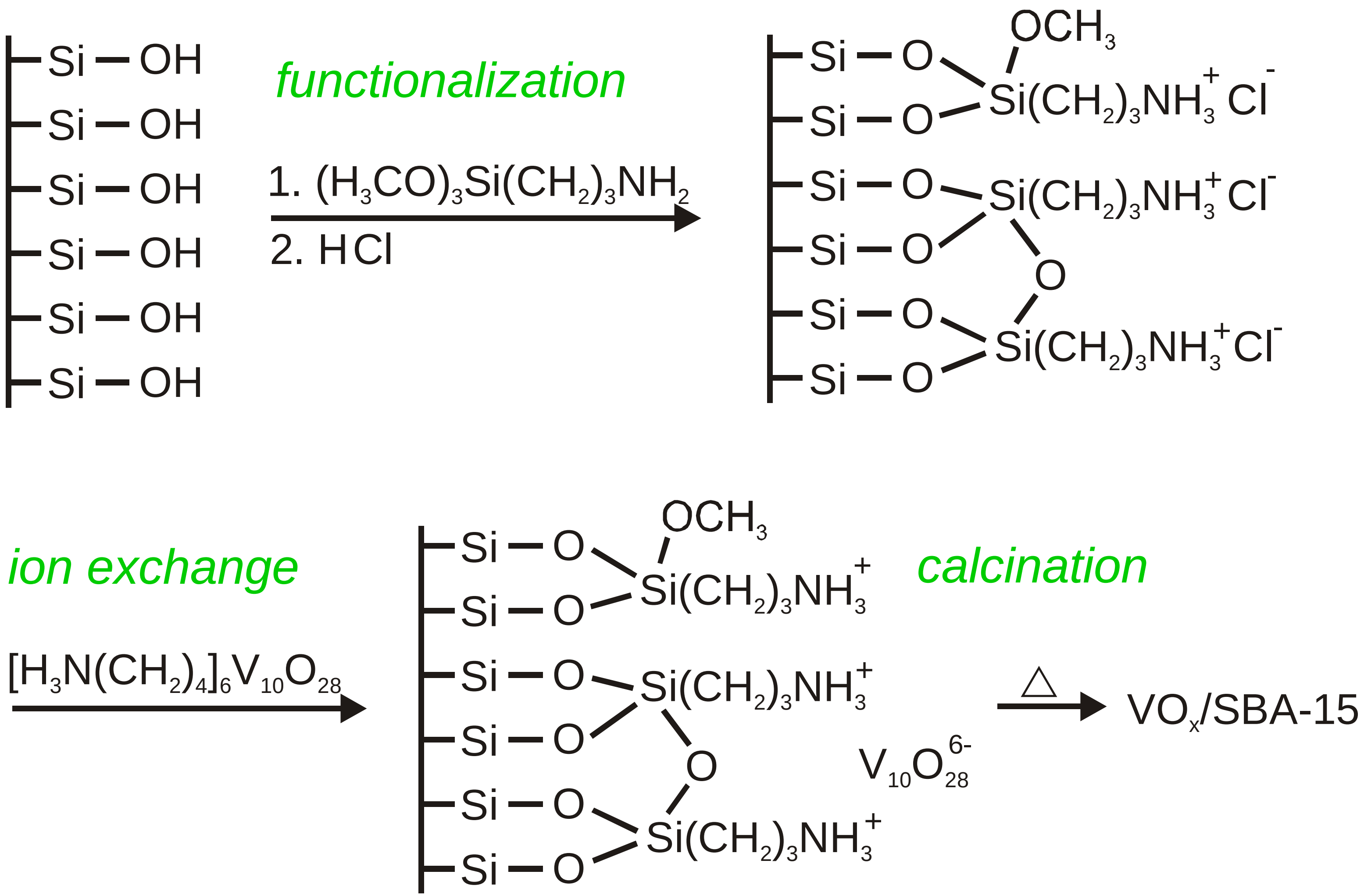
⇨ Redshift with loading indicates increasing coordination of V

Visible Raman characterization of VO_x/SBA-15



⇨ **Raman allows for sensitive detection of V=O in cryst. V_2O_5**

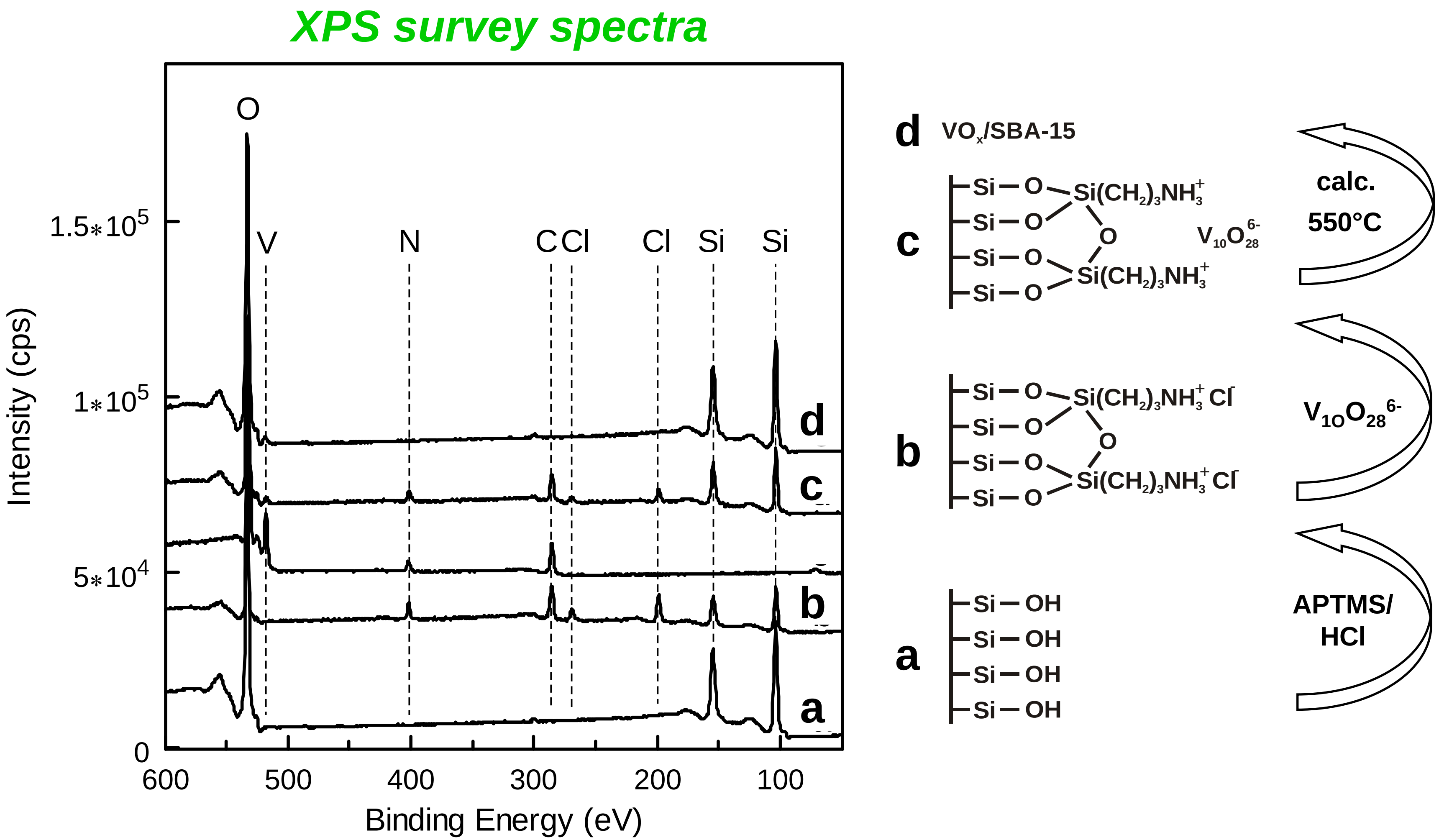
Synthesis of vanadia supported on silica SBA-15



⇨ Novel method to anchor TM oxides on mesoporous supports

C. Hess, J.D. Hoefelmeyer, T.D. Tilley, JPCB 108 (2004) 9703

XPS during synthesis of VO_x/SBA-15

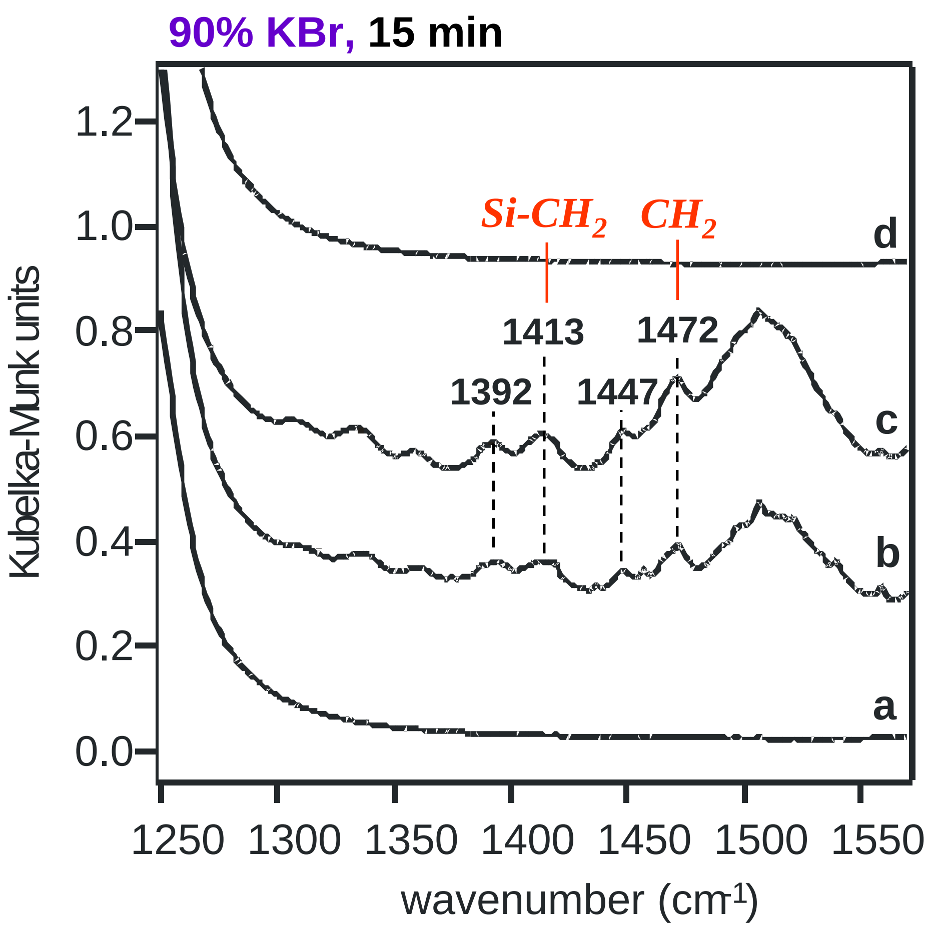


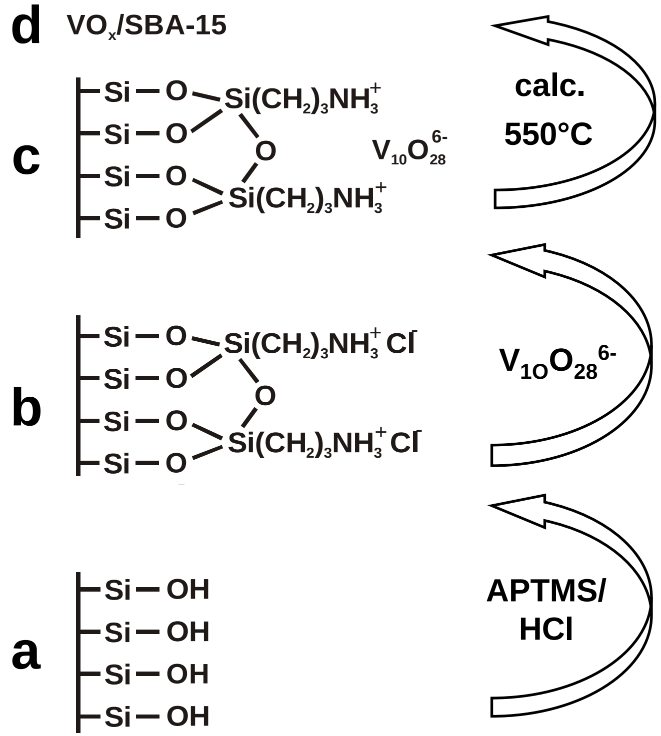
⇨ XPS confirms well-defined nature of VO_x/SBA-15 synthesis

C. Hess, U. Wild, R. Schlögl, Microp. Mesop. Mater. 95 (2006) 339

DRIFTS characterization during synthesis

C-H bending vibrations

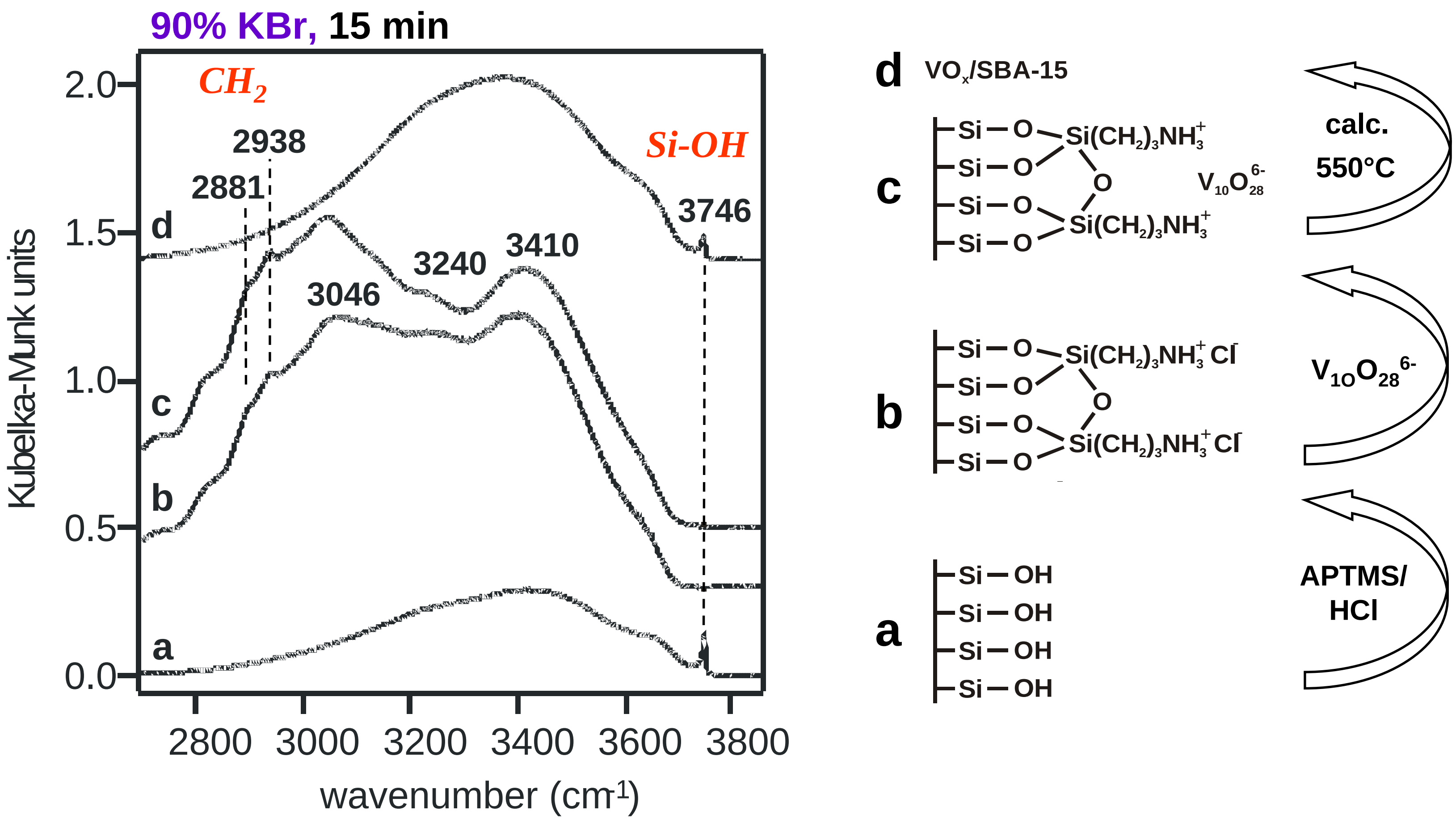




⇨ **DRIFTS data demonstrates removal of C upon calcination**

DRIFTS characterization during synthesis

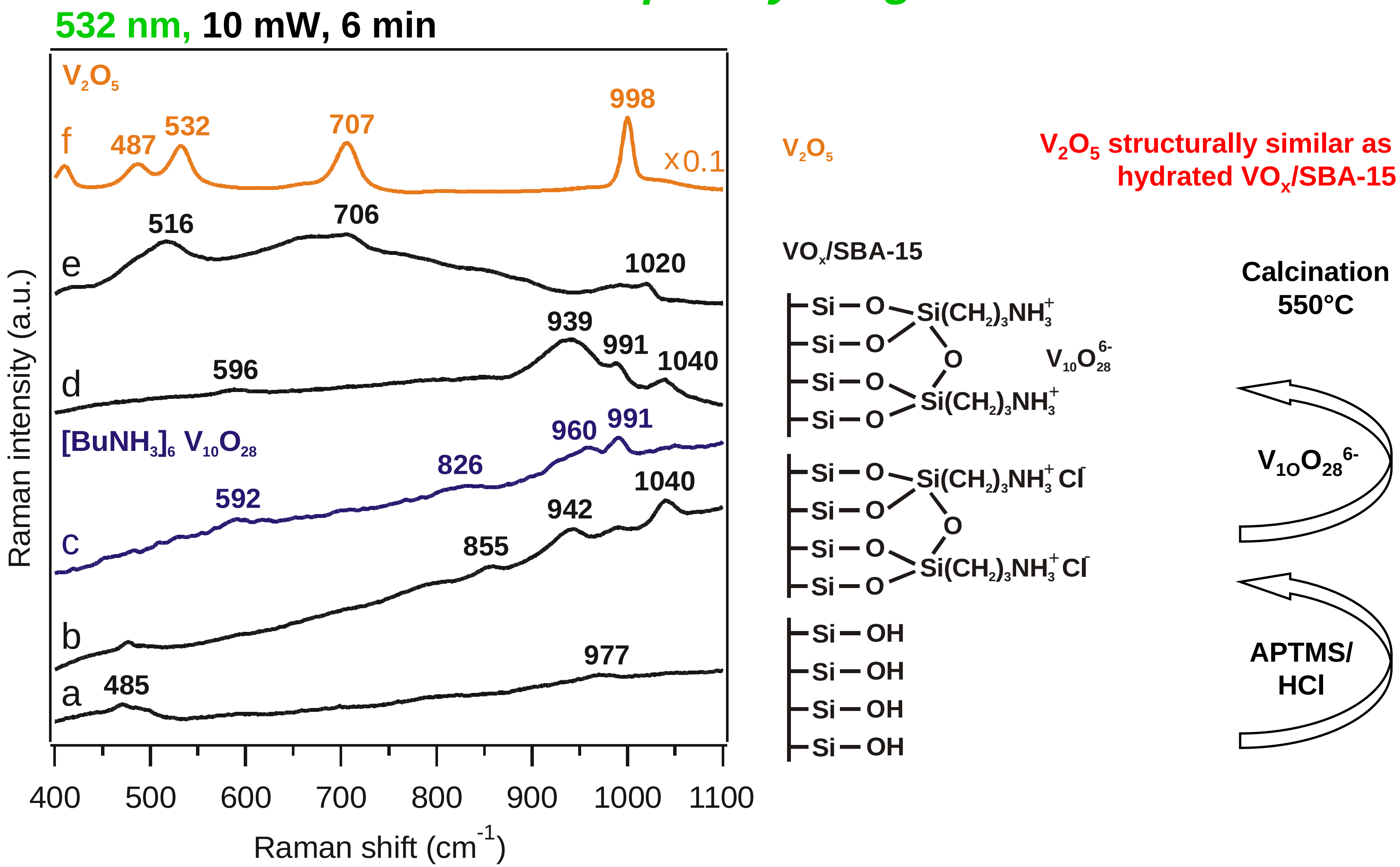
C-H/O-H stretch vibrations



⇨ **C-H range allows to monitor anchoring of vanadia via Si-OH**

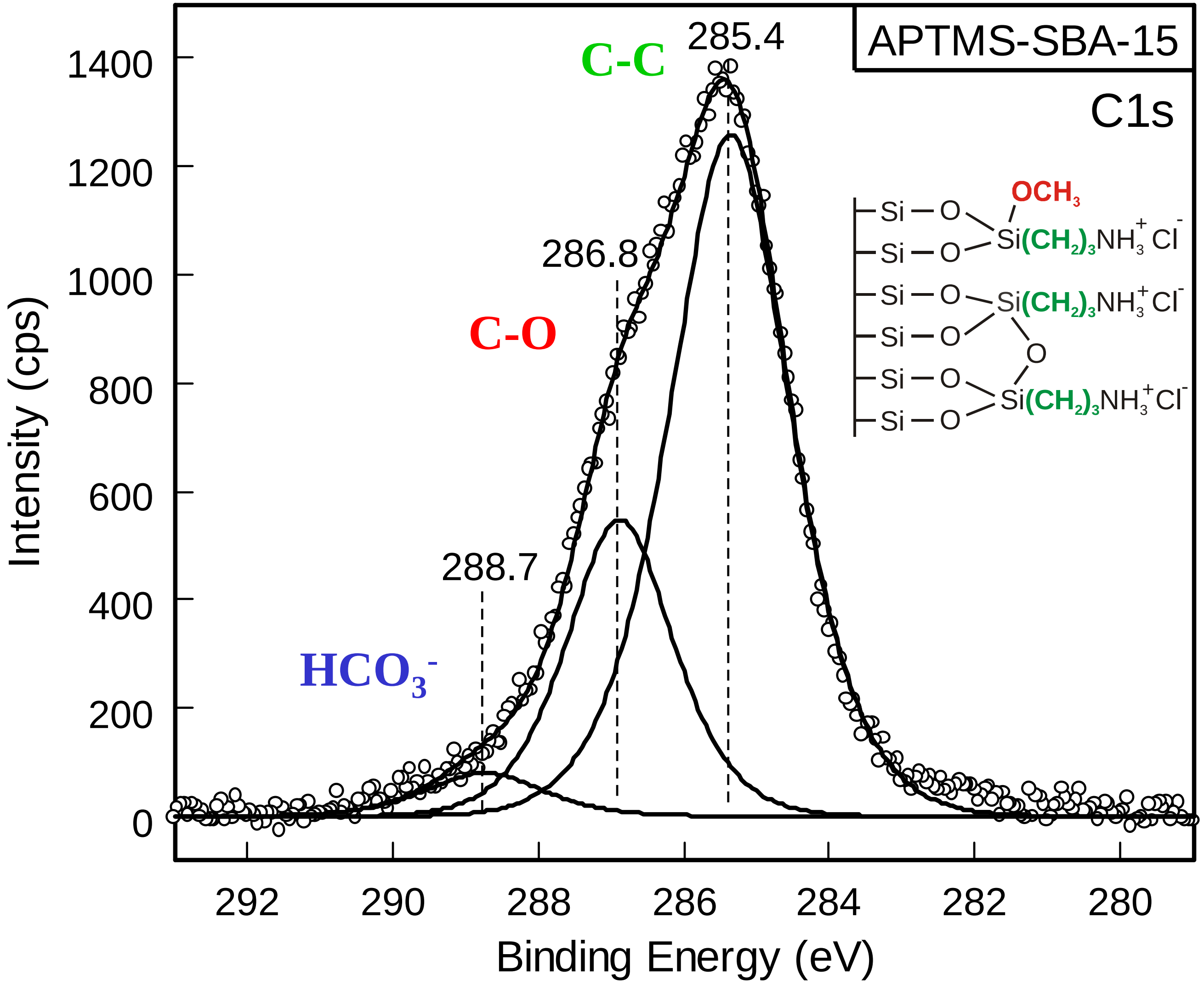
Raman characterization during synthesis

V-O frequency range



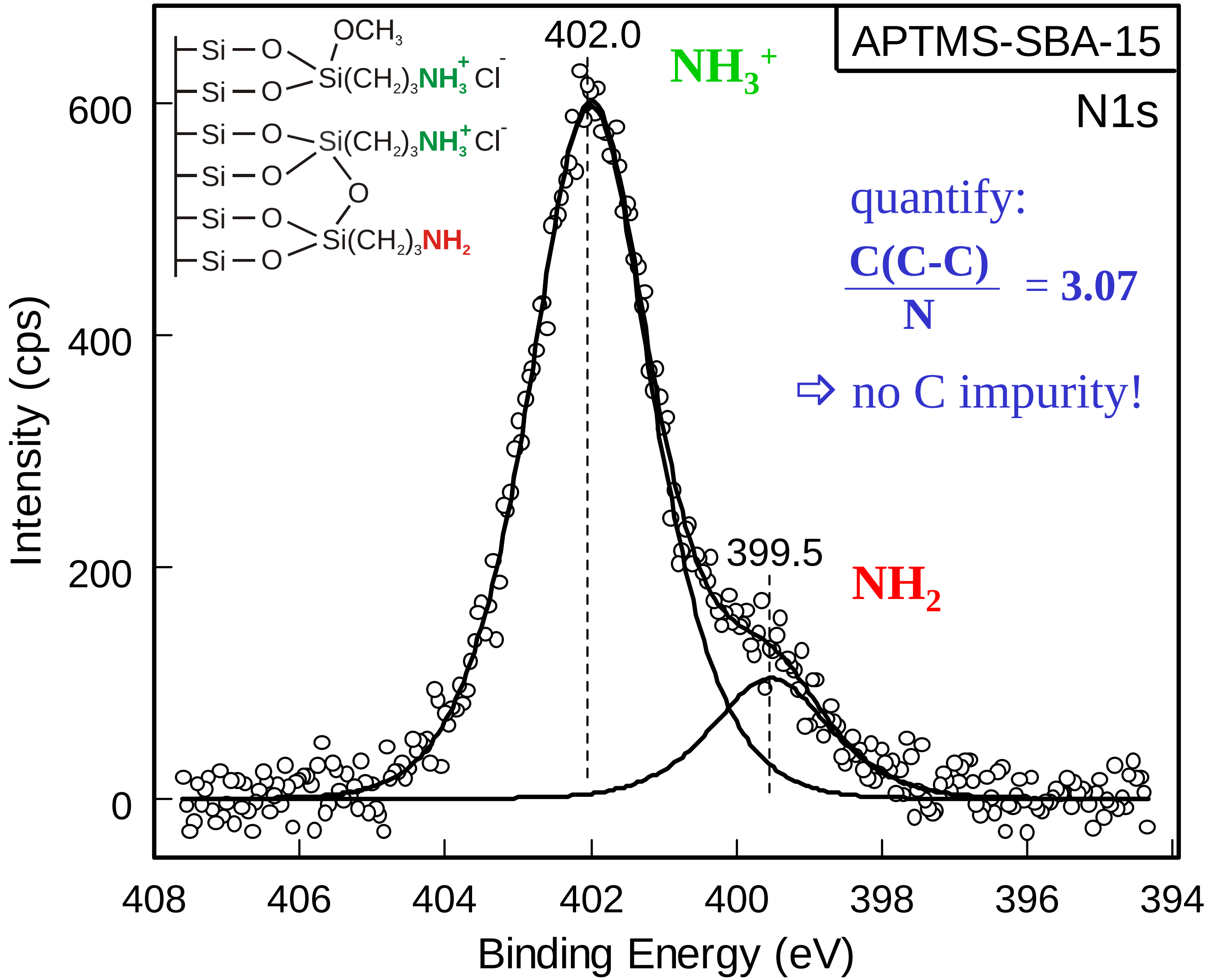
⇨ **V-O range allows to monitor ion-exchange and calcination**

C1s XP spectra during synthesis of VO_x/SBA-15



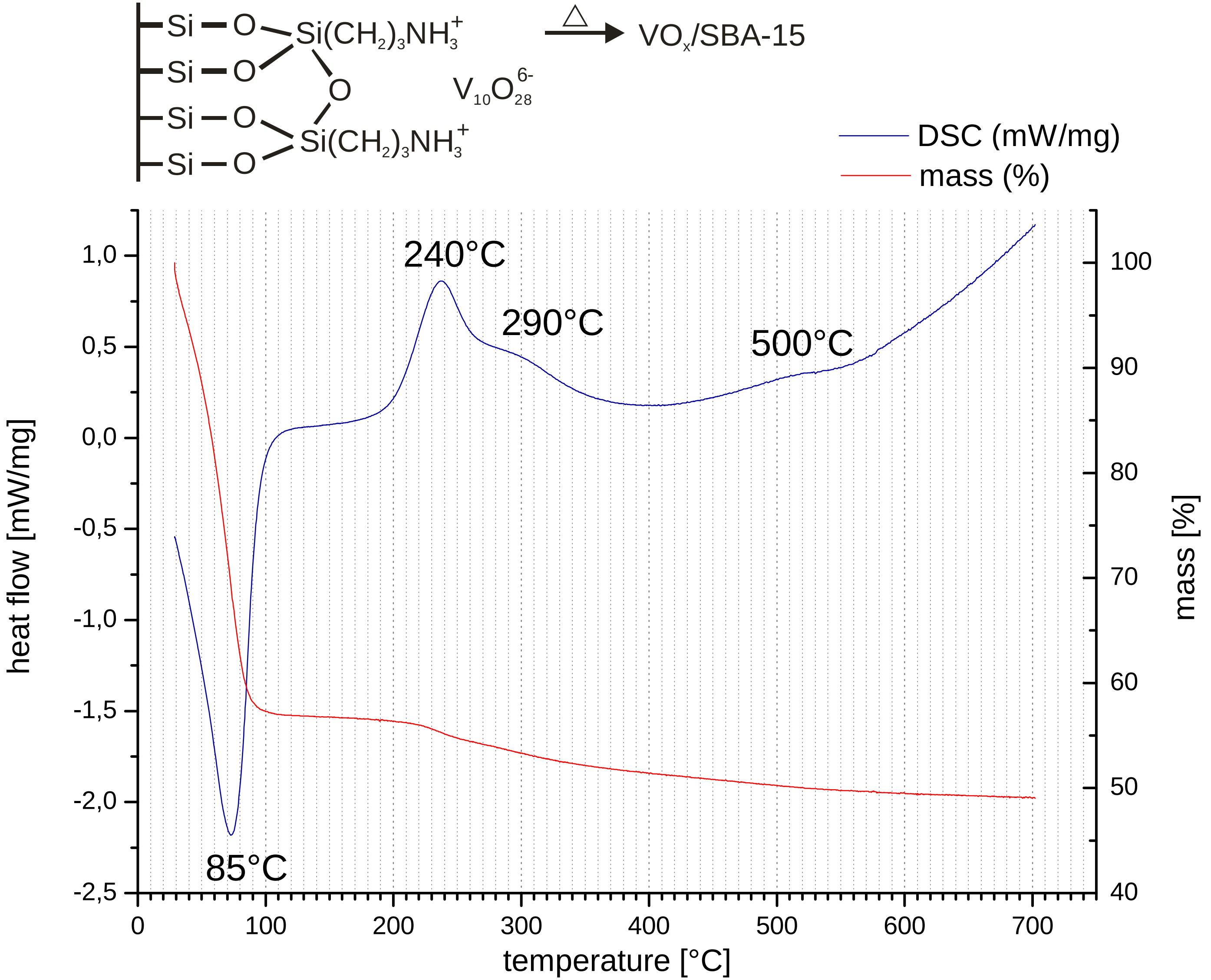
⇨ Detailed information on framework structure

N1s XP spectra during synthesis of VO_x/SBA-15

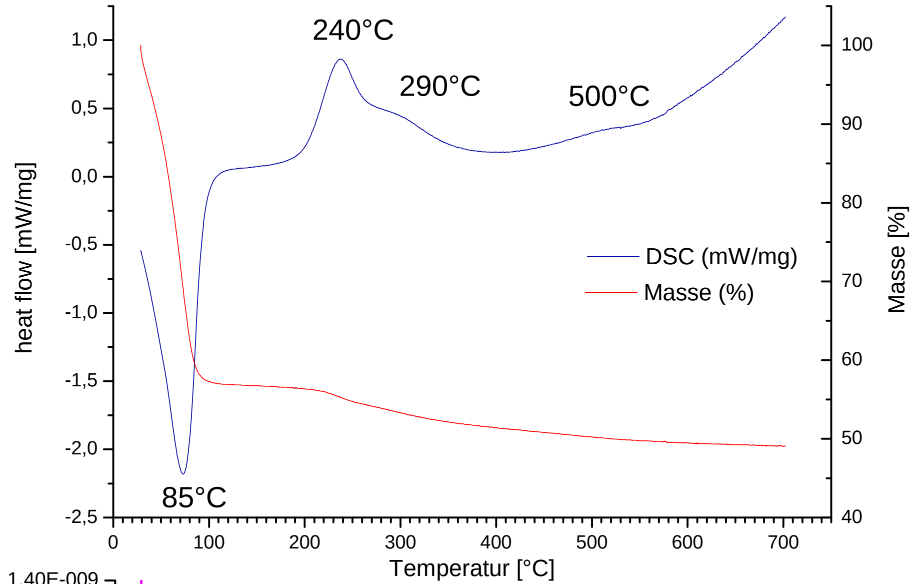


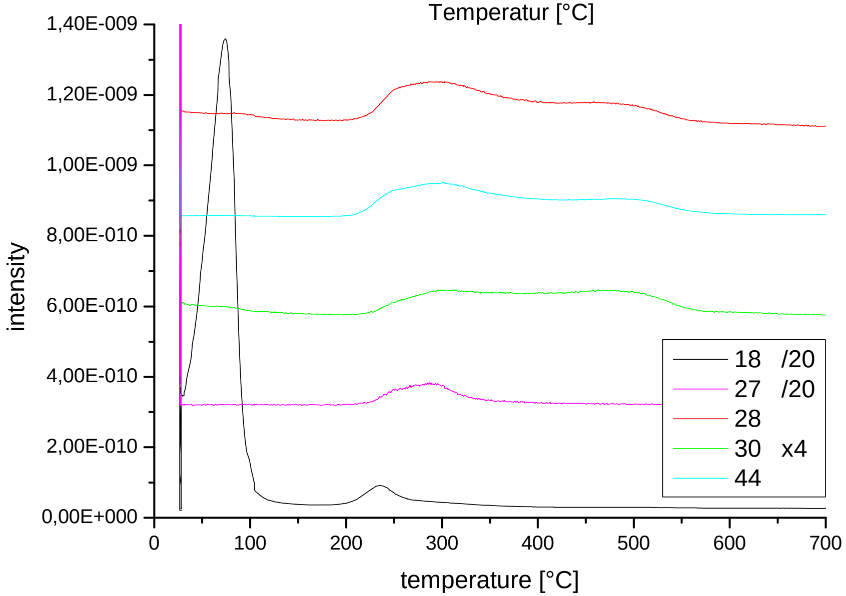
⇨ **Quantitative surface composition of intermediates**

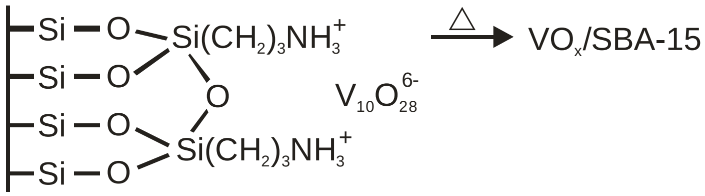
TG/MS characterization of calcination step



TG/MS characterization of calcination step

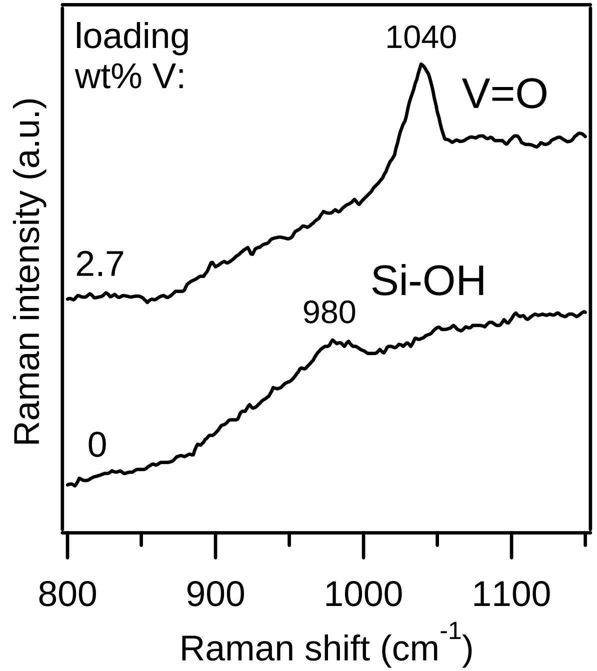






⇨ **organic framework is fully removed during calcination**

… and VO_x is anchored via OH



• Model catalysts based on nanostructured materials

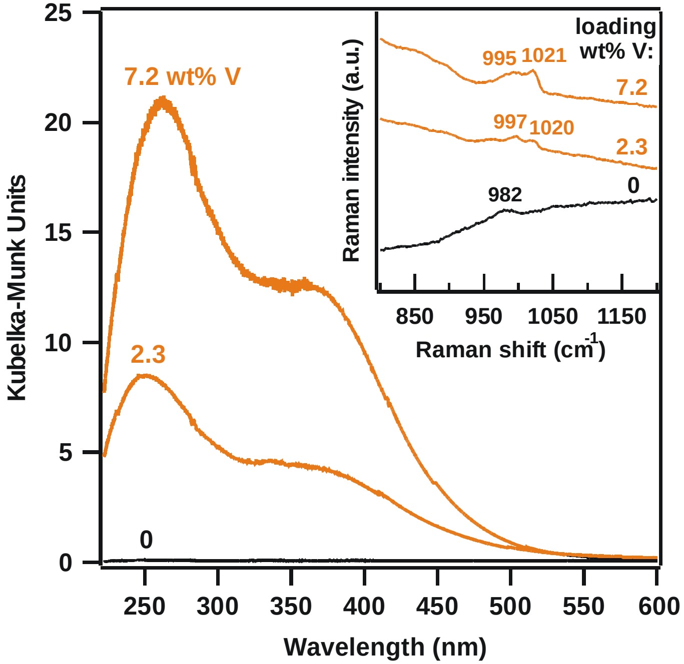
• Spectroscopic characterization

- Synthesis
- Catalyst surface structure and dispersion

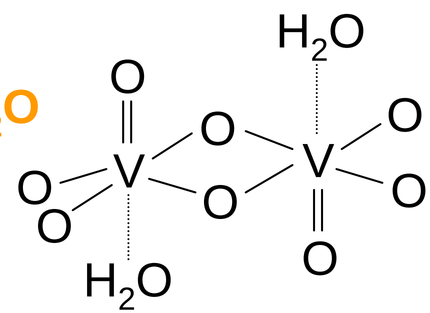
• Selective oxidation over highly dispersed vanadia

Structural changes of vanadia during activation

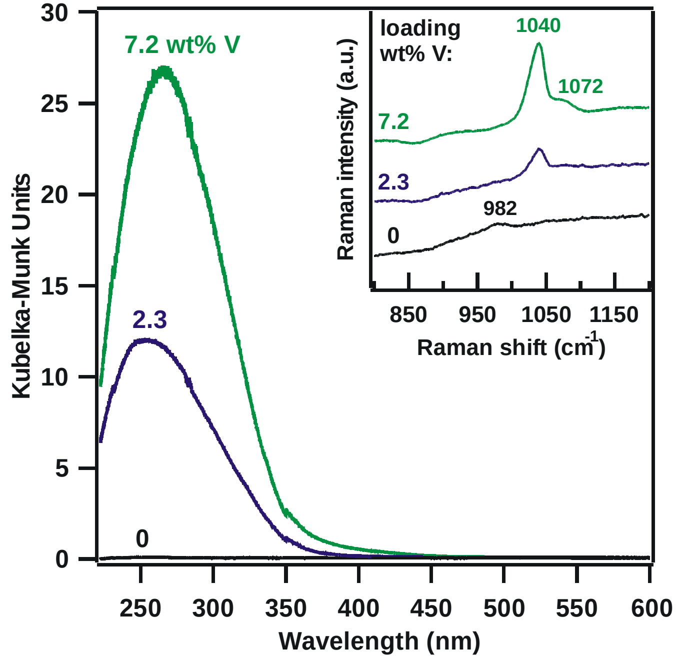
'as is': hydrated

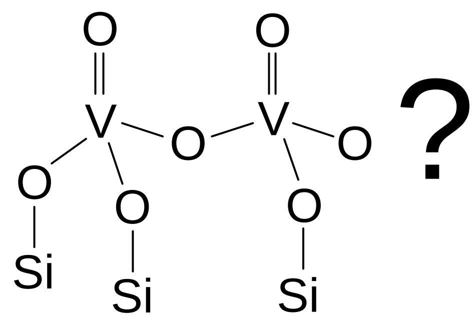


$V_2O_5 \cdot n\ H_2O$



dehydrated

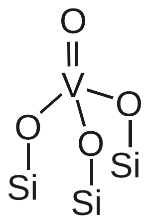




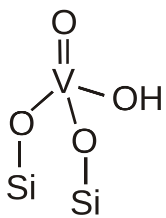
⇨ **Dehydration dramatically changes the surface VO_x structure!**

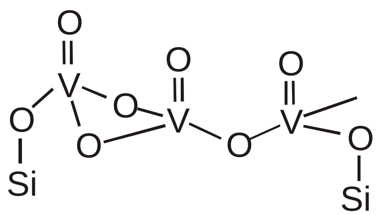
Structure of silica supported vanadia: Literature

Structural motifs proposed for dispersed vanadia

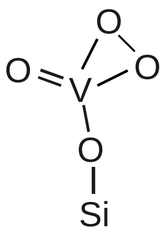


Oyama/Bell et al. (1989)
Wachs et al. (1991)





Wokaun et al. (1991)
Vansant et al. (1998)
Hess, Hoefelmeyer, Tilley (2004)
Freund/Sauer/Stair et al. (2004)

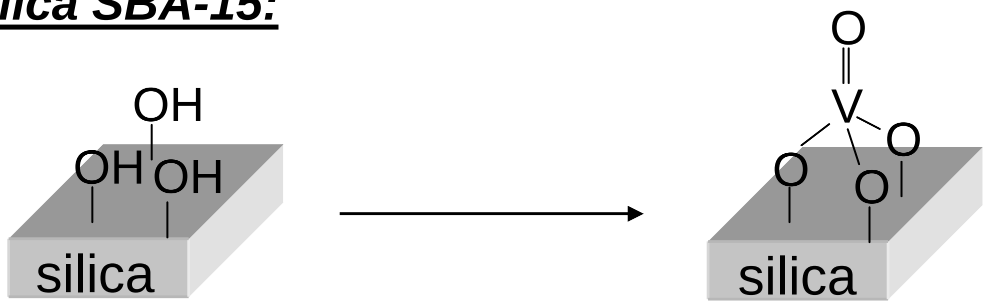


Weckhuysen et al. (2006)

?

Structure of VO_x/SBA-15: OH concentration

Silica SBA-15:



Fully hydroxylated SiO_2:

*[OH] = 4.6/nm^2**

(despite pore size, surface area etc.)

*From NMR** on SBA-15:*

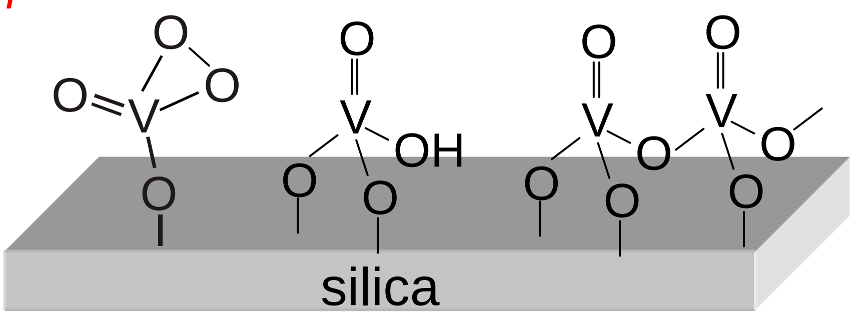
[OH] = 3.7/nm^2

all-isolated three-legged $O=VO_3$ would require:

(3 x 0.8 = 2.4) OH/nm^2 for 3.3 wt% V

(3 x 2.3 = 6.9) OH/nm^2 for 7.2 wt% V

but: would also require high local [OH]!



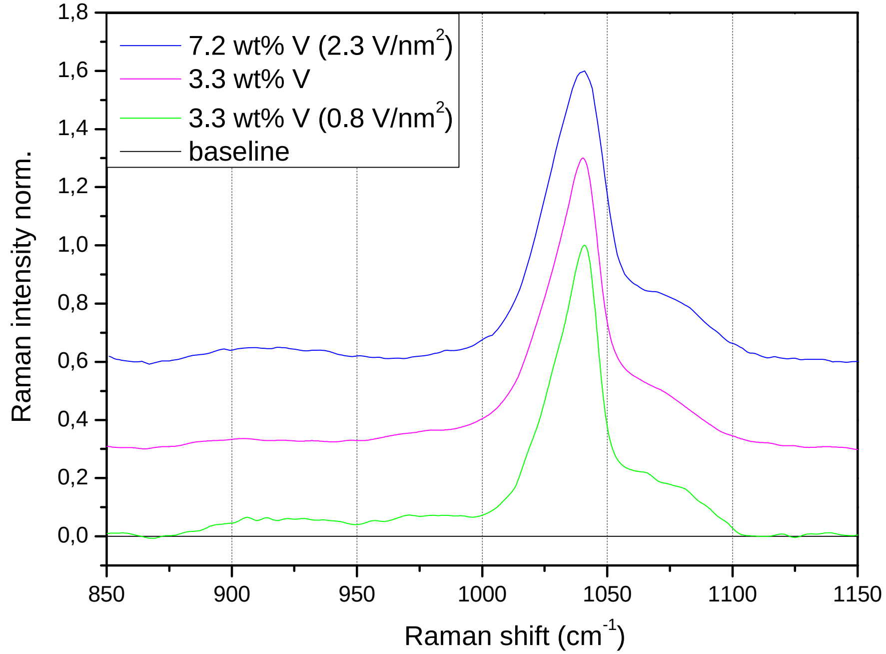
⇨ one/two-legged
⇨ dimeric
⇨ polymeric species

* Zhuravlev et al, Langmuir 3 (1983) 316*

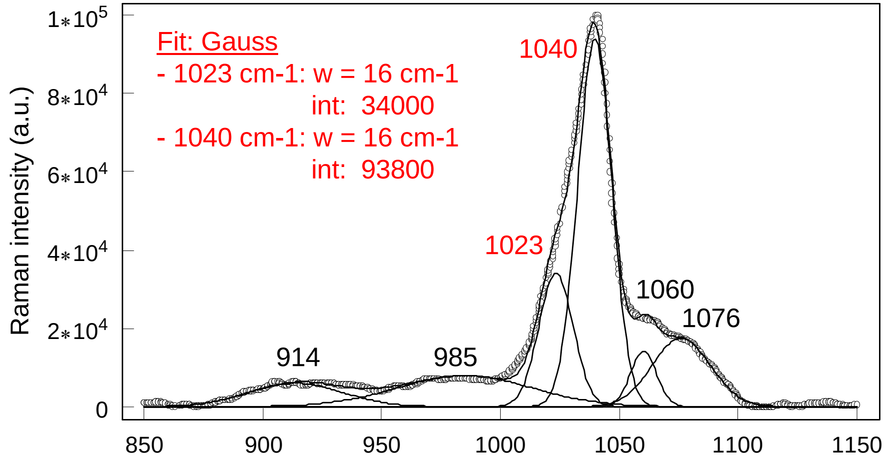
** *Limbach et al, JPCB 107 (2003) 11924*

Visible Raman characterization of VO_x/SBA-15

- VO_x/SBA-15 vanadyl band shape is representative of silica supported vanadia
- No change in V=O band shape with increasing vanadia loading

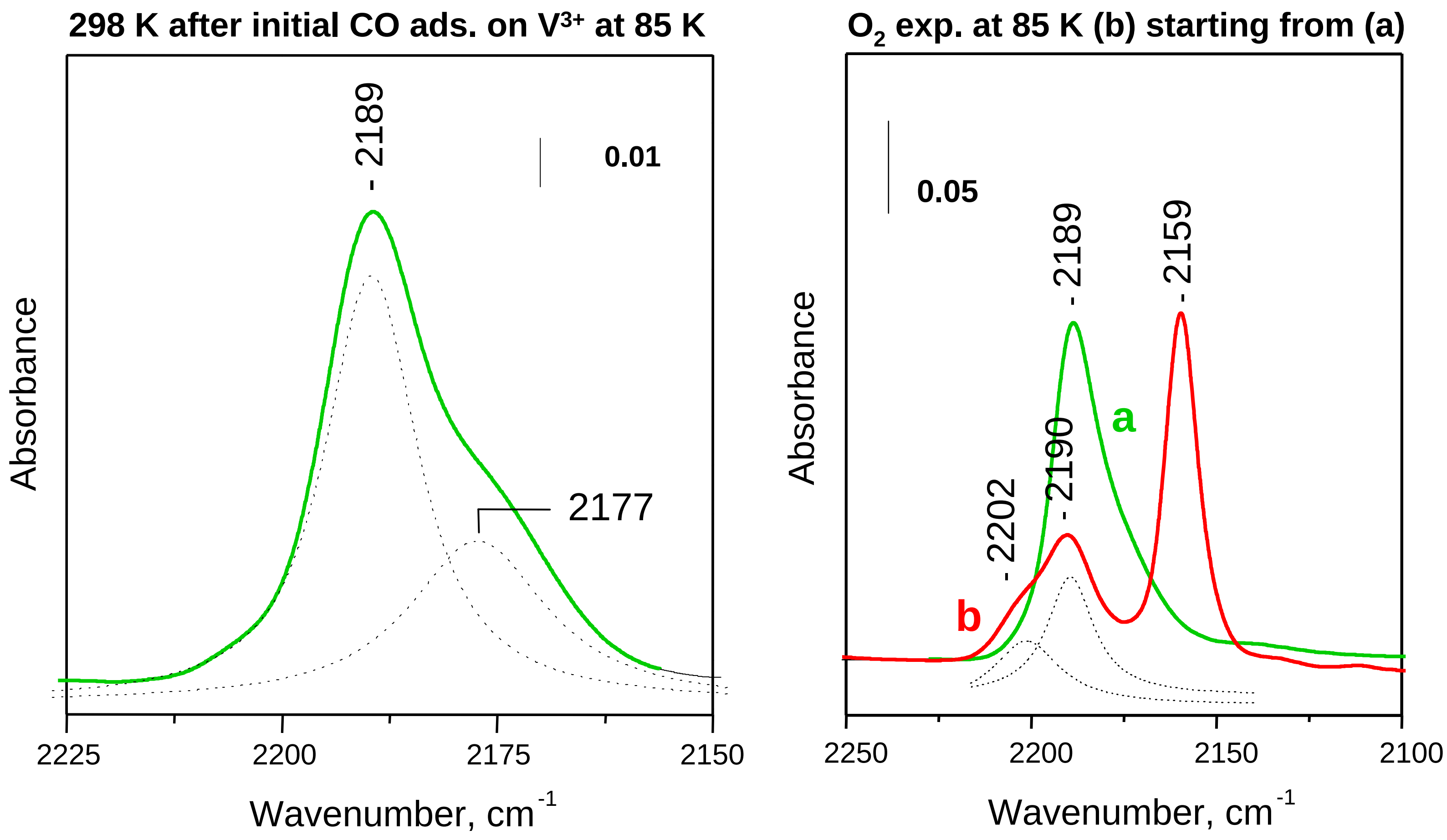


- Asymmetric V=O band shape
  → fitting with Gauss functions
  V=O band consists at least of two contributions



Red-ox properties of VO_x/SBA-15: IR at low T

Using CO as probe molecule



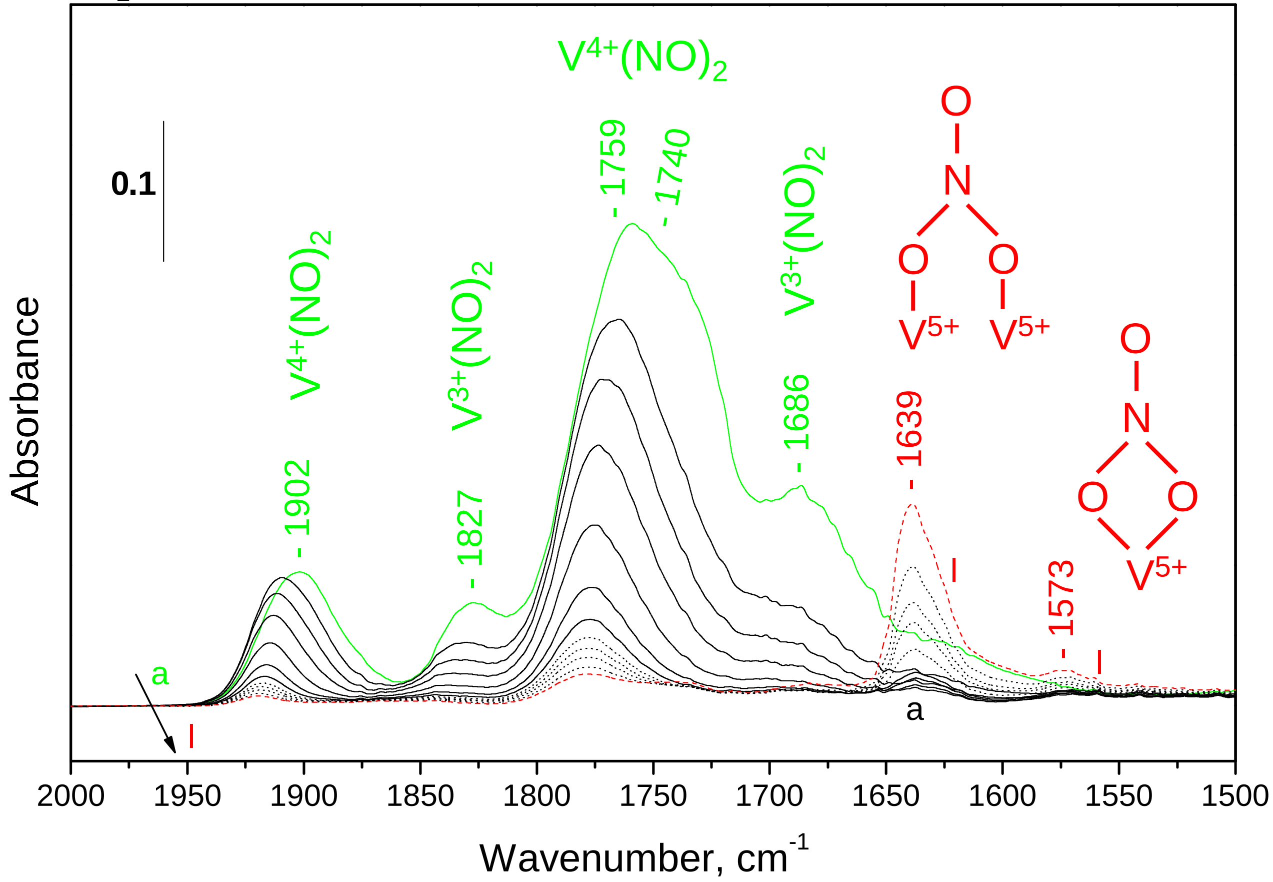
⇨ **Pair of CO-bands due to different $V^{3+/4+}$ sites observed**

C. Venkov, C. Hess, F.C. Jentoft, Langmuir (in press)

Red-ox properties of VO_x/SBA-15: FTIR

Using NO as probe molecule

O_2 exp. at 298 K after adsorption of NO to form V-NO complexes

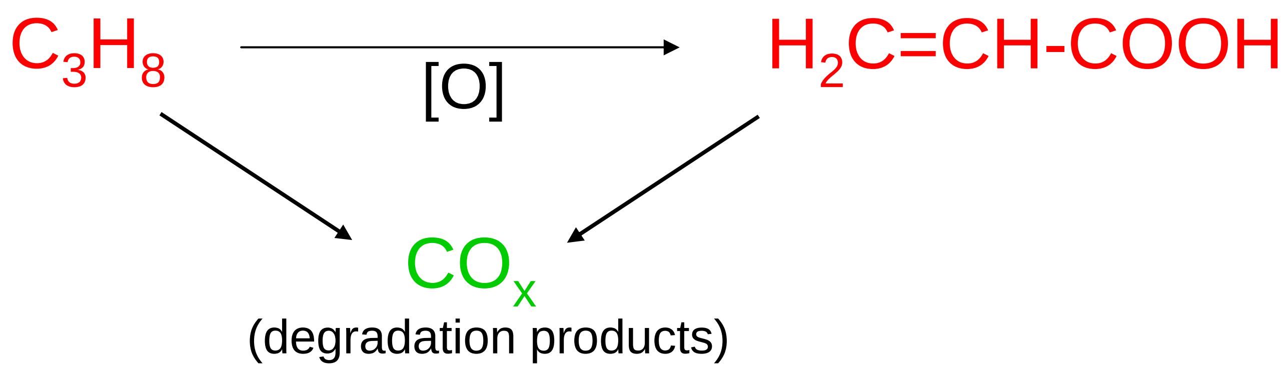


⇨ Bridging nitrates points to presence of polymeric vanadia

C. Venkov, C. Hess, F.C. Jentoft, Langmuir (in press)

- Model catalysts based on nanostructured materials
- Spectroscopic characterization
  - Synthesis
  - Catalyst surface structure and dispersion
- Selective oxidation over highly dispersed vanadia

Selective oxidation of propane over VO_x/SBA-15



1200 h^{-1}, 0.5 ml, $C_3H_8/O_2/N_2/H_2O$ = 1/2.2/17.9/14.1

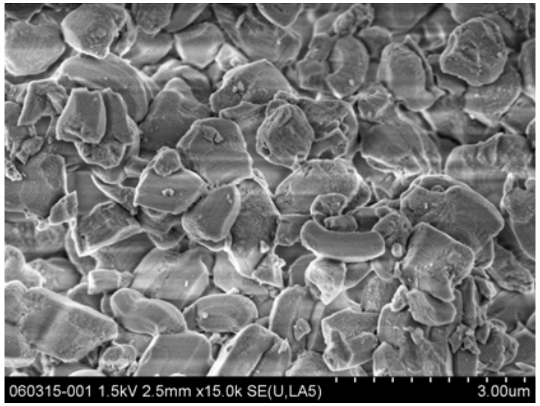
400°C	**C_3H_8 Conversion (%)**	**Time on stream (min)**			**Selectivity (%)**		**Yield of AA (%)**
			AA	**C_3H_6**	**AceA**	**CO_x**	
SBA-15	0	165	0	0	0	0	0
3.3 wt% V/SBA-15	**8**	165	**84**	10	2	**4**	**6.8**
	5	345	86	13	1	0	4.5

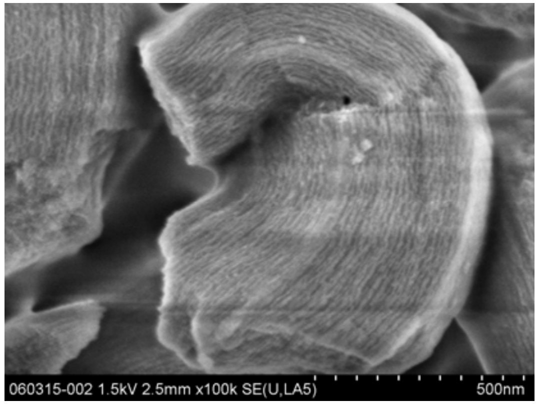
⇨ Highly dispersed vanadia shows high selectivity towards AA

C. Hess, M.H. Looi, S.B. Abd Hamid, R. Schlögl, Chem. Comm. (2006) 451

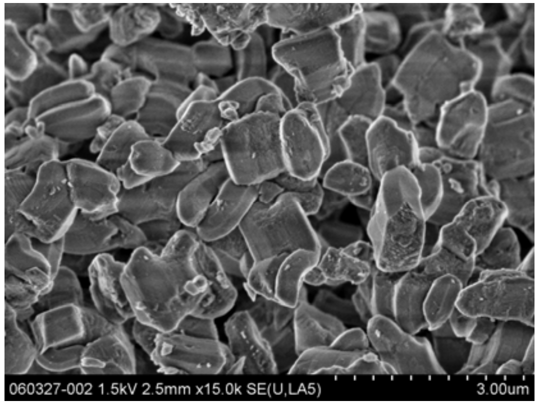
Selective oxidation of propane over VO_x/SBA-15

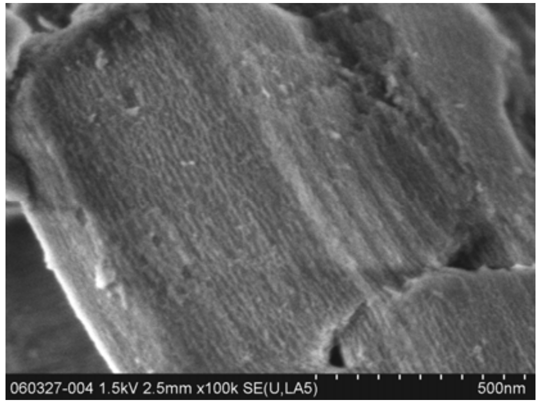
before

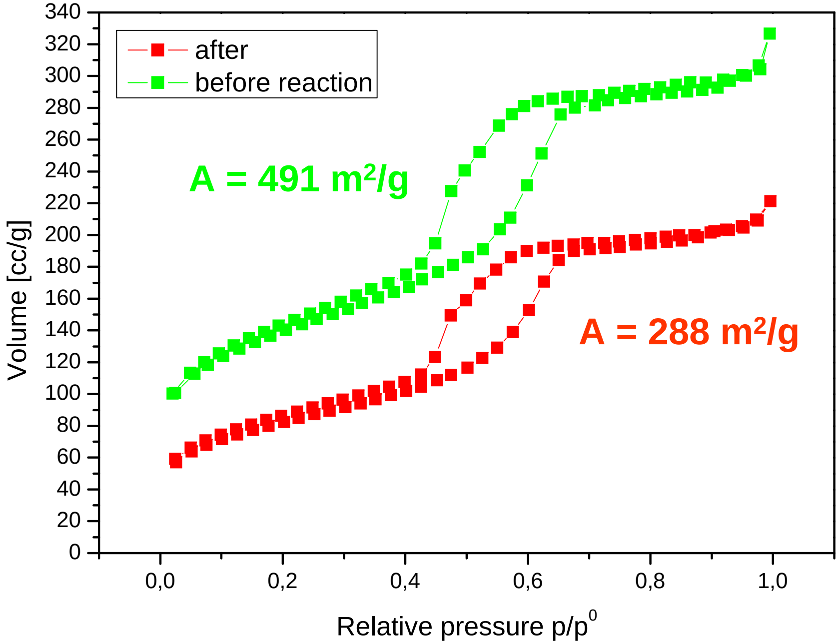




after

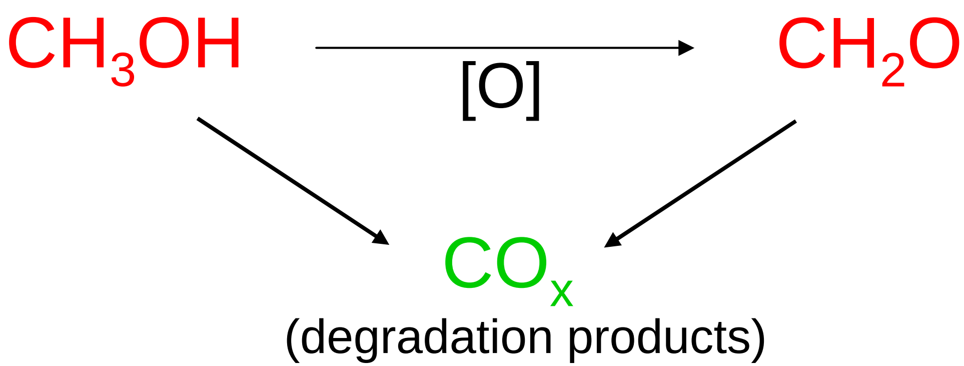






⇨ **Mesoporous structure is largely conserved!**

Selective oxidation of MeOH over VO_x/SBA-15



10 mm plug-flow reactor, 200 mg, MeOH/O_2/He = 3/7/90

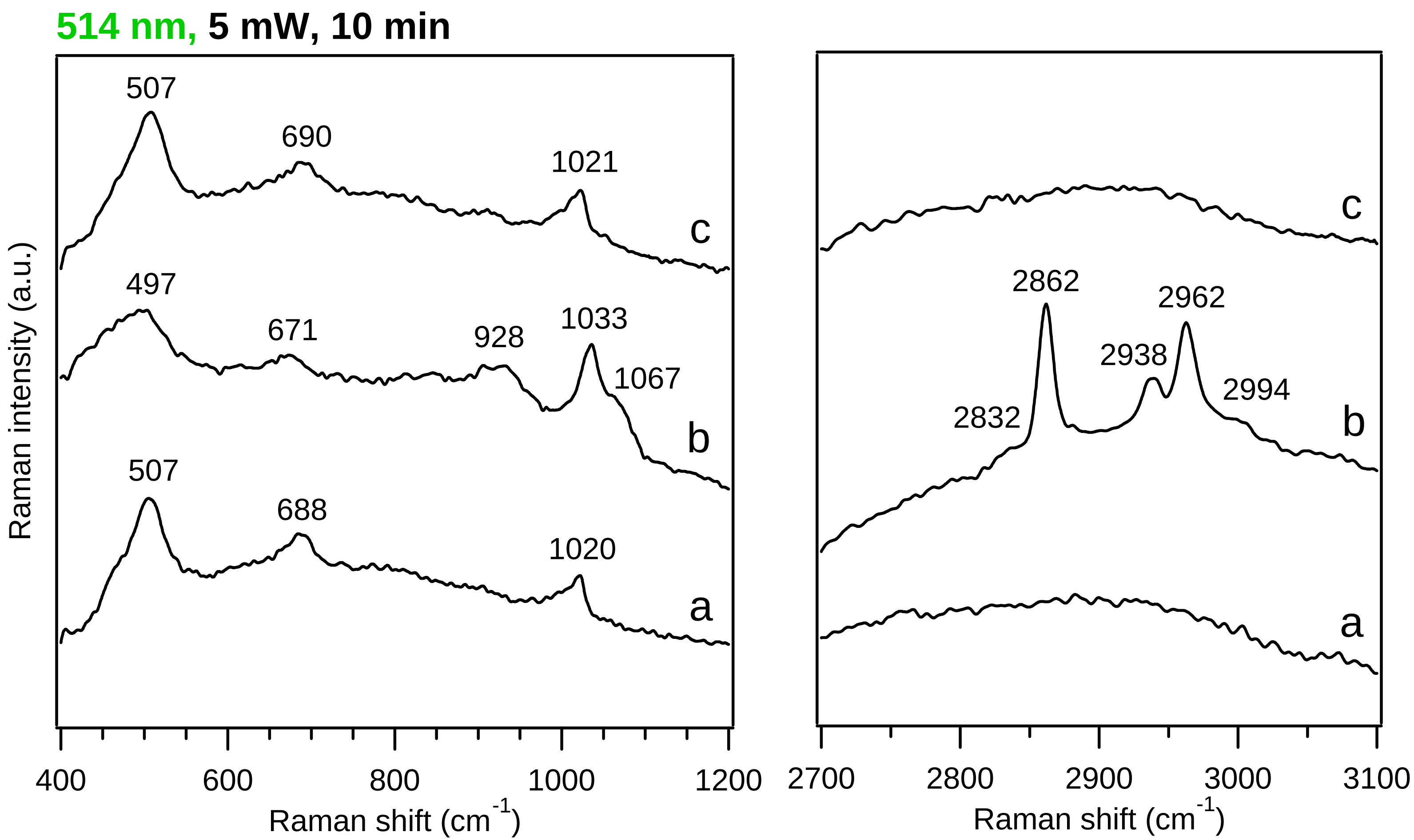
350°C	**Conversion (%)**	**TOF ($\times 10^3$ s^{-1})**	**Selectivity (%)**				
			FA	**MF**	**DMM**	**DME**	**CO_x**
SBA-15	16.4		48.2	1.8	0	0	50
2.7 wt% V/SBA-15	**13**	3.7	**94**	0.3	0	0.1	**5.6**
7.2 wt% V/SBA-15	38.6	2.6	93.3	0.4	0.1	0.9	5.3

⇨ Highly dispersed vanadia shows high selectivity towards FA

C. Hess, I.J. Drake, J.D. Hoefelmeyer, T.D. Tilley, A.T. Bell, Catal. Lett. 105 (2005) 1

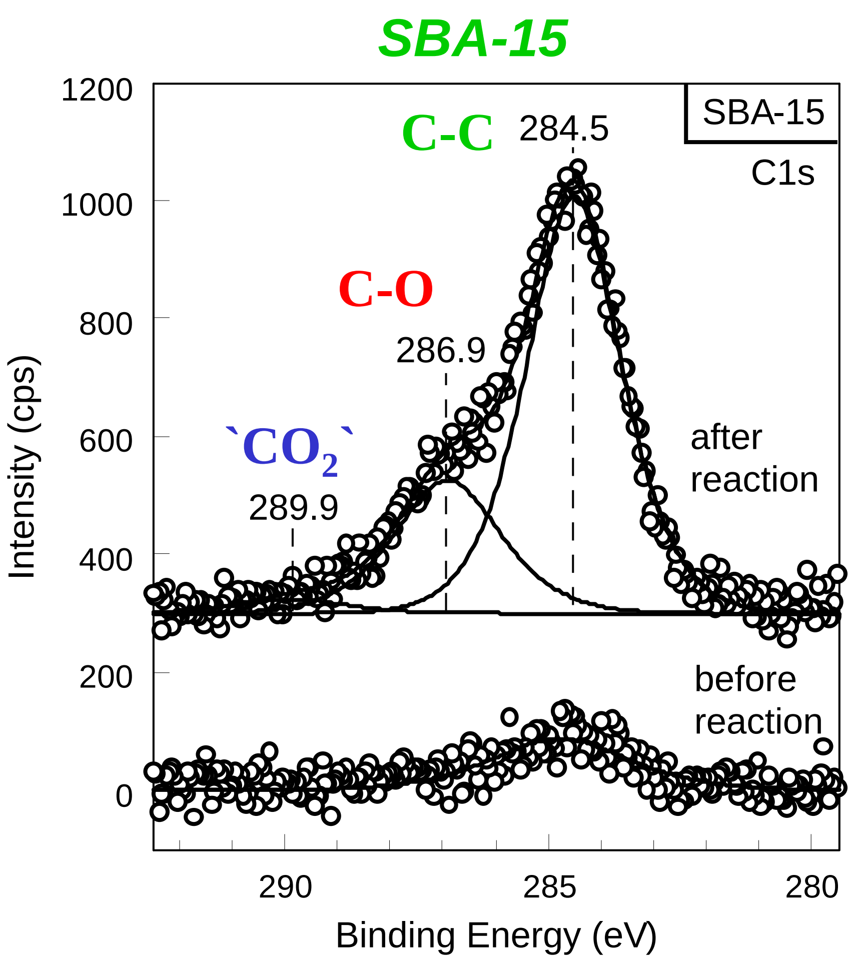
Selective oxidation of MeOH over VO_x/SBA-15

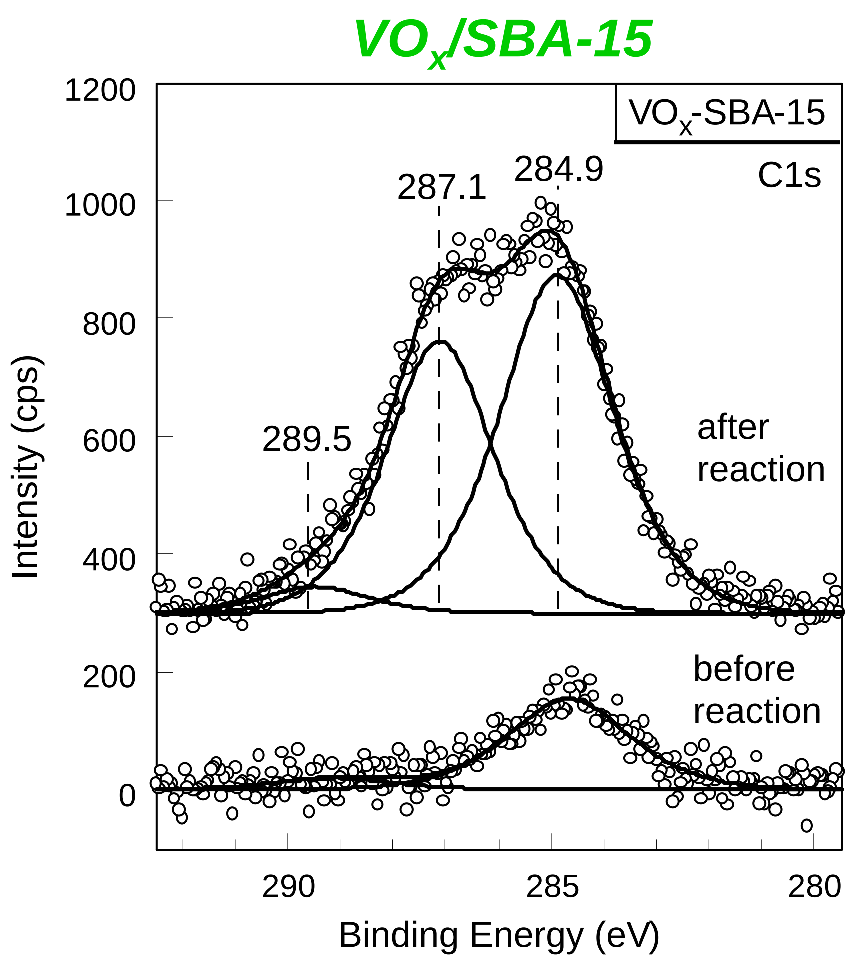
Raman before (a) and after (b,c) MeOH oxidation



⇨ 2.7 wt% VO_x/SBA-15 shows stability towards sintering

XPS analysis before/after MeOH oxidation – C1s

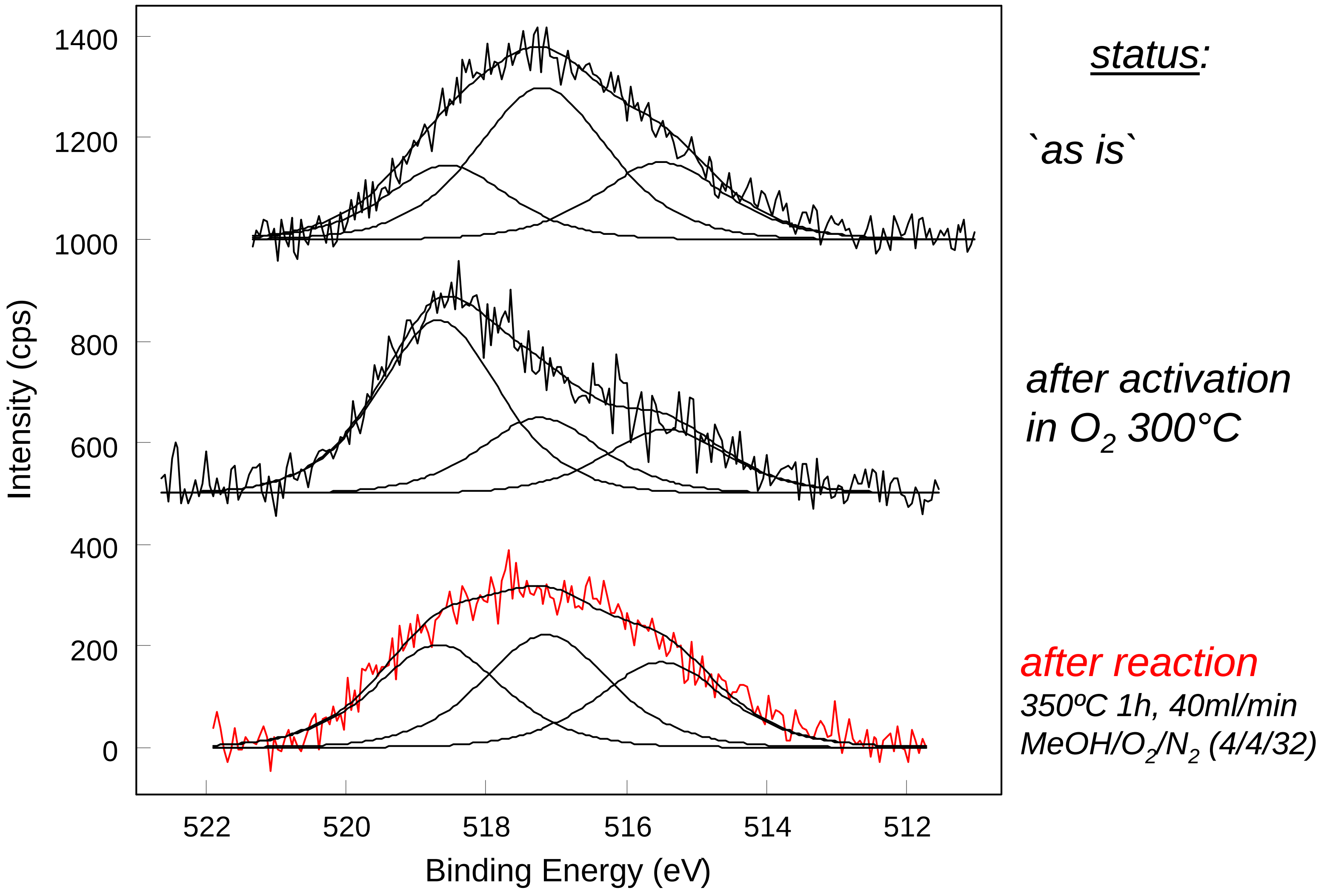




⇨ Correlation XPS/Raman allows for detailed chemical analysis

C. Hess, Surf. Sci. 600 (2006) 3695

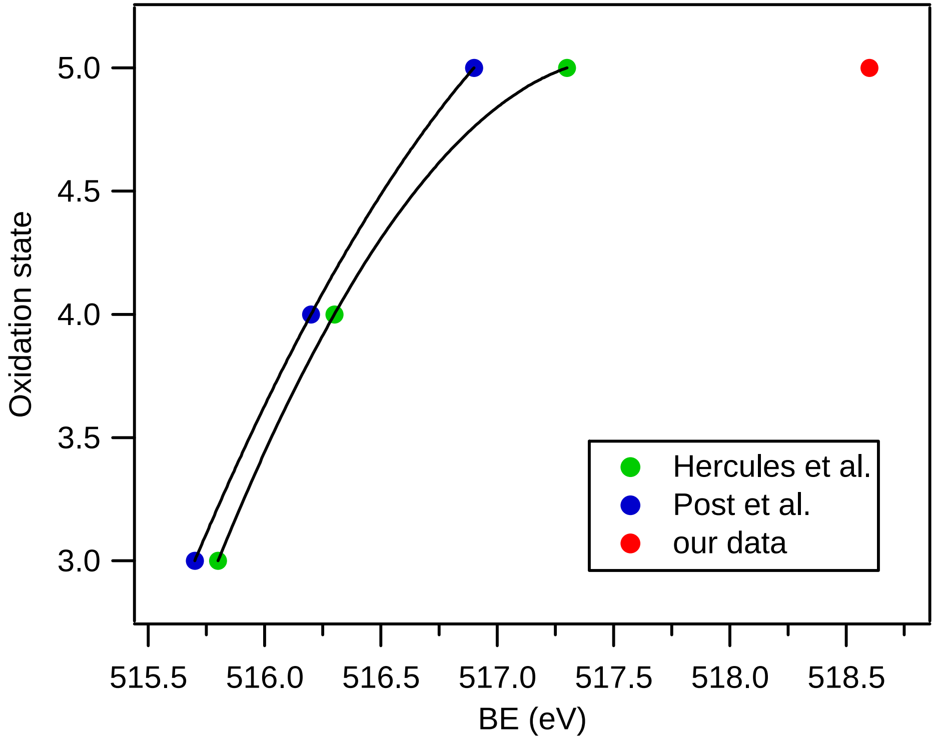
Quasi in situ XPS: XPS data – V2$p_{3/2}$



⇨ **V2$p_{3/2}$ shows dramatic changes after activation and reaction!**

Quasi in situ XPS: XPS data – V2p$_{3/2}$

BE in vanadium oxides



dispersion

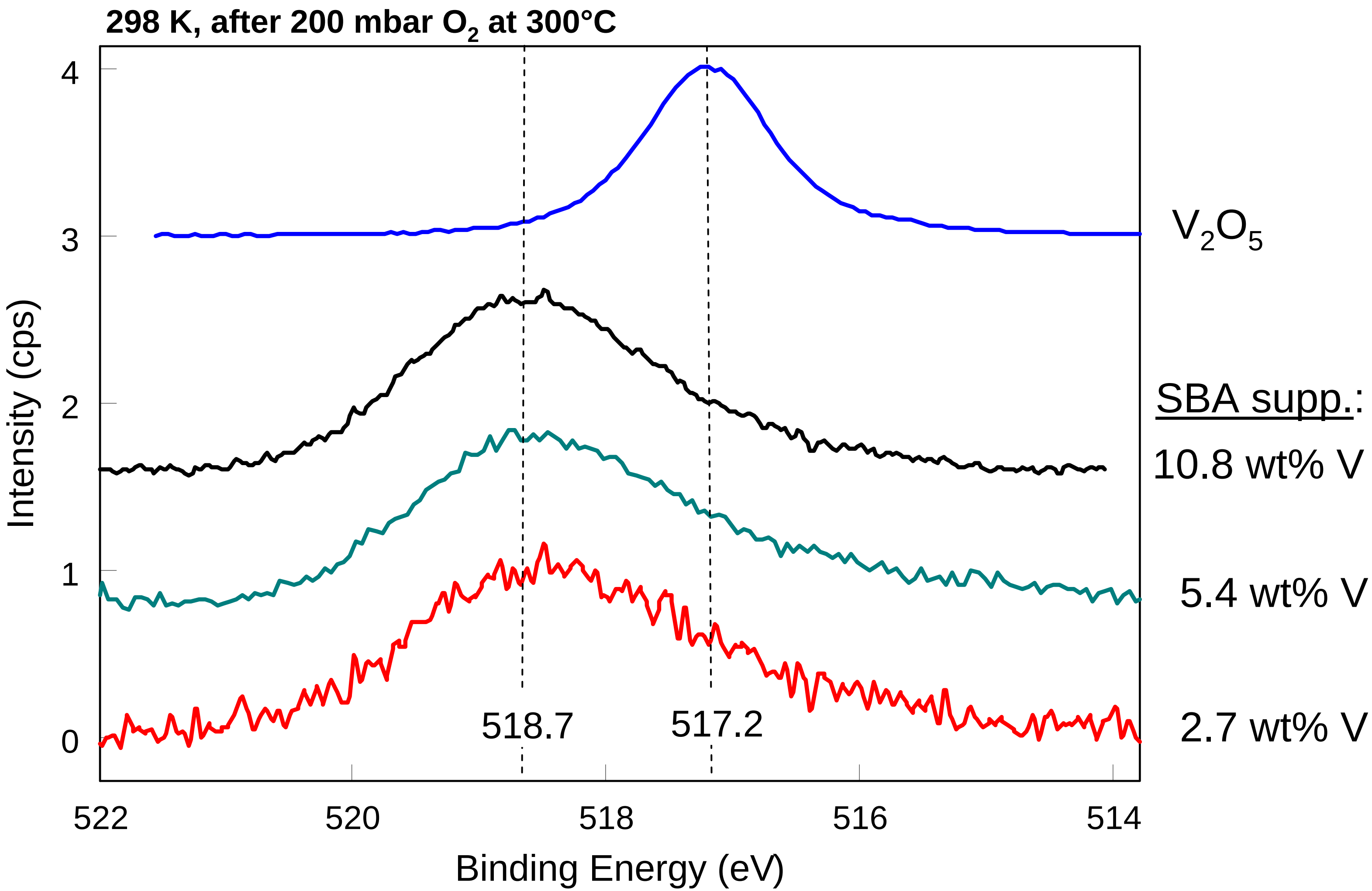
	V/Si
\`as is\`	0.0239
after activation in O_2	0.0294
after MeOH/O_2/N_2 at 250ºC - no reaction	0.0278
after MeOH/O_2/N_2 at 350ºC - reaction	0.0277

⇨ Positive BE shift after activation due to increased dispersion?

⇨ Partial BE backshift due to V_xO_y agglomeration in MeOH/O_2?

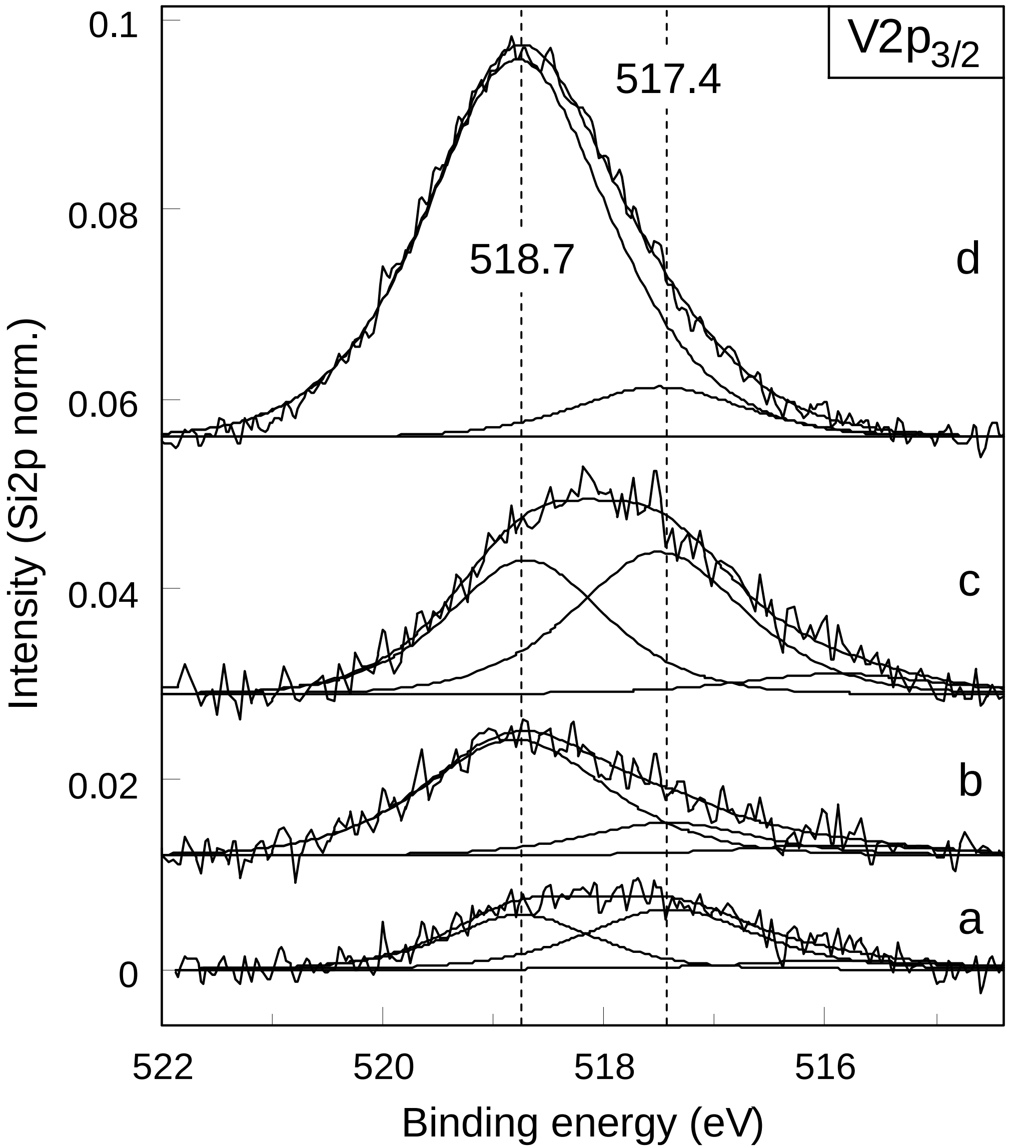
- Model catalysts based on nanostructured materials
- Spectroscopic characterization
    - Synthesis
    - Catalyst surface structure and dispersion
- Selective oxidation over highly dispersed vanadia

Quasi in situ XPS: XPS data – V2p$_{3/2}$



⇨ **XPS reveals strong positive BE shift for silica supported VO$_x$**

Quasi in situ XPS: XPS data – V2p$_{3/2}$



5.4 wt% V
O$_2$ treated

5.4 wt% V (1.4 V/nm^2)
'as is'

2.7 wt% V
O$_2$ treated

2.7 wt% V (0.7 V/nm^2)
'as is'

C. Hess, R. Schlögl, CPL (2006)

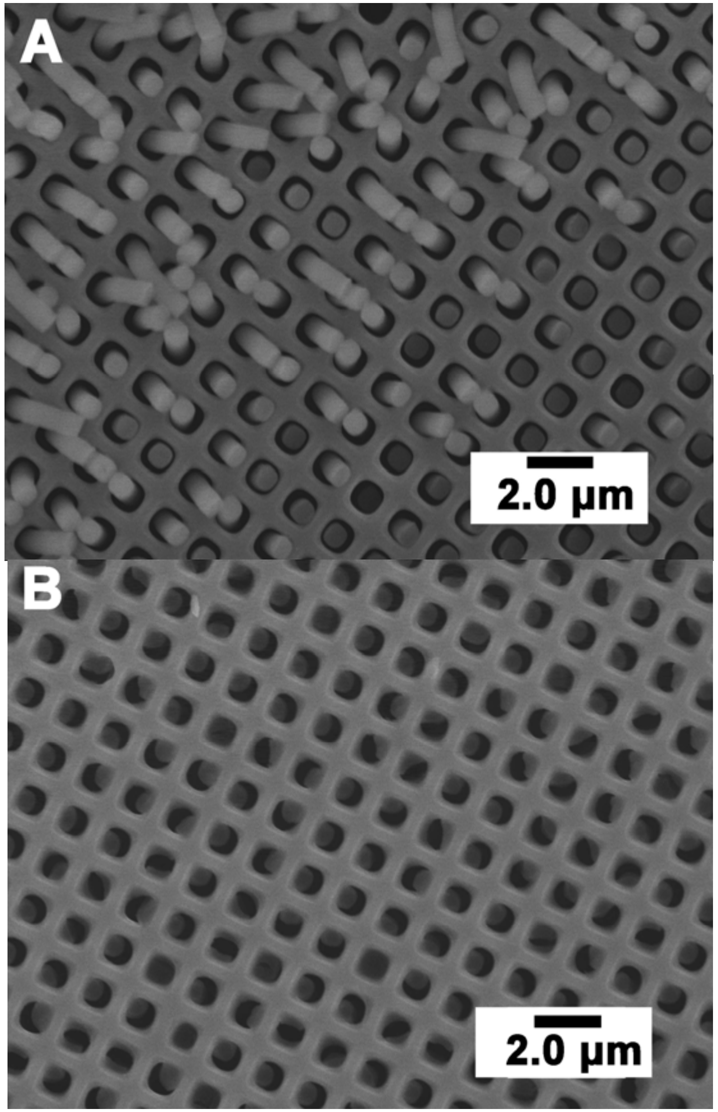
Quasi in situ XPS: XPS data – V2p$_{3/2}$

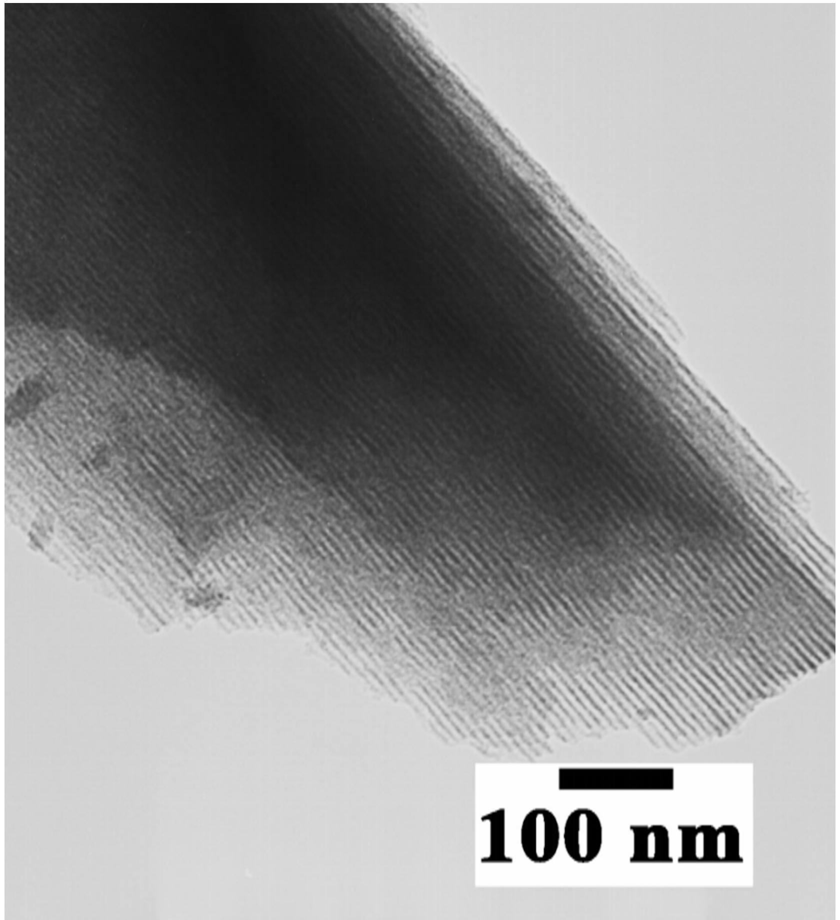
fit results

	Position (eV)	Width (eV)	% (t = 100 min)	% (t = 0 min)	V/Si
after activation O_2 5.4 wt% V	518.6 517.4 515.9	2.0 2.0 2.0	74.5 23.9 1.6	72.0 28.0	0.061
\`as is\` 5.4 wt% V	518.7 517.4 515.9	2.0 2.0 2.0	51.3 42.2 6.5	51.1 48.9	0.052
after activation O_2 2.7 wt% V	518.7 517.4 515.9	2.0 2.0 2.0	66.6 30.1 3.3	65.0 35.0	0.029
\`as is\` 2.7 wt% V	518.7 517.4 515.9	2.0 2.0 2.0	45.0 46.6 8.4	46.0 54.0	0.024

⇨ **XPS provides direct info on dispersion of supported vanadia**

Other model approaches: VO_x/SBA-15/SiO_2/Si

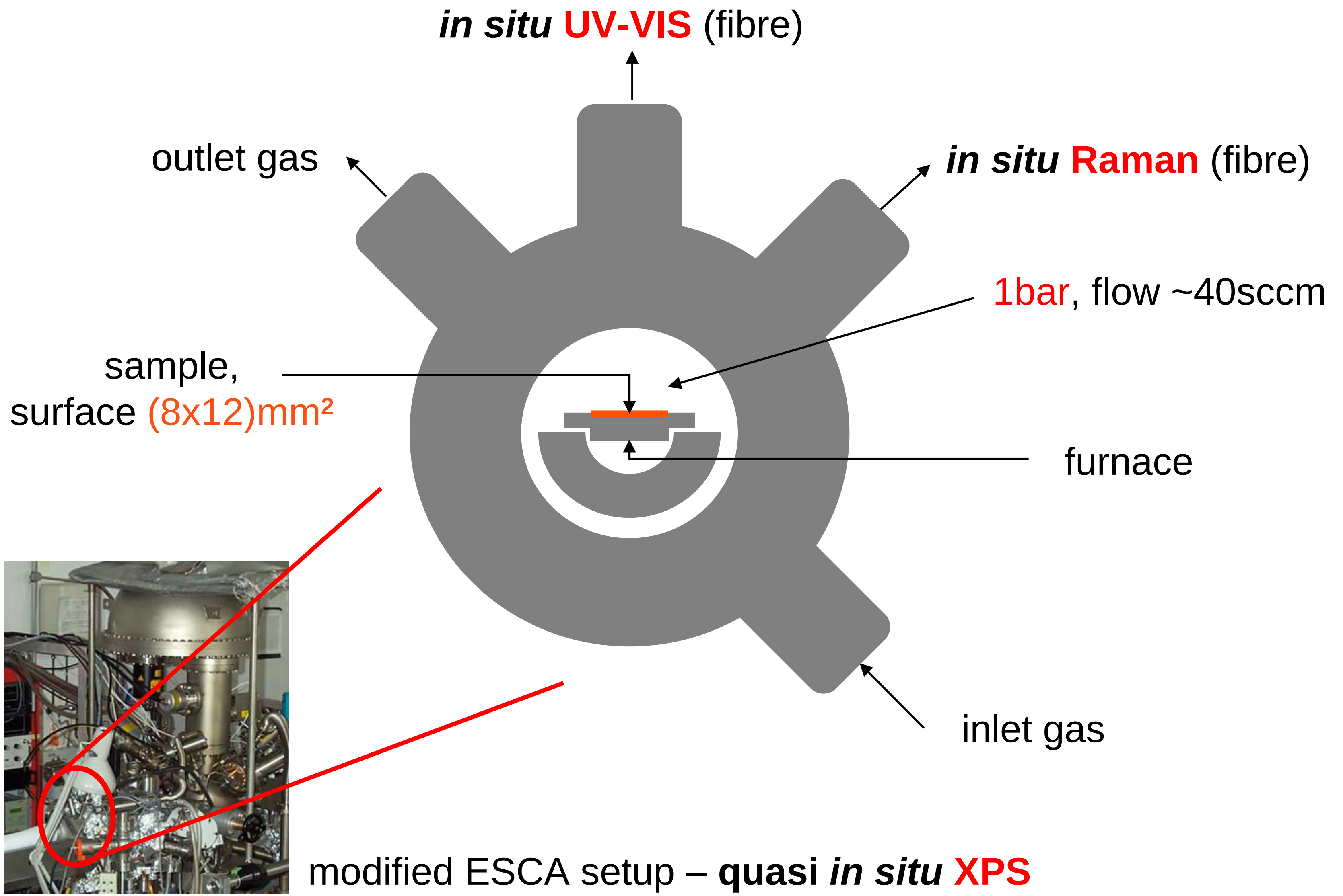




⇨ **Ordered microrods of silica SBA-15 using Si templates**

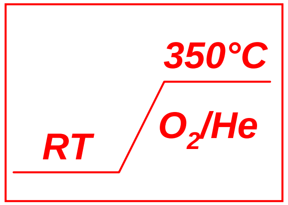
X. Chen , M. Steinhart, C. Hess, U. Gösele, Adv. Mater. 18 (2006) 2153

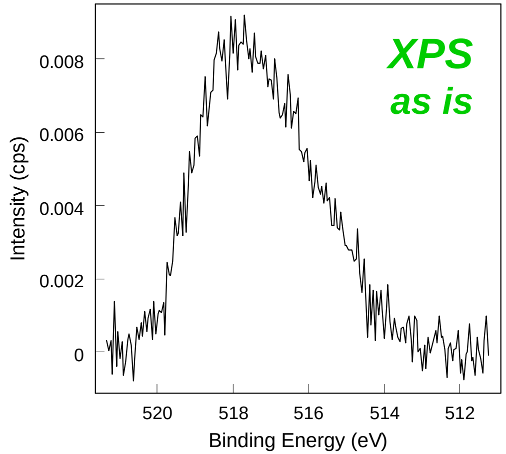
Multi in situ spectroscopy - experimental setup

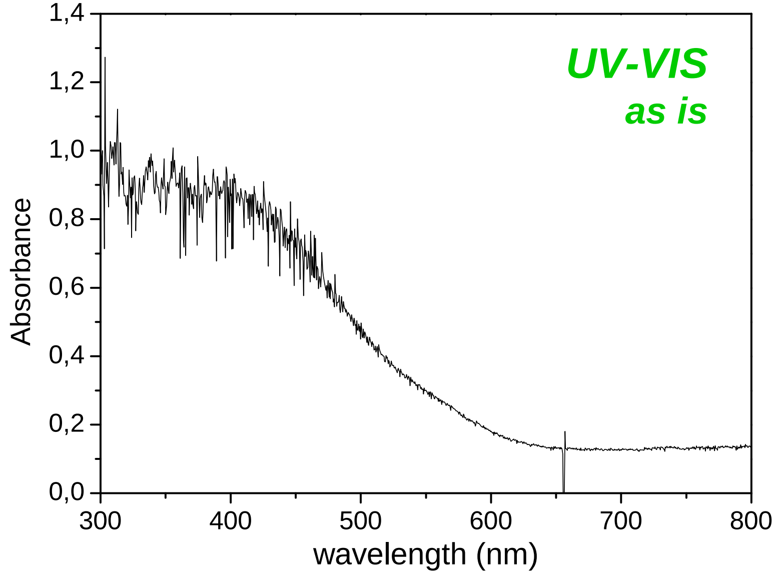


Multi in situ spectroscopy – VO_x/SBA-15 structure

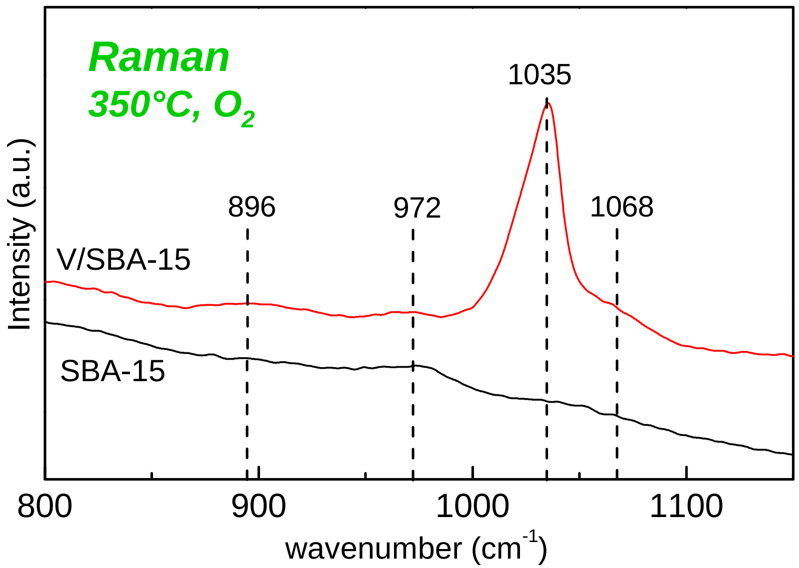
<u>VO_x/SBA-15:</u>
0.8 V/nm
491 m^2/g

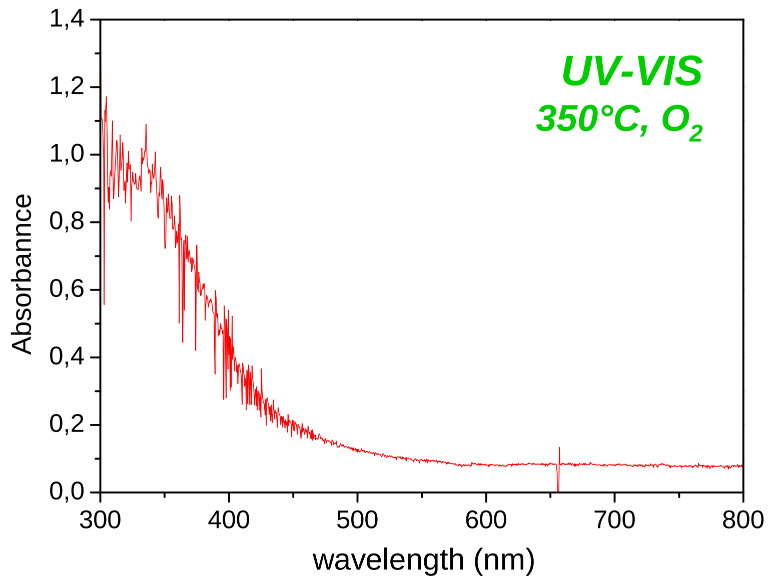






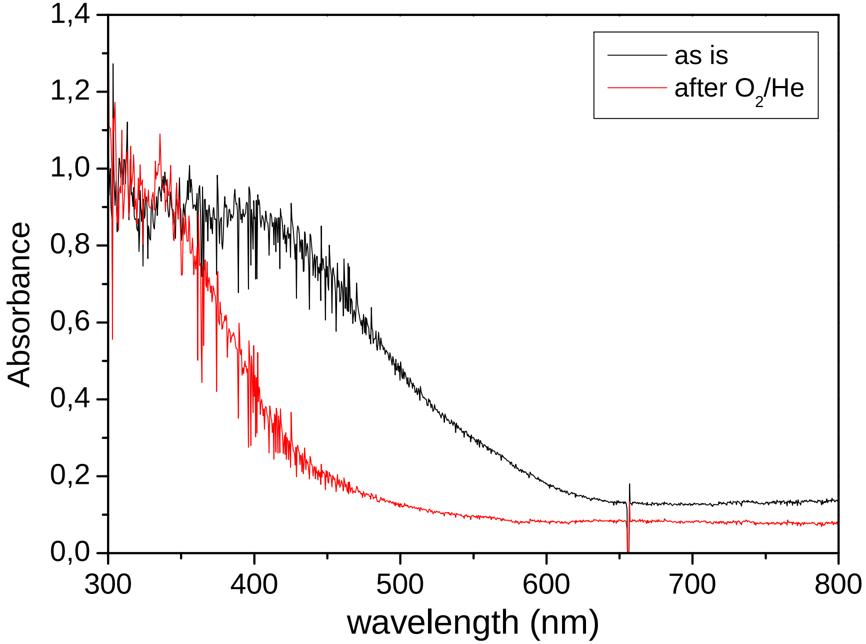
632 nm, 5mW, 1000s





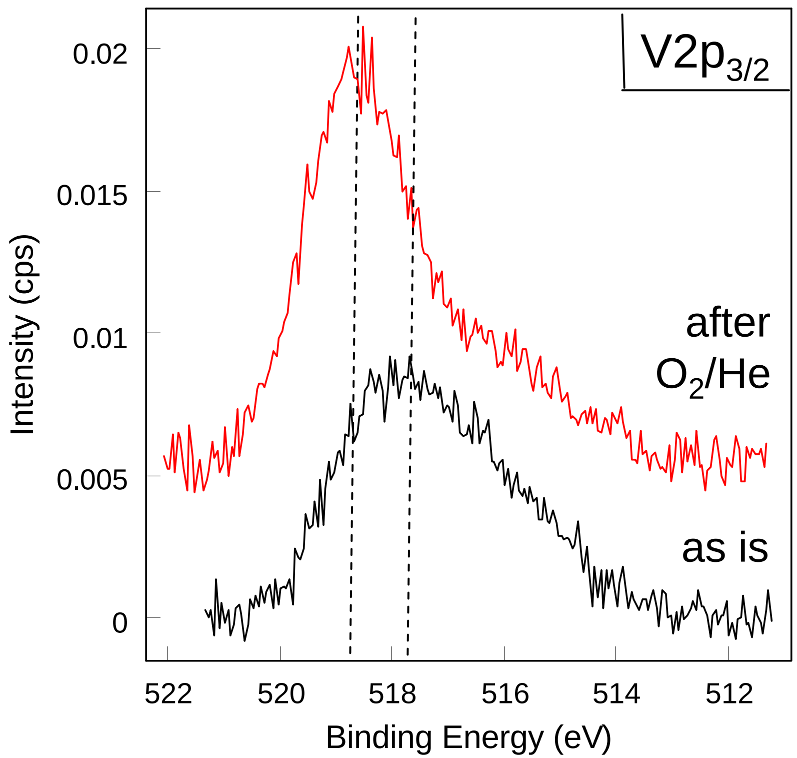
Multi in situ spectroscopy – VO_x/SBA-15 structure

UV-VIS



- Vanadia initially partly reduced
- coordination/aggregation reduced upon O_2 treatment → dehydration
- **Structural changes correlated with changes in V_xO_y dispersion**

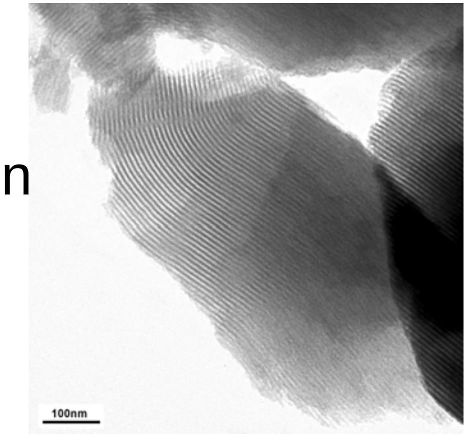
XPS



	V/Si	C
after	0.032	1.1
as is	0.028	0.8

Summary and Outlook

- New class of vanadia model catalysts using nanostructured SBA-15
  - ⇨ high density of uniform vanadia sites
  - ⇨ full catalytic function



- Synthesis: detailed spectroscopic characterization
  - ⇨ reaction mechanism
  - ⇨ controlled synthesis

- Well-suited model catalyst to study
  - vanadia surface structure - dispersion – C deposition
  - structure-activity relation of propane selective oxidation reactions

Acknowledgements

Rita Herbert,
Jörg Thielemann,
Ute Wild,
Robert Schlögl

Emmy Noether Research Group
@ Fritz Haber Institute

Emmy Noether-Programm
Deutsche Forschungsgemeinschaft
DFG