Synthesis, characterization and application of nanostructured vanadia model catalysts for partial oxidation reactions

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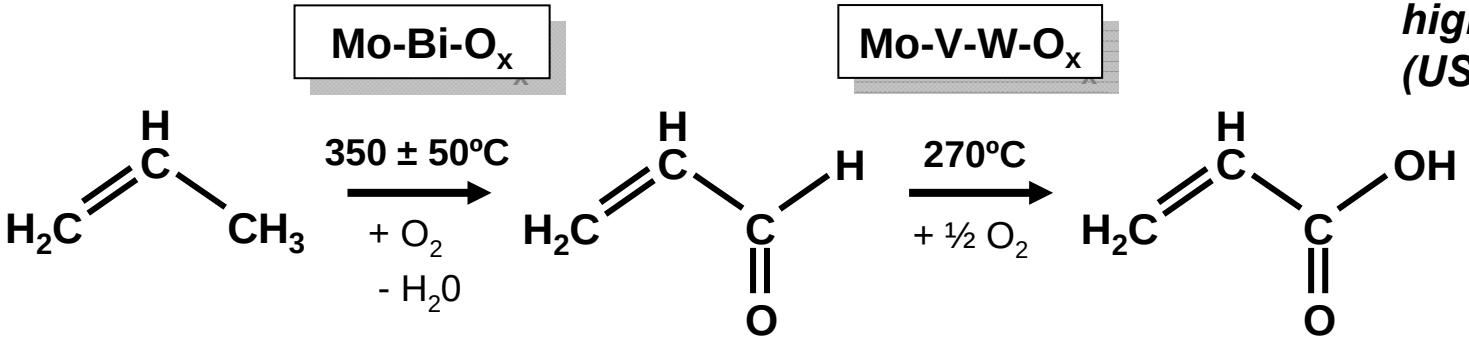
- **Model catalysts based on nanostructured materials**
- **Spectroscopic characterization of the synthesis**
- **Propane partial oxidation over highly dispersed vanadia**
- **Influence of water on surface structure and dispersion**

Motivation: Propane to acrylic acid conversion

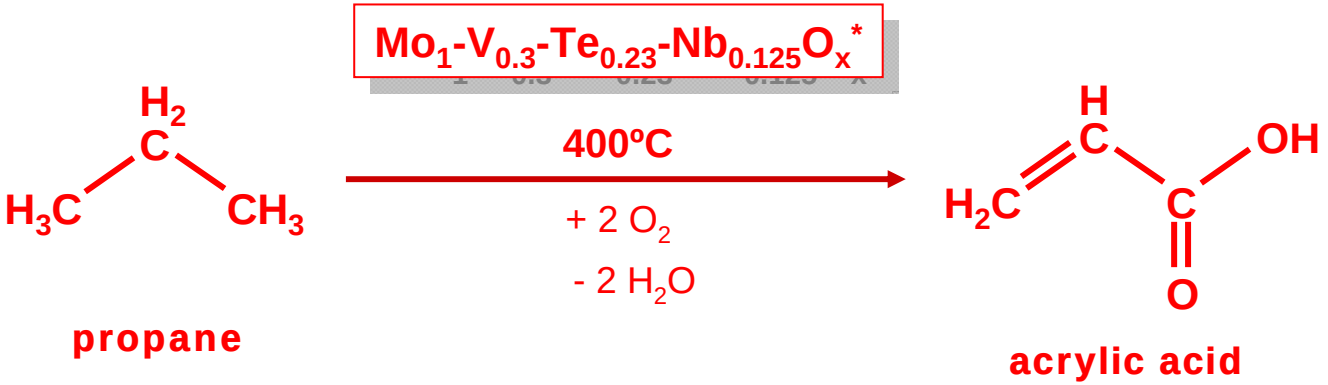
Industrial process: 2-stage oxidation of propene



high costs: (US$ 420/t)

Y ≤ 87%

Alternative process: Direct oxidation of propane



low costs: (US$ 200/t)

Y ≈ 50%

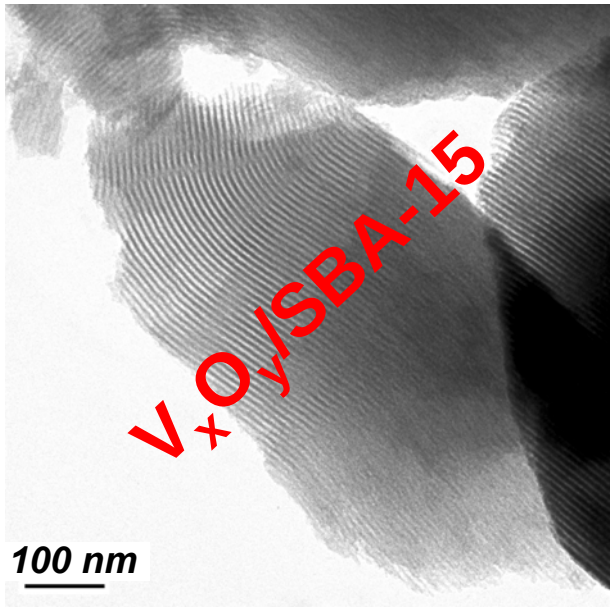
* *T. Ushikubo, H. Nakamura, Y. Koyasu, S. Wajiki, Mitsubishi Kasei Corporation, US 005380933A (1995)*

Model catalysts based on nanostructured silica

Limited understanding of MoVTeNb oxides:

- Structural complexity
- Similar composition/structure of surface and bulk

⇨ 3-D model catalyst with full catalytic function



- *well-known preparation*
- *isolates/mimics active V sites*
- *detailed insight into structure*

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

- Model catalysts based on nanostructured materials
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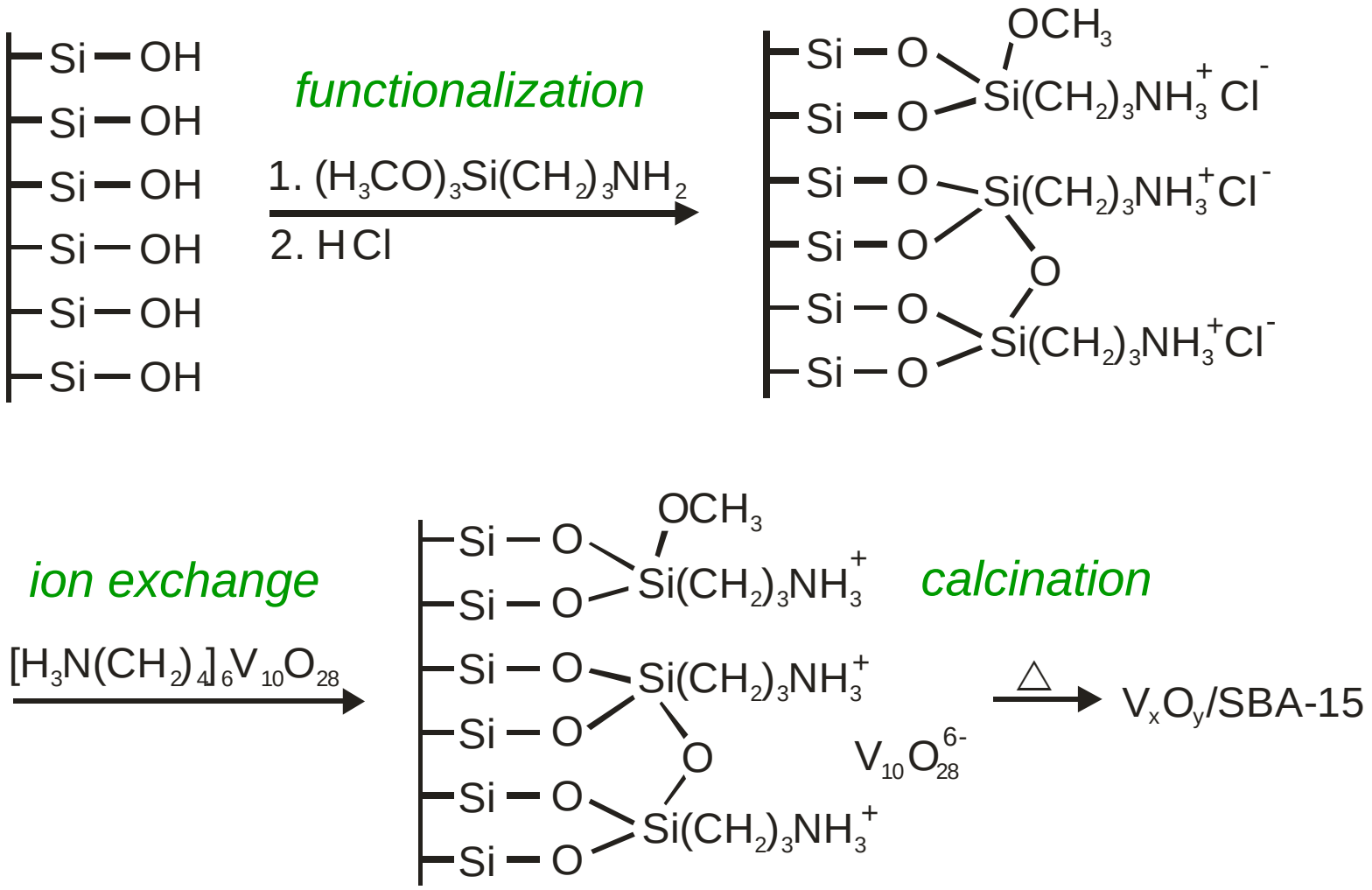
- Propane partial oxidation over highly dispersed vanadia
- Influence of water on surface structure and dispersion

Synthesis of vanadia supported on silica SBA-15



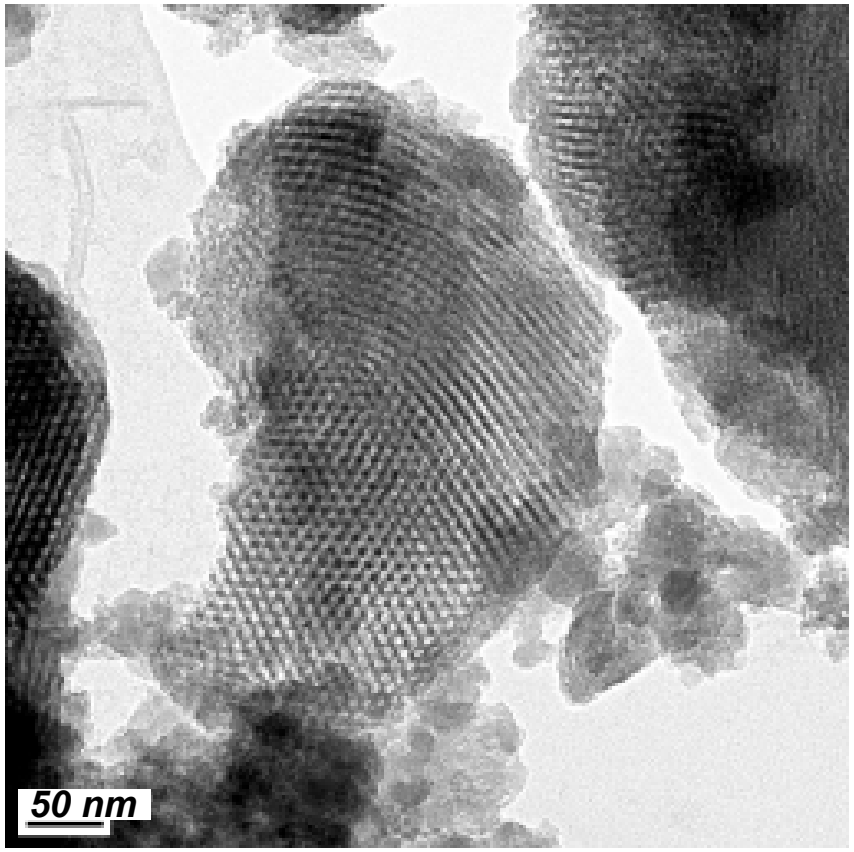
⇨ **Novel method to anchor TM oxides on mesoporous supports**

C. Hess, J.D. Hoefelmeyer, T.D. Tilley, J. Phys. Chem. B 108 (2004) 9703

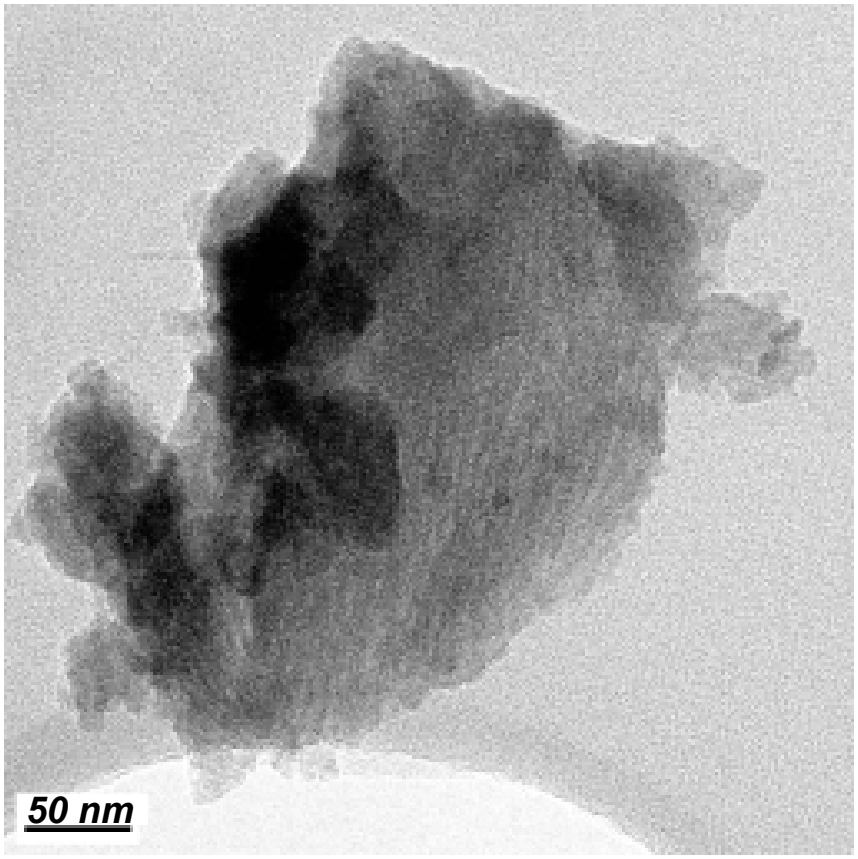
Synthesis of vanadia supported on silica SBA-15

Mechanical stability: Pressure treatment at 750 MPa

functionalized + ion exchanged



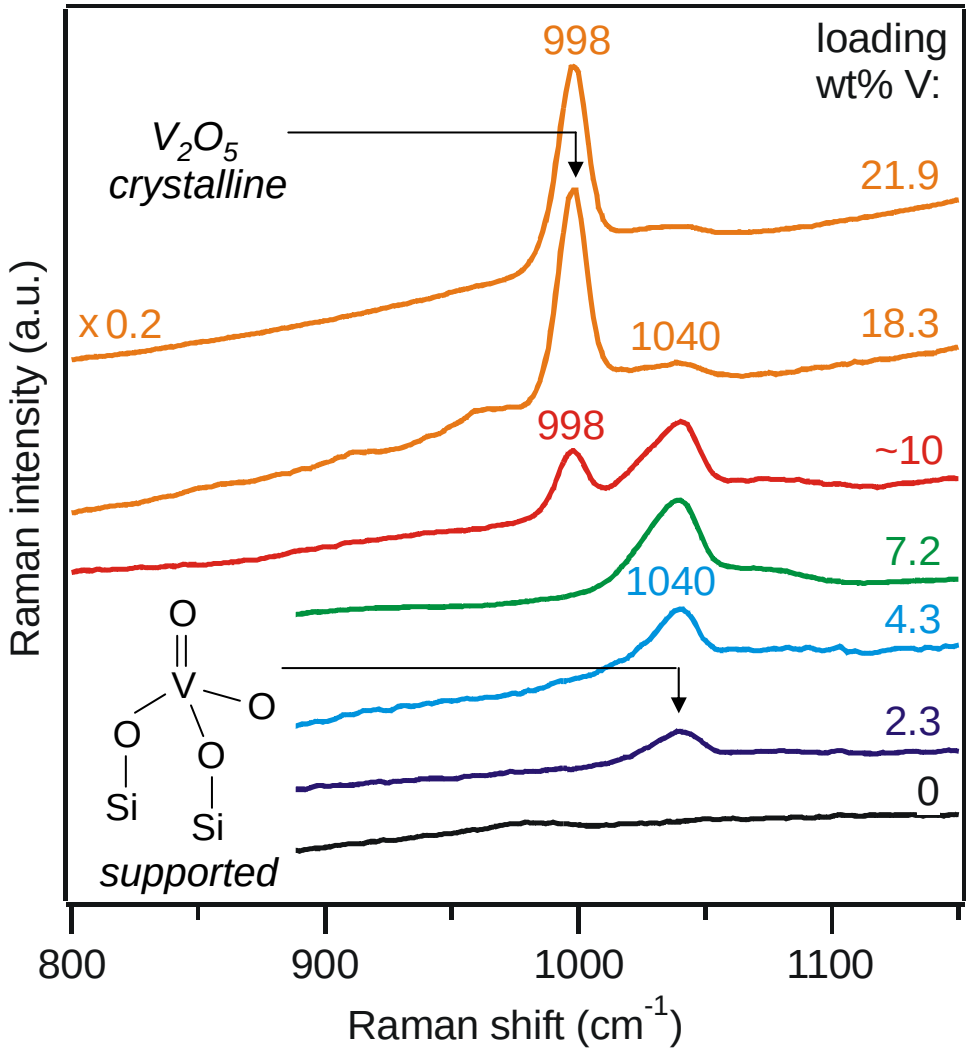
incipient wetness



⇨ Significant increase in stability of mesoporous support matrix

R. Herbert, U. Wild, C. Hess, R. Schlögl, Chem.-Ing.-Tech. 78 (2006) 1263

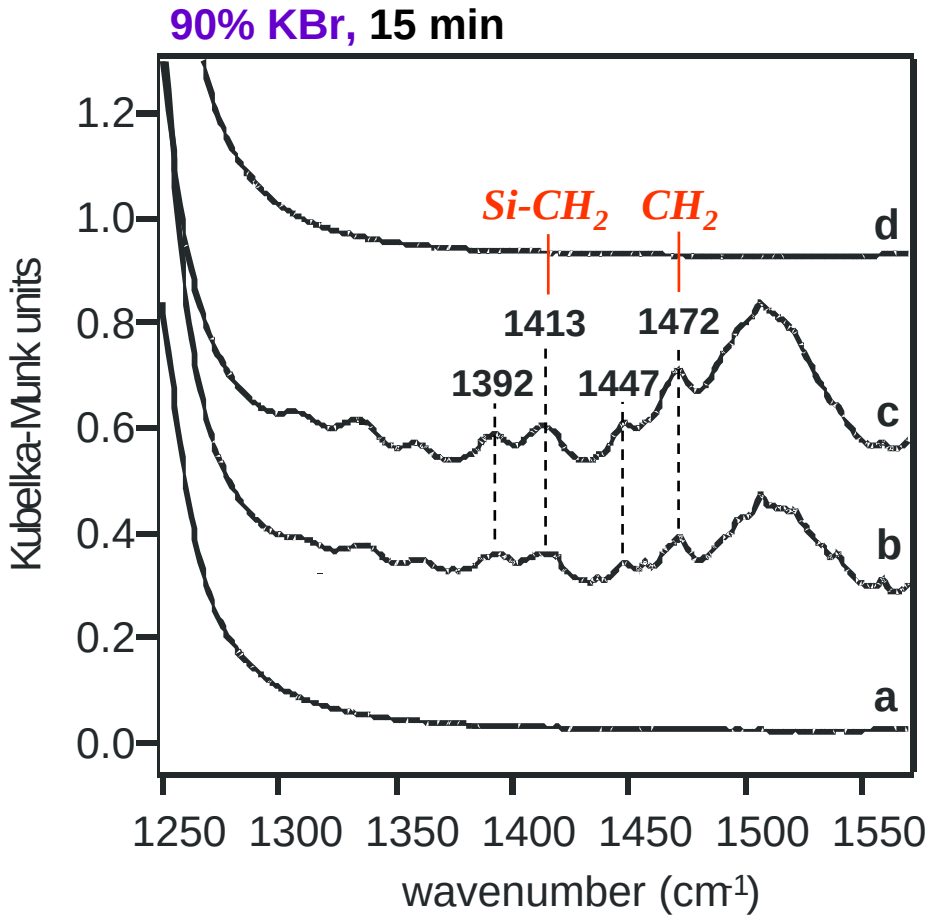
Visible Raman characterization of V_xO_y/SBA-15

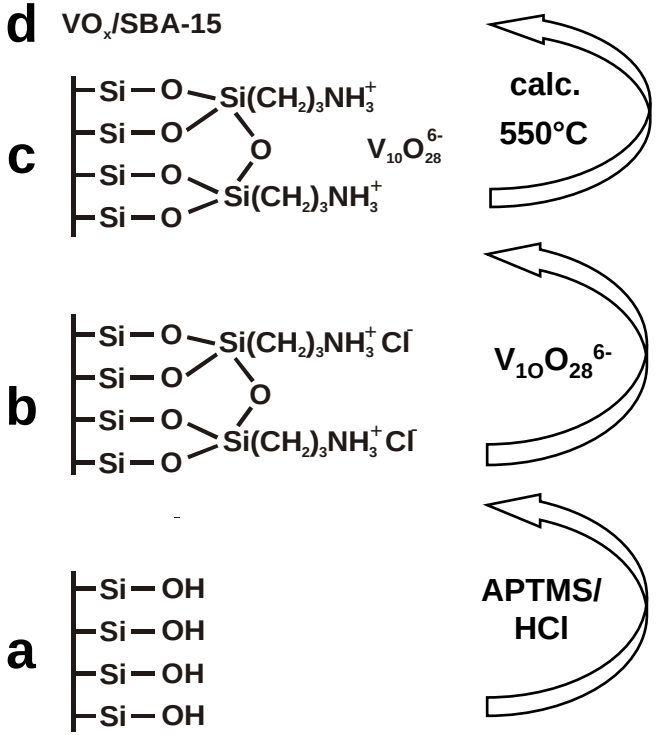


⇨ **Raman allows for sensitive detection of V=O in cryst. V_2O_5**

DRIFTS characterization during synthesis

C-H bending vibrations

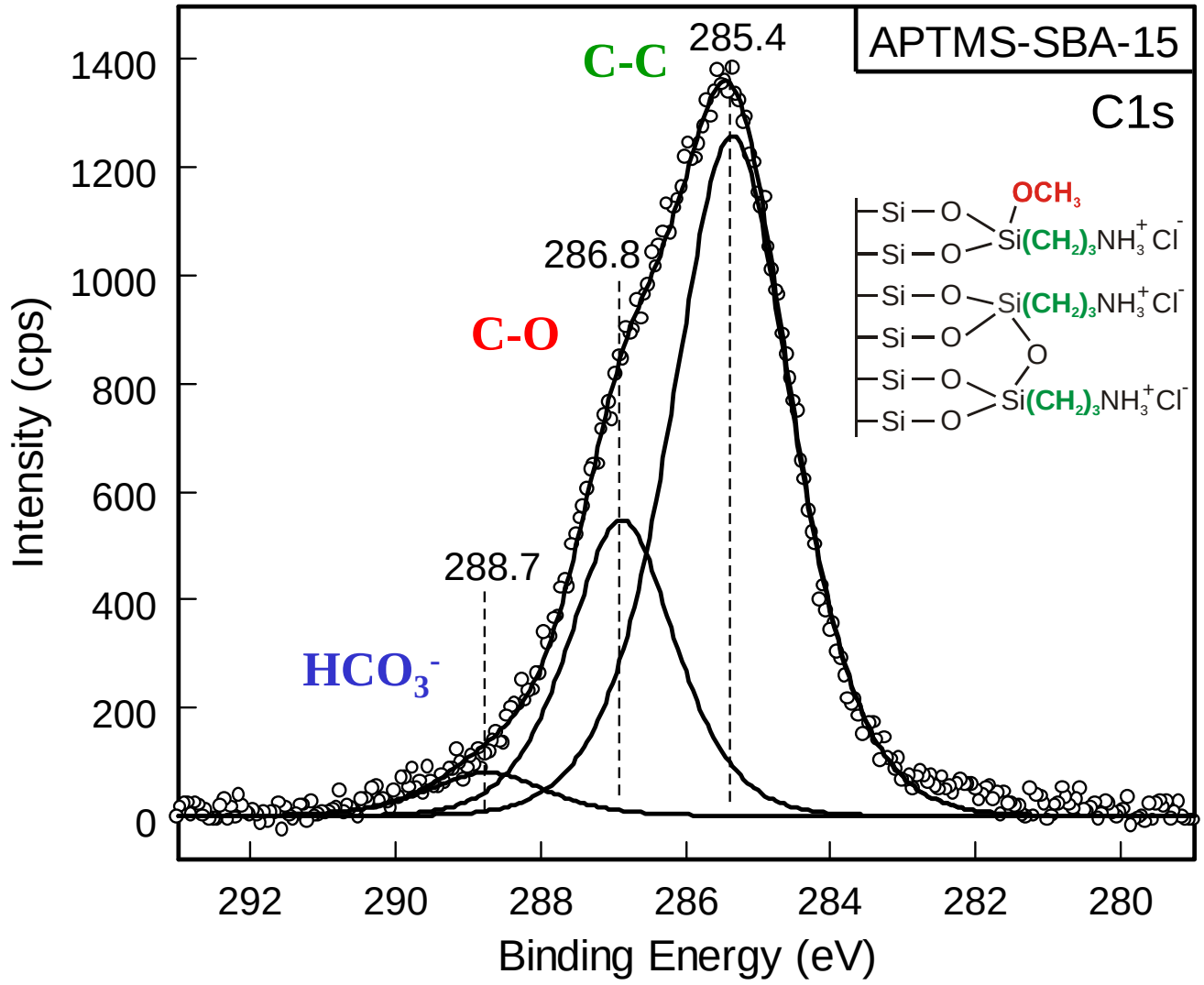




⇨ **DRIFTS data demonstrates the presence of Si-propyl chain**

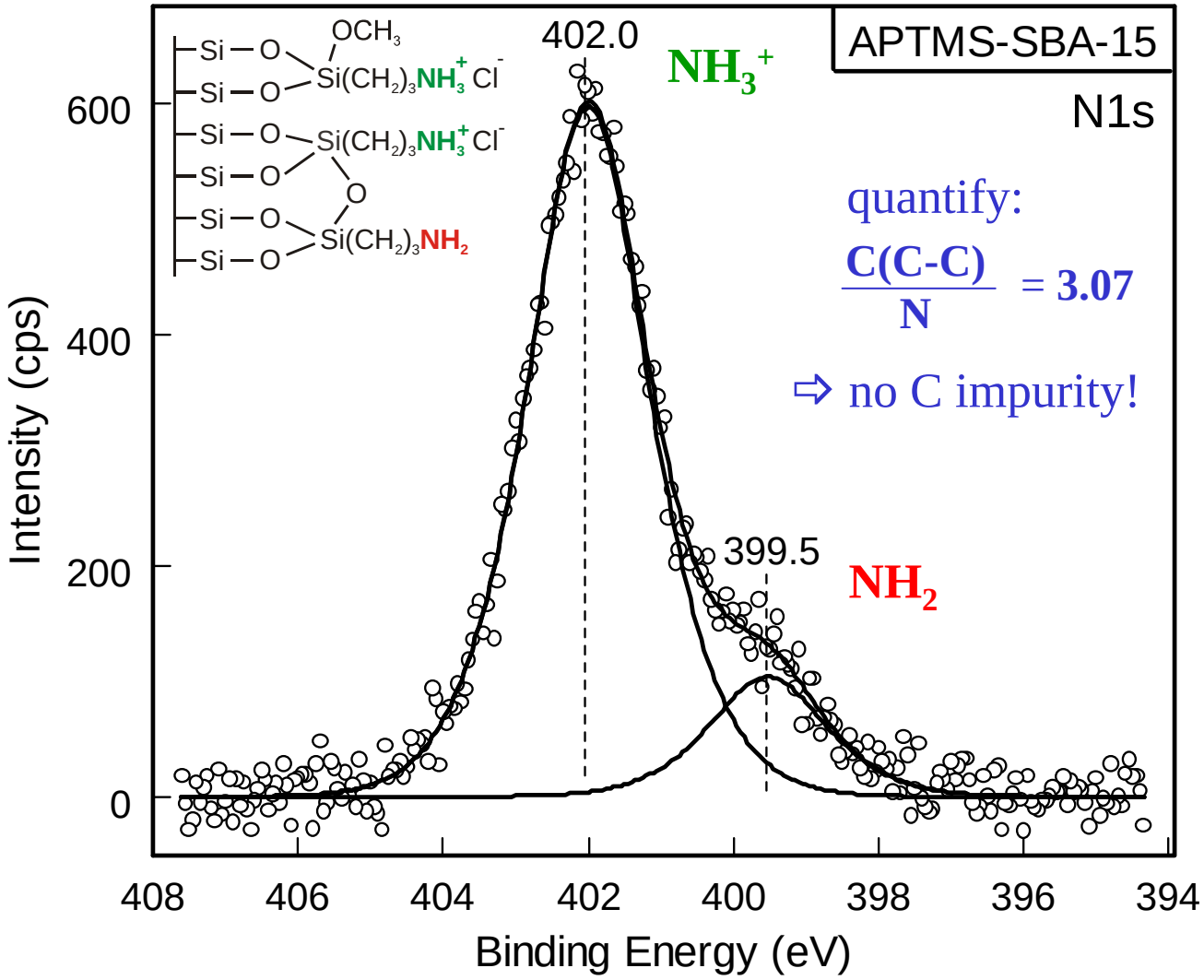
C. Hess, U. Wild, R. Schlögl, Microp. Mesop. Mater. 95 (2006) 339

C1s XP spectra during synthesis of V_xO_y/SBA-15



⇨ **Detailed information on framework structure**

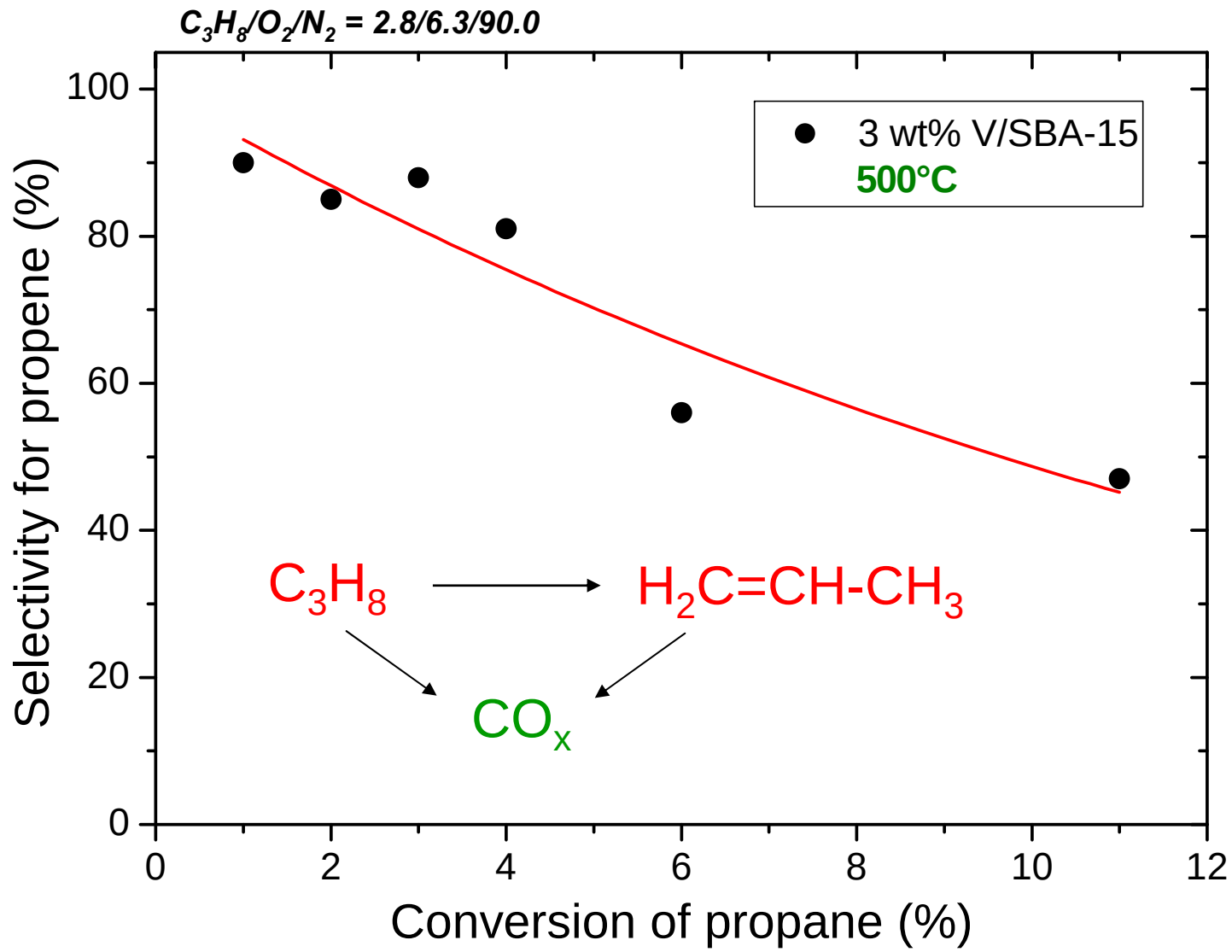
N1s XP spectra during synthesis of V_xO_y/SBA-15



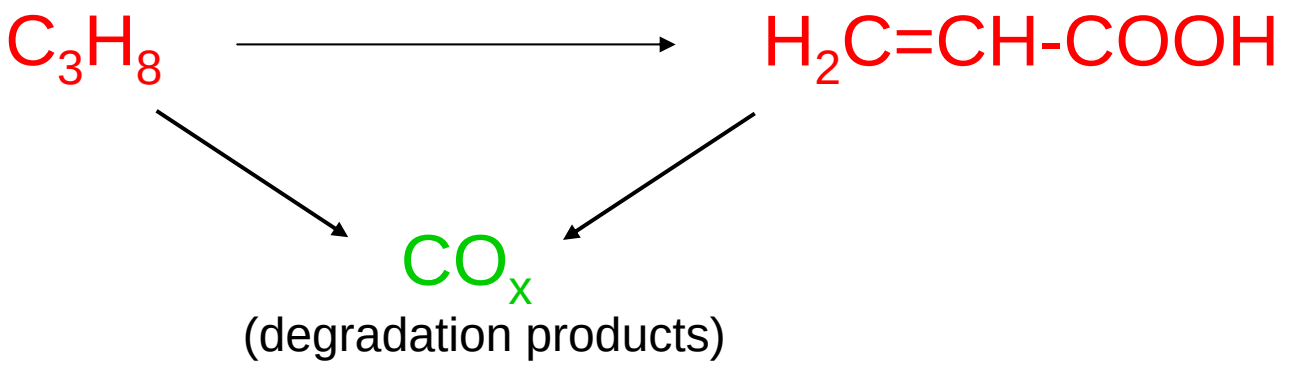
⇨ **Quantitative surface composition of intermediates**

- Model catalysts based on nanostructured materials
- Spectroscopic characterization of the synthesis
- Propane partial oxidation over highly dispersed vanadia
- Influence of water on surface structure and dispersion

Propane selective oxidation to propene



Selective oxidation of propane: Effect of steam



1200 h^{-1}, 0.5 ml, $C_3H_8/O_2/N_2/H_2O$ = 2.8/6.3/50.8/40

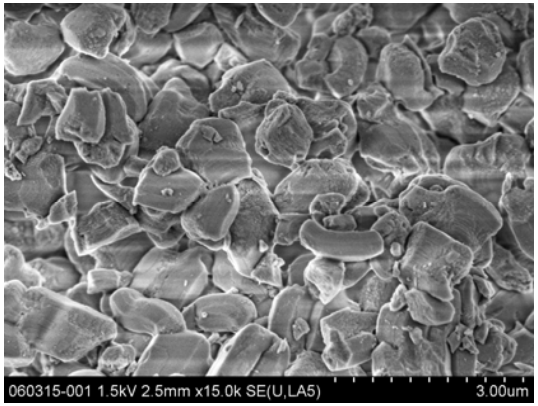
400°C	C_3H_8 Conversion (%)	Time on stream (min)	Selectivity (%) AA	C_3H_6	AcetAc	CO_x	Yield of AA (%)
SBA-15	0	165	0	0	0	0	0
3.3 wt% V/SBA-15	**8**	165	**84**	10	2	**4**	**6.8**
	5	345	86	13	1	0	4.5

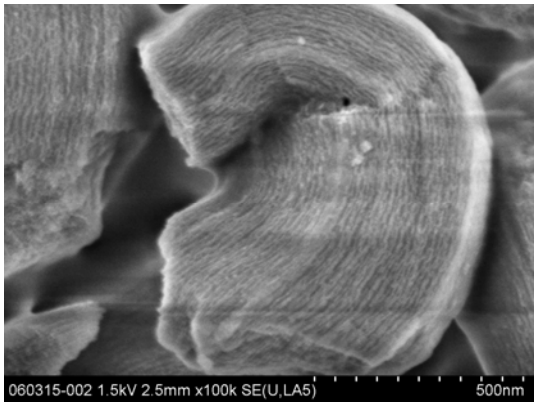
⇨ Highly dispersed vanadia shows high selectivity towards AA

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

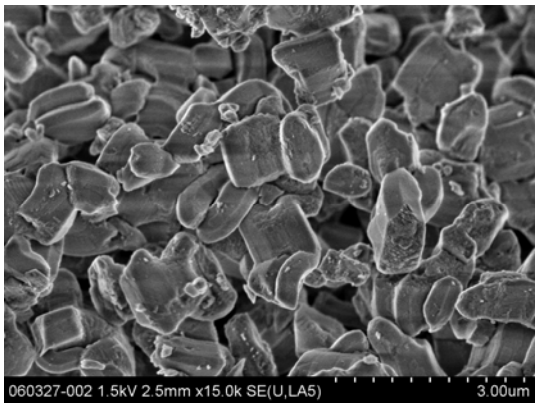
Selective oxidation of propane over V_xO_y/SBA-15

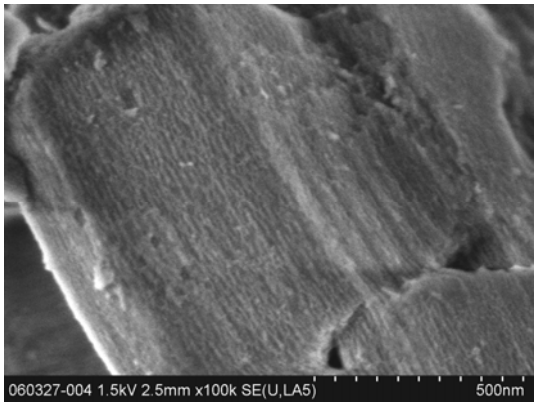
before

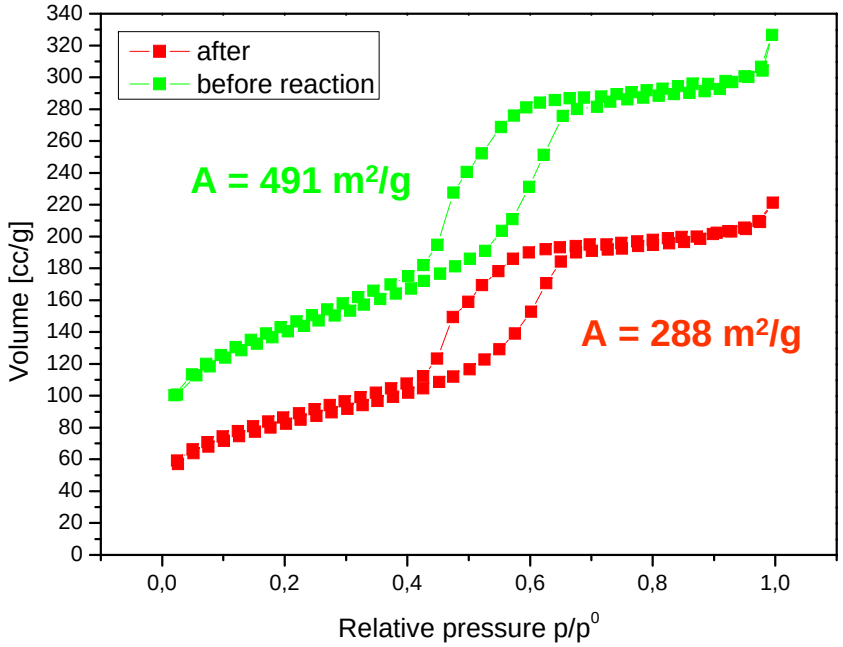




after





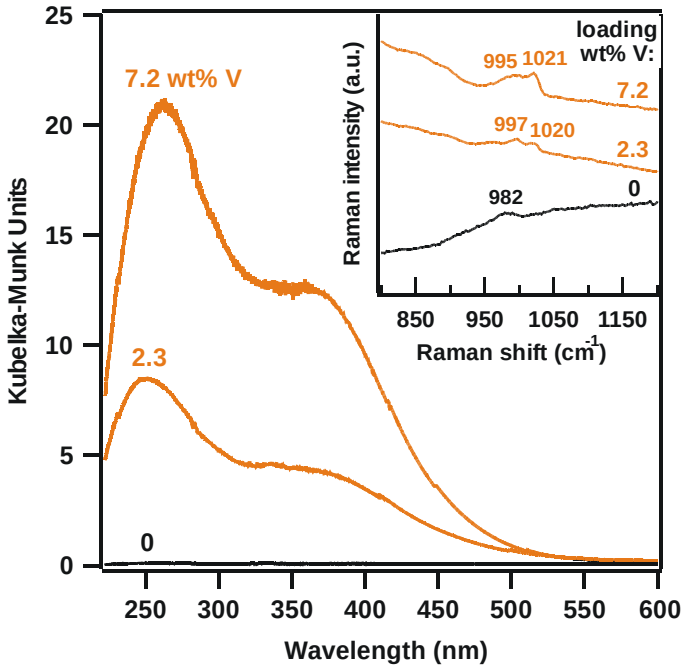


⇨ **Mesoporous structure is largely conserved!**

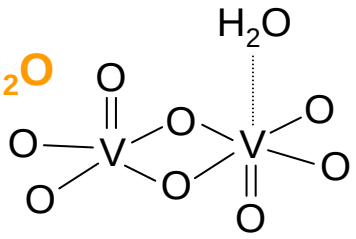
- Model catalysts based on nanostructured materials
- Spectroscopic characterization of the synthesis
- Propane partial oxidation over highly dispersed vanadia
- Influence of water on surface structure and dispersion

Structural changes of vanadia during dehydration

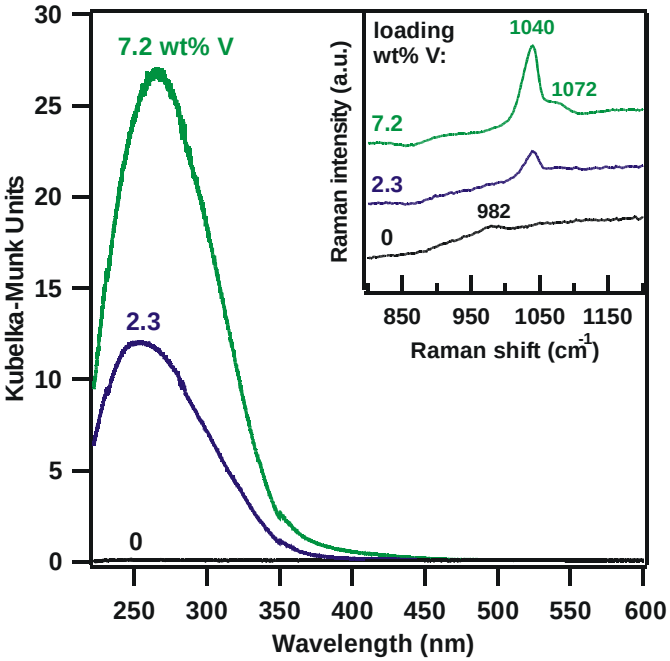
‘as is’: hydrated



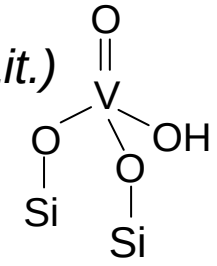
$V_2O_5 \cdot 1.2\ H_2O$



dehydrated



(Lit.)



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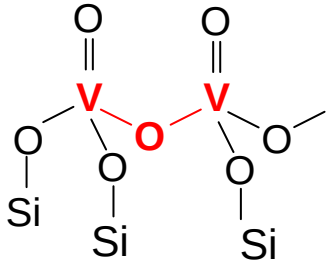


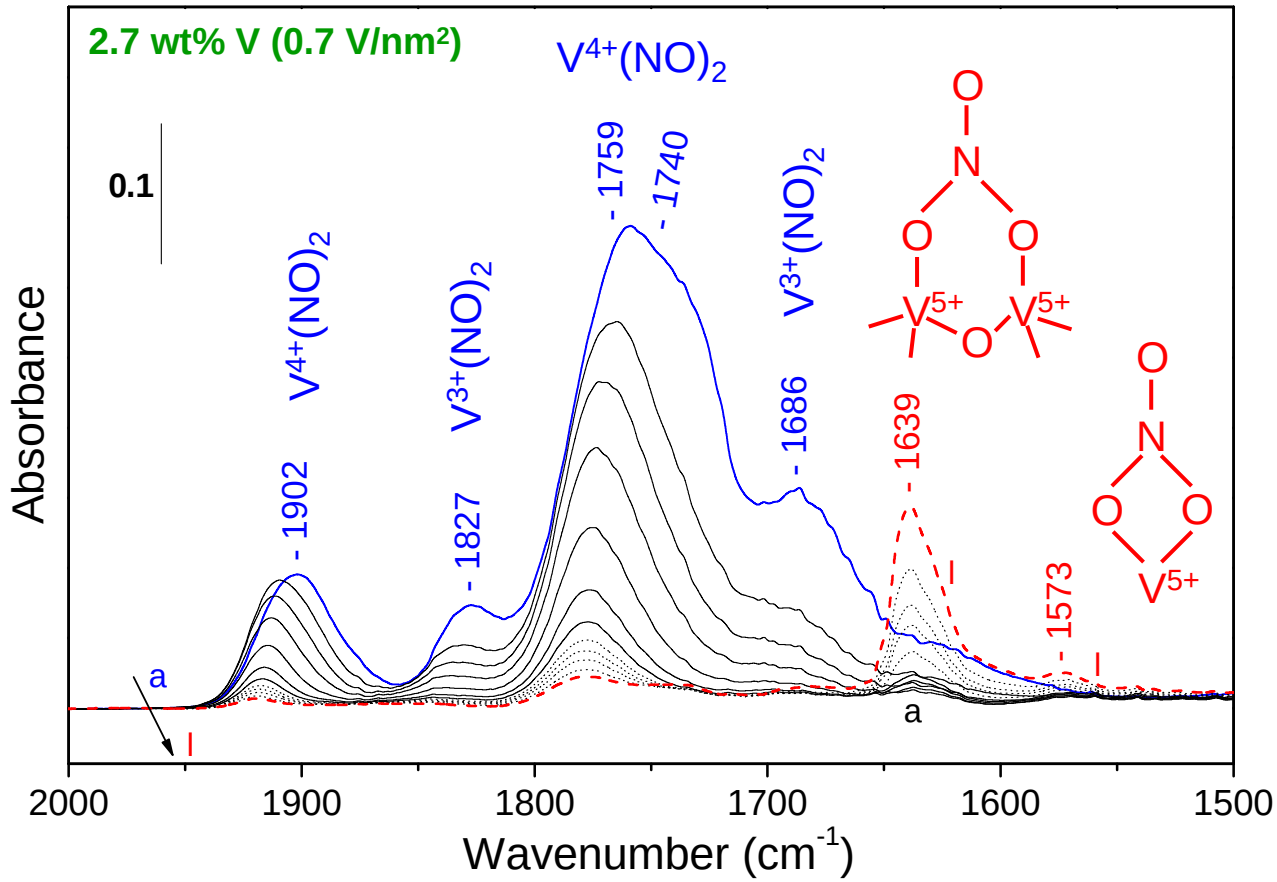
⇨ **Dehydration dramatically changes surface vanadia structure**

C. Hess, I.J. Drake, J.D. Hoefelmeyer, T.D. Tilley, A.T. Bell, Catal. Lett. 101 (2005) 1

Structure of highly dispersed V_xO_y/SBA-15: FTIR

Using NO to probe the structure

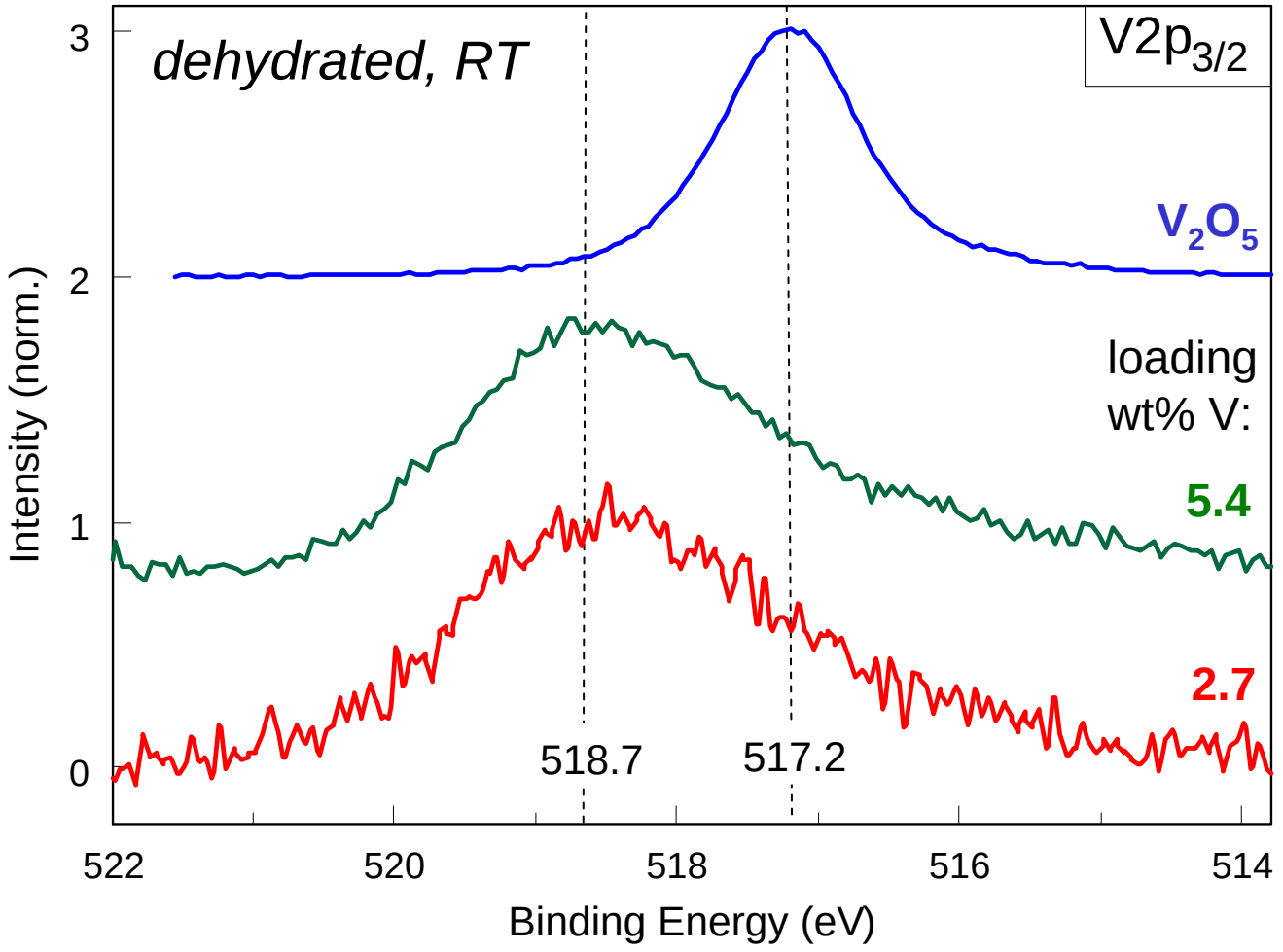
O_2 exp. at 298 K after adsorption of NO to form V-NO complexes



⇨ Bridged nitrates imply presence of dimeric/polymeric vanadia

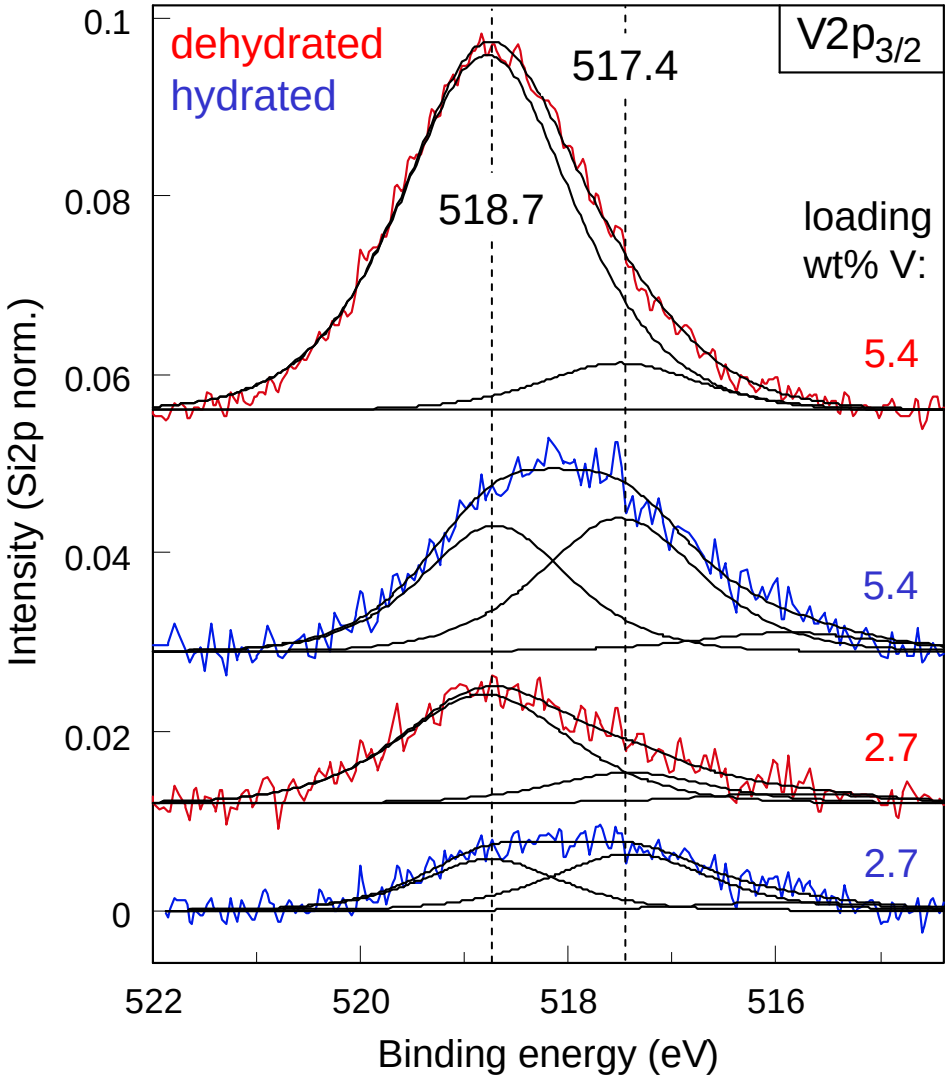
C. Venkov, C. Hess, F.C. Jentoft, Langmuir 23 (2007) 1768

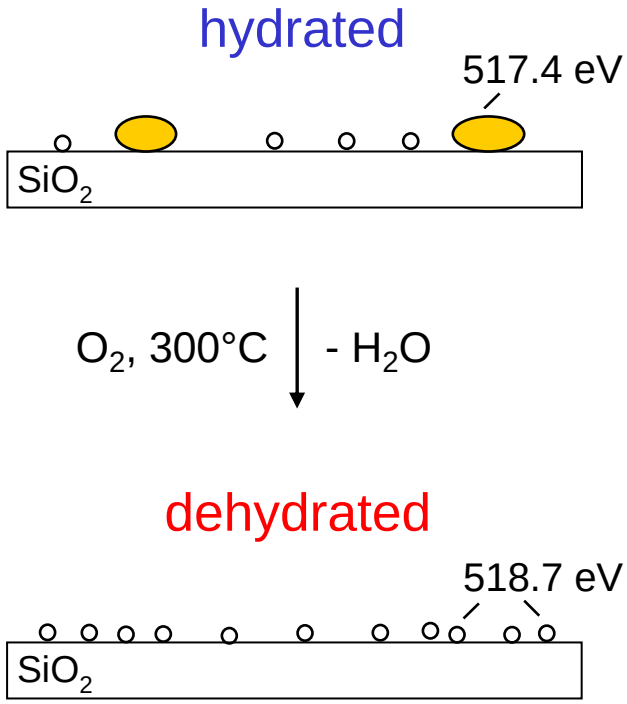
Quasi in situ XPS of V_xO_y/SBA-15: V2p$_{3/2}$



⇨ **XPS reveals strong positive BE shift for silica supported V_xO_y**

Effect of water on dispersion of V_xO_y/SBA-15

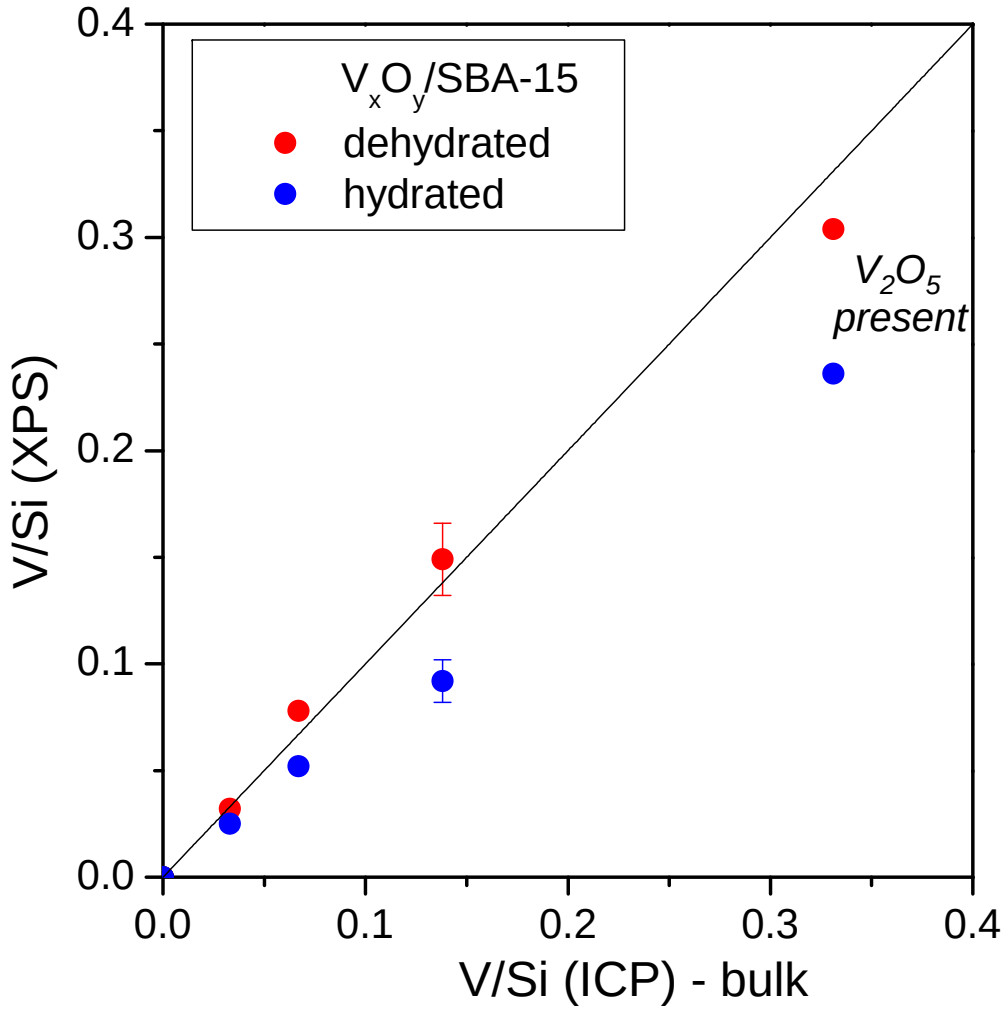




⇨ **XPS yields information on vanadia dispersion**

C. Hess, R. Schlögl, Chem. Phys. Lett. 432 (2006) 139

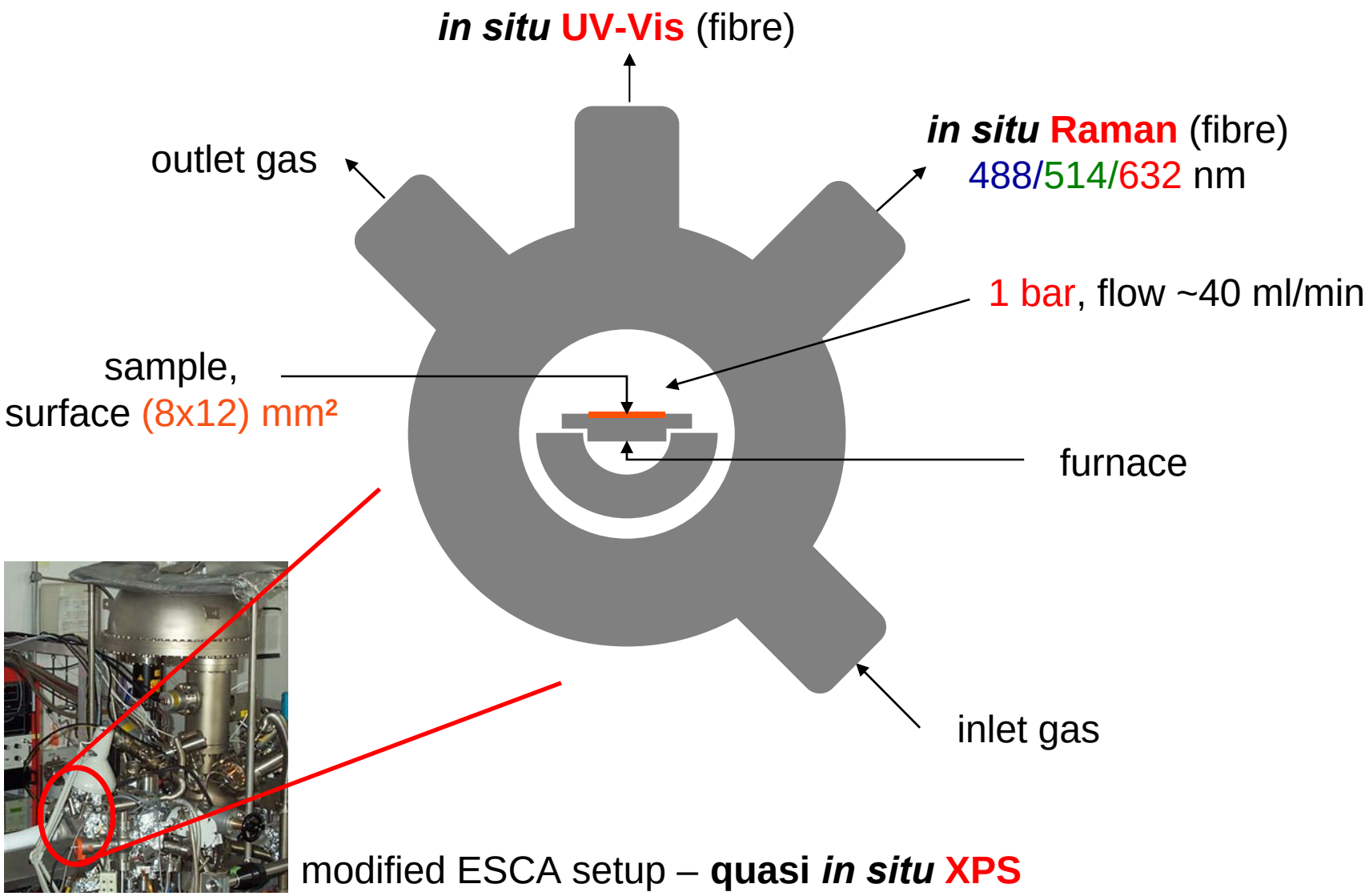
V loading in V_xO_y/SBA-15: XPS vs. bulk



⇨ Close resemblance of V/Si XPS-bulk: Correlation XPS-Raman

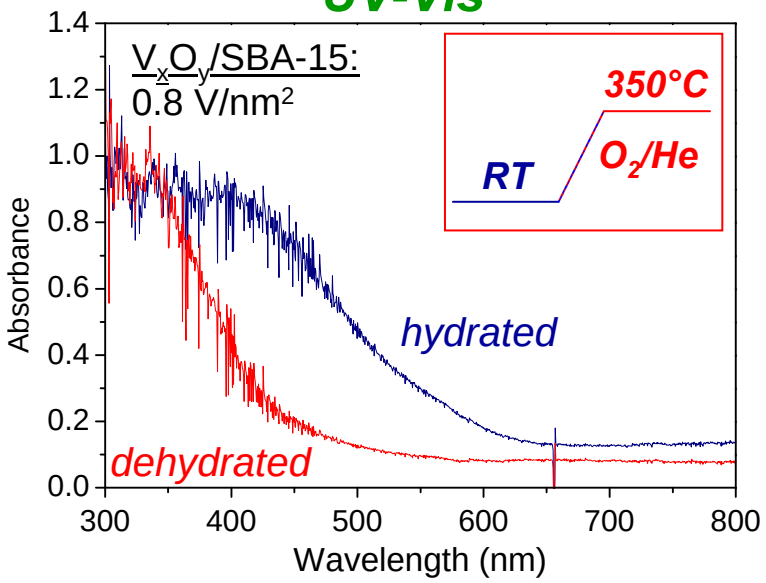
C. Hess, G. Tzolova-Müller, R. Herbert, J. Phys. Chem. C (accepted)

Multi in situ spectroscopy - experimental setup

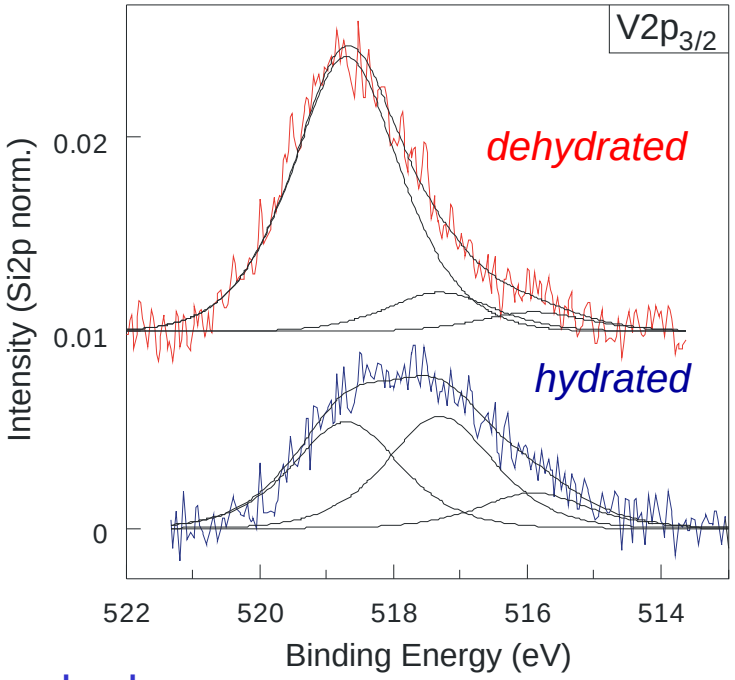


Direct correlation of structure and dispersion

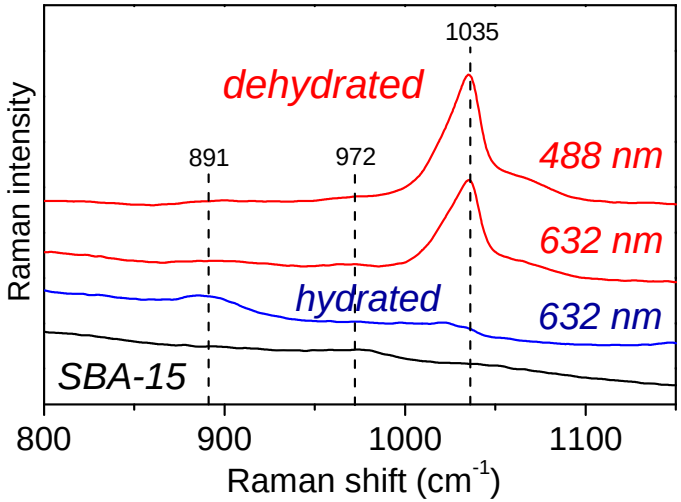
UV-Vis

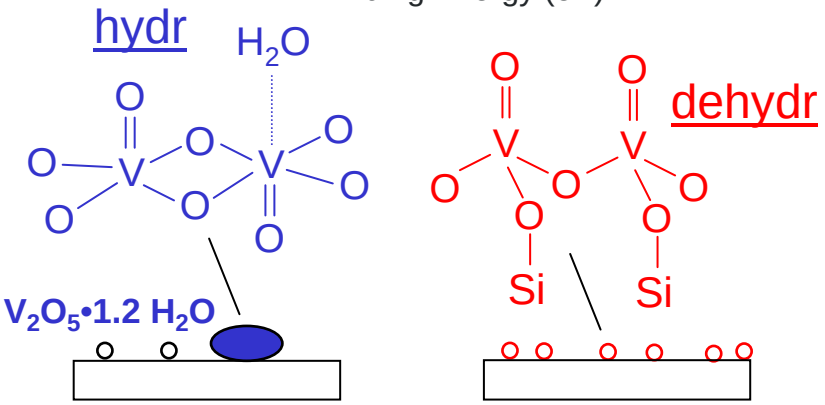


XPS



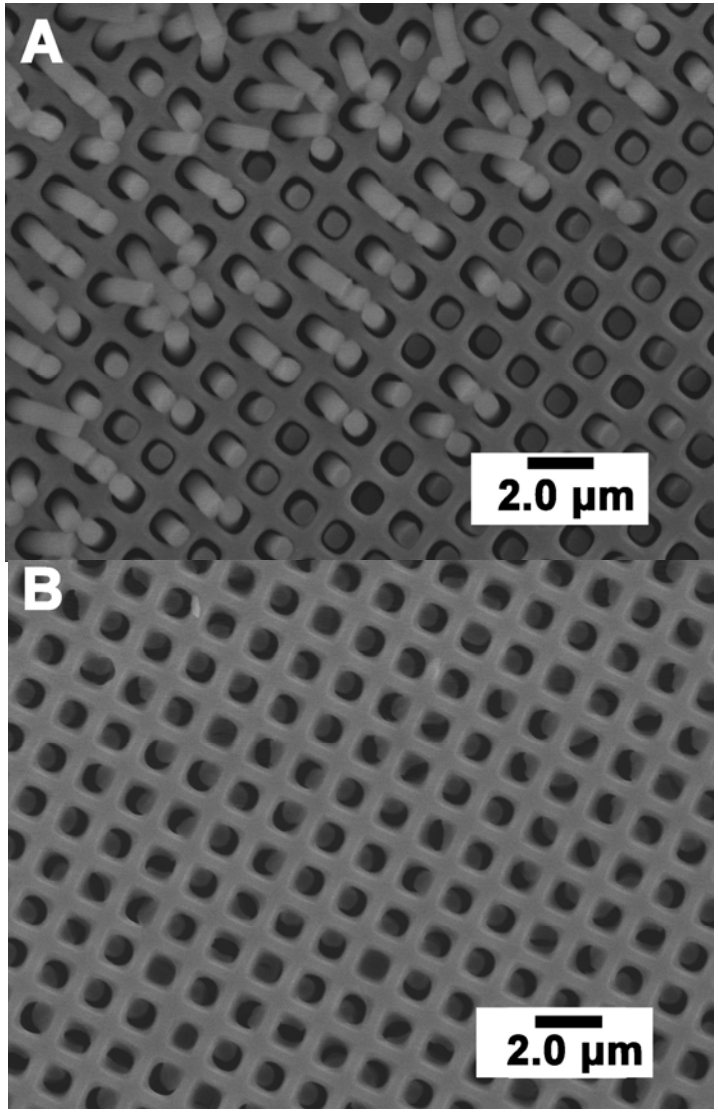
Raman

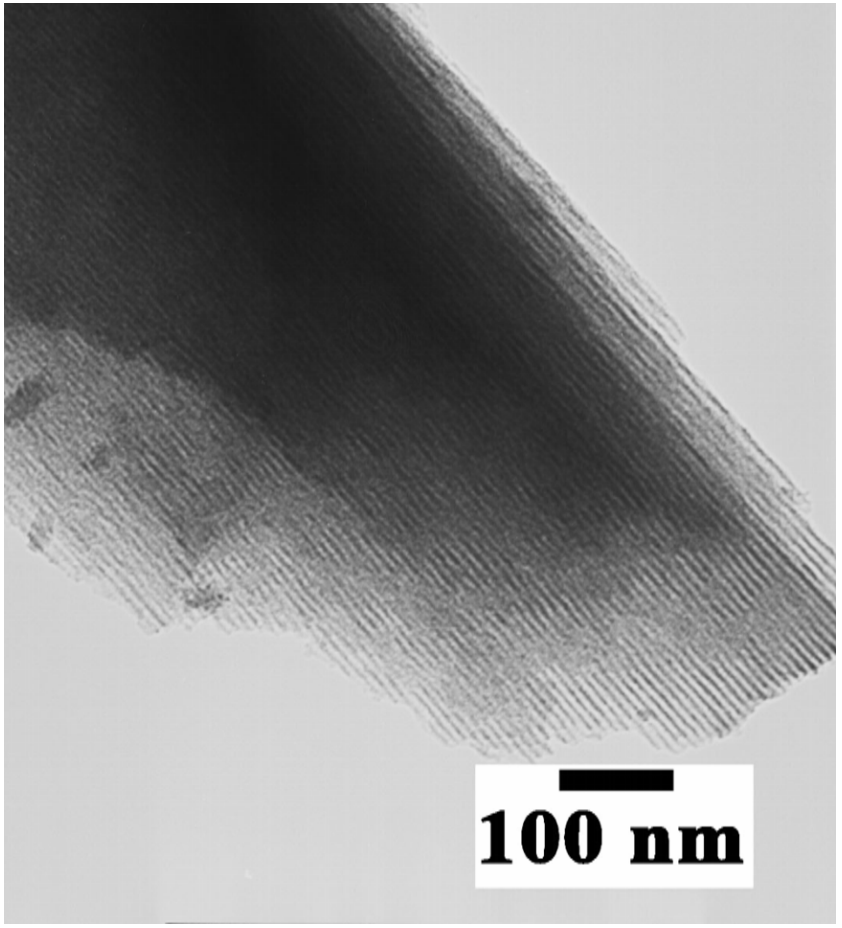




C. Hess, J. Catal. 248 (2007) 120

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



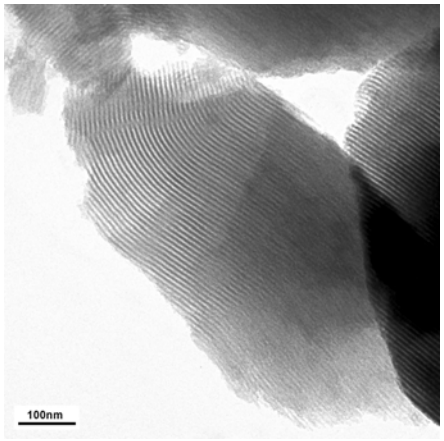


⇨ **Ordered microrods of silica SBA-15 using Si templates**

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

Summary and Outlook

- Controlled synthesis of vanadia model catalysts using silica SBA-15
  - ⇨ reaction mechanism
  - ⇨ increased mechanical stability
  - ⇨ isolate/mimic vanadia sites of complex oxides
  - ⇨ new insight in structure of supported vanadia



- Multi *in situ* spectroscopy (Raman, UV-Vis, XPS)
  - ⇨ correlation of vanadia structure and dispersion
- Dehydrated state is perfect starting point
  - ⇨ structure-activity relation of propane selective oxidation reactions
- Support effects
  - ⇨ TiO_x/SBA-15, positive binding energy shift at low titania loadings

Acknowledgements

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MPI of Microstructure Physics, Halle:

Dr. Xin Chen

Dr. Martin Steinhart

SFB 546 (TP B2)

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