Struktur und Reaktivität von Vanadia/Silica Modell Katalysatoren

Structure and Reactivity of Vanadia/Silica Model Catalysts

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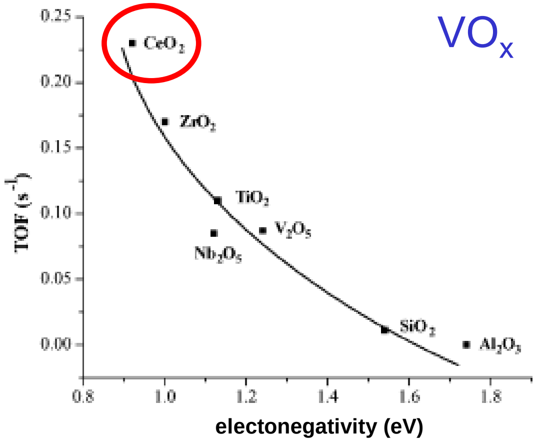
reactivity of VO_x particles in chemical reactions (e.g. ODH) is strongly dependent on the <u>support</u>

Methanol → Formaldehyde



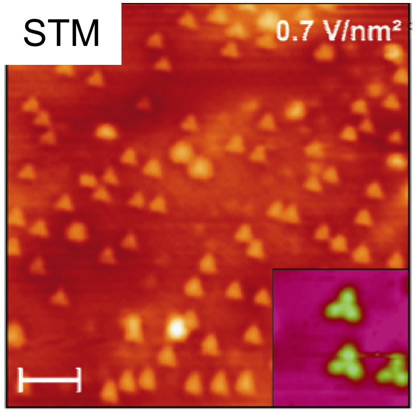
I. Wachs, Catal. Today, 100 (2005), 79.

VO_x on CeO_2

STM: formation of monomers, dimers, trimers or oligomers as function of coverage and temperature

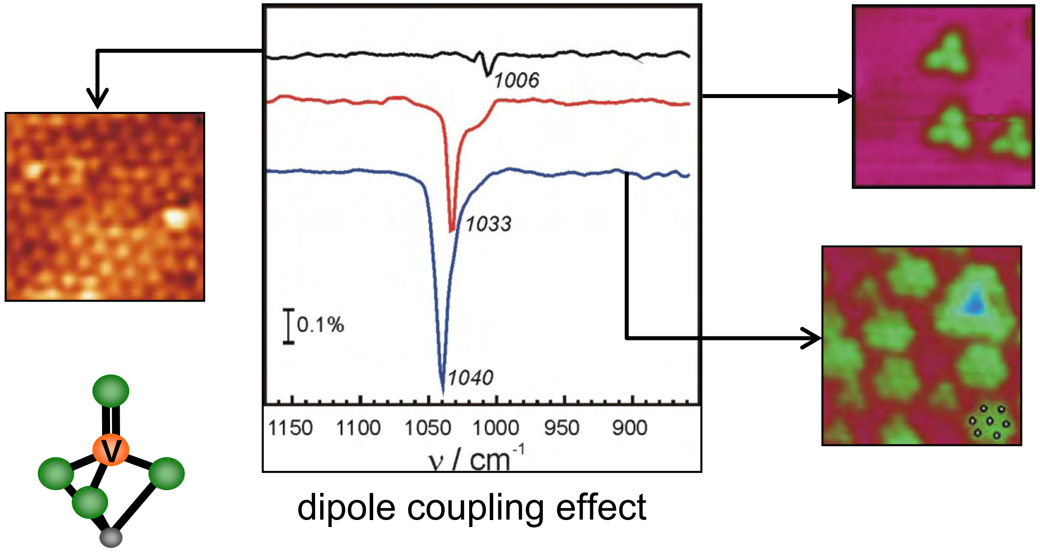
IRAS: direct relationship between the nuclearity of vanadia clusters and the V=O frequency

monomers → dimers (trimers) → nanoparticles



Baron et al., Angew. Chem. 2009, 121, 8150

IRAS



dipole coupling effect

objectives

reactivity of VO_x particles in chemical reactions (e.g. ODH) is strongly dependent on the <u>support</u>

VO_x on CeO_2

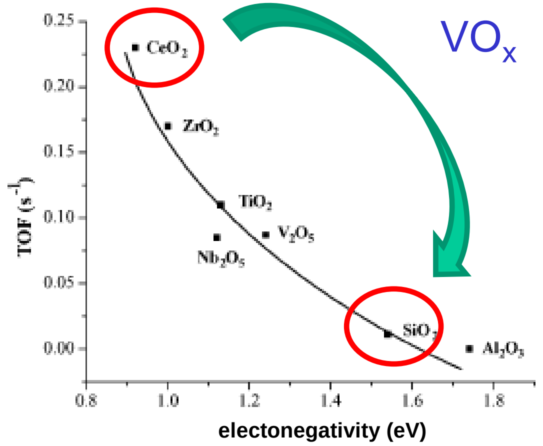
STM: formation of monomers, dimers, trimers or oligomers as function of coverage and temperature

IRAS: direct relationship between the nuclearity of vanadia clusters and the V=O frequency

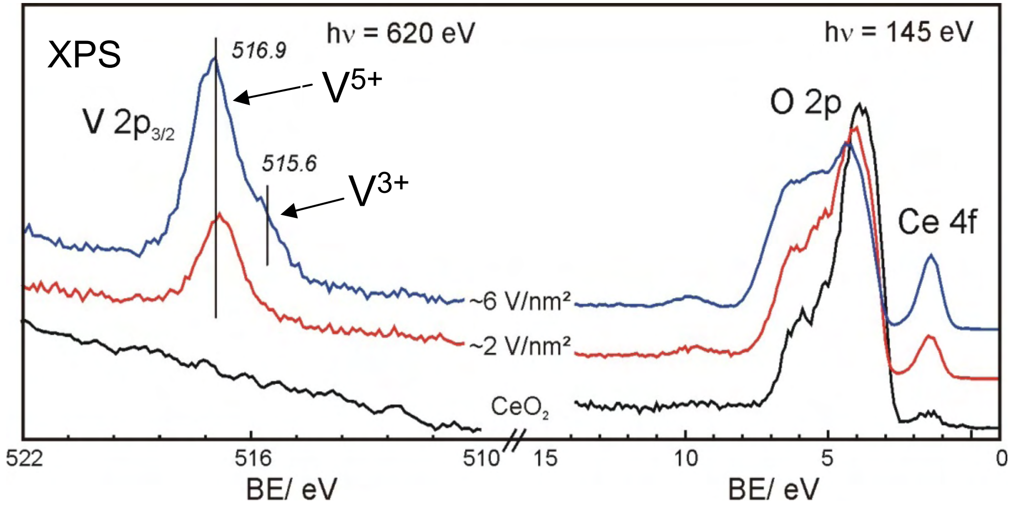
XPS: V in +5 state

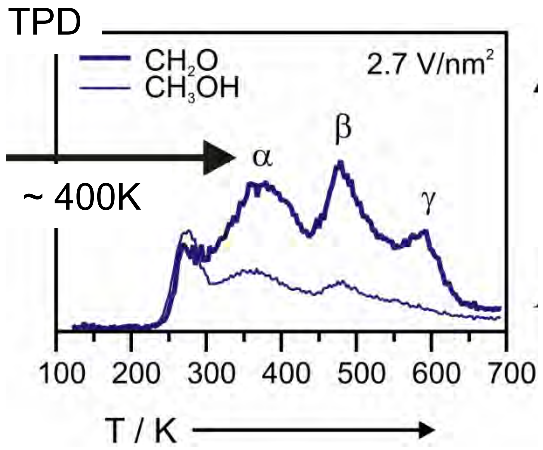
TPD: low-temperature reactivity of small VO_x particles

Methanol → Formaldehyde



I. Wachs, Catal. Today, 100 (2005), 79.



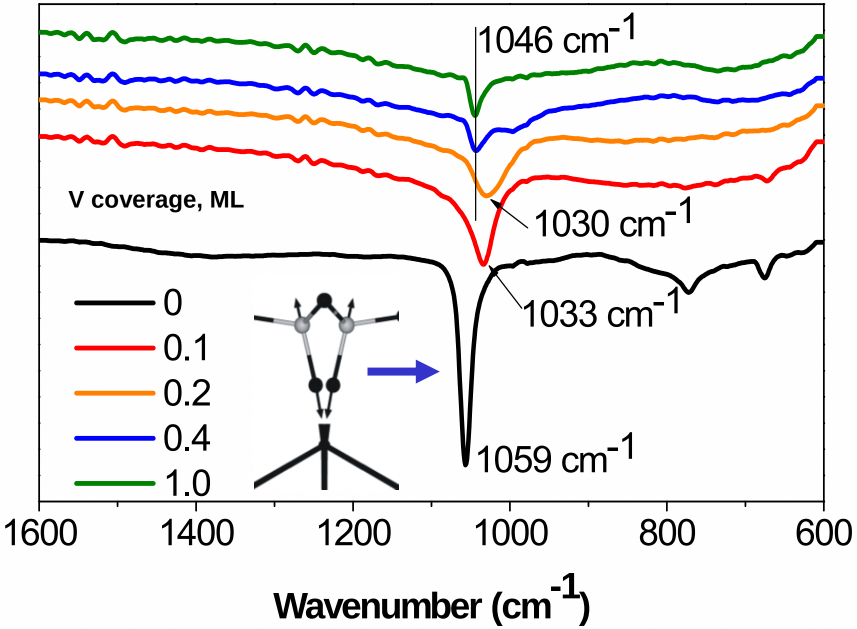


M. V. Ganduglia-Pirovano, et al., JACS, 2009

→ <u>correlation between structure and reactivity</u>

monolayer crystalline SiO_2/Mo(112)

- ➢ SiO_2 phonon (~1060 cm^{-1}) interferes/ couples with V=O stretch frequency (1010-1050 cm^{-1})
- ➢ only ML → interaction to metal underneath
- ➢ thicker SiO_2 /Mo(112) films are amorphous



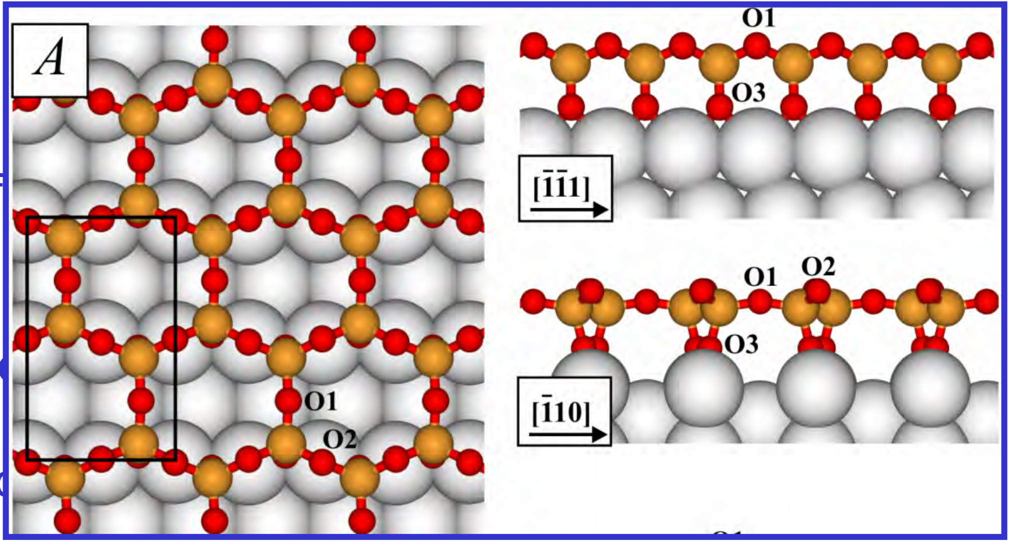
Kaya et al., Surface Science (2007), 601, 4849–4861

Research Goals:

1) synthesis and characterization of
SiO_2 substrate (Ru(0001))

2) characterize VO_x model catalyst

3) relate the structure of VO_x/SiO_2 to

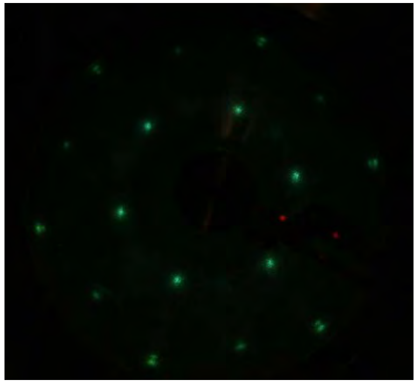


preparation of SiO_2 on Ru(0001)

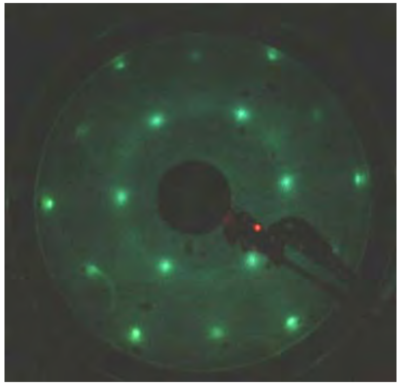
1. step: PVD of Si in O_2 ambient (~$2*10^{-7}$ mbar) at 633 K on O precovered Ru(0001)

2. step: O_2 at 1025 K in font of doser (→ high local O_2 pressure, > 10^{-5} mbar)

LEED



60 eV

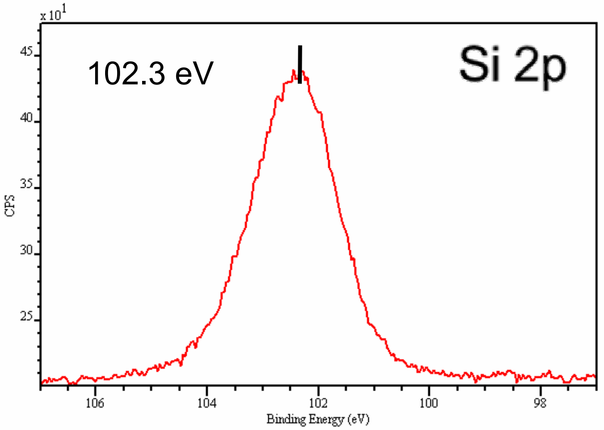


60 eV

p(2x2)/Ru (+ weak ring)

→ crystalline

XPS

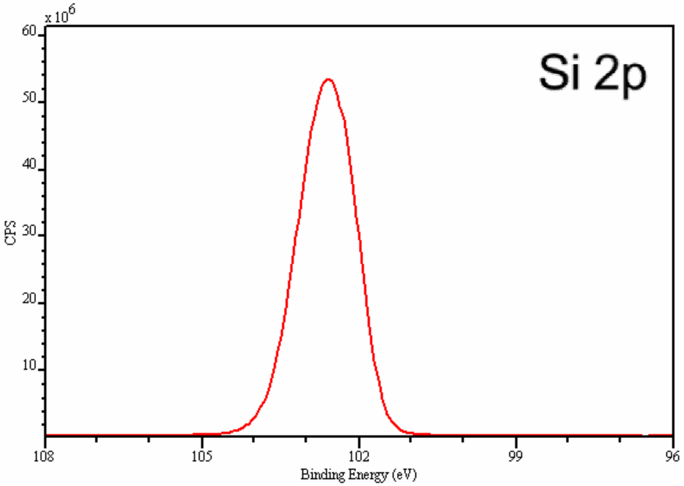


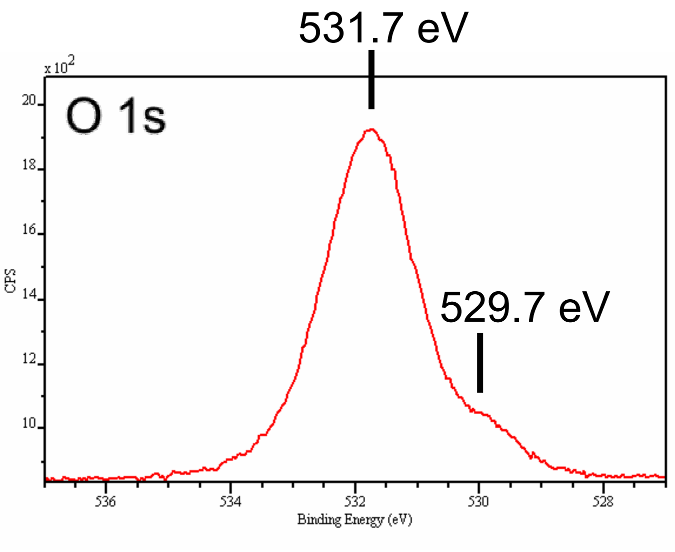
only one state at 102.3 eV (+4)

→

BESSY

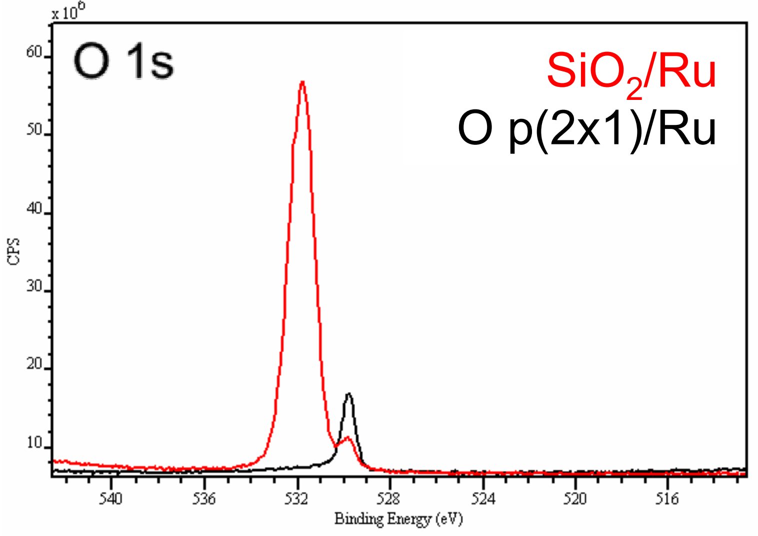
syn. XPS





BESSY →

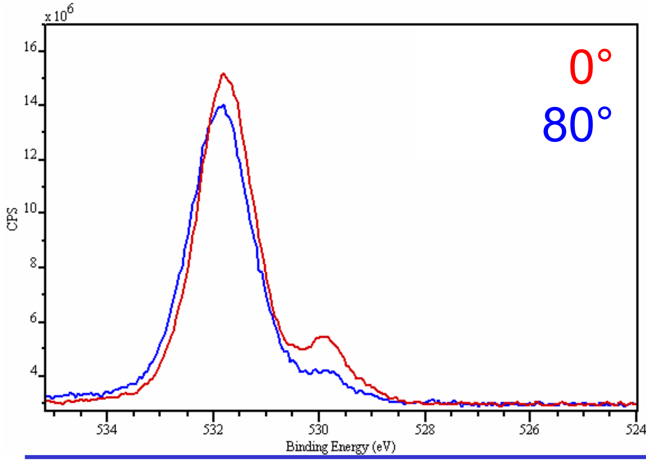
syn. XPS



E_B (SiO$_2$/Ru) = 531.7 eV and 529.8 eV (ratio ~ 12:1)

E_B (O p(2x1)/Ru) = 529.8 eV

grazing emission

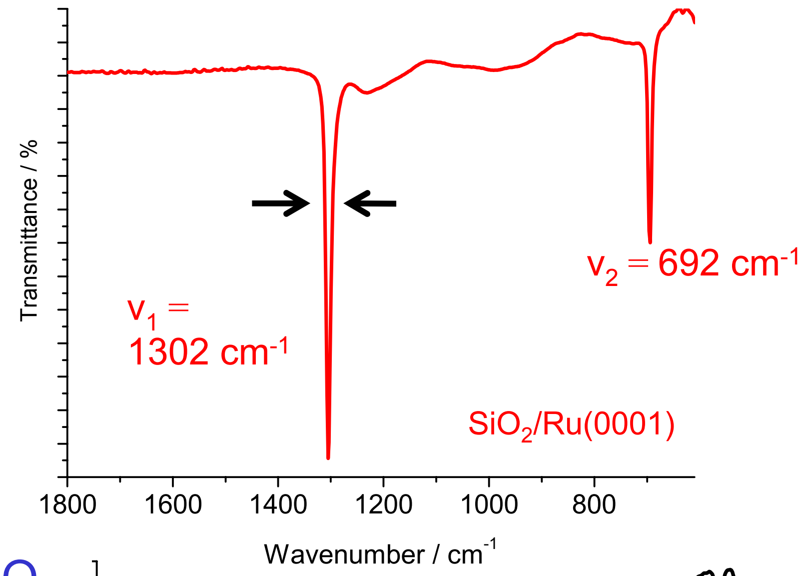


decreasing of low binding state at grazing emission

→ not on surface

→ on SiO$_2$/Ru interface

IRAS



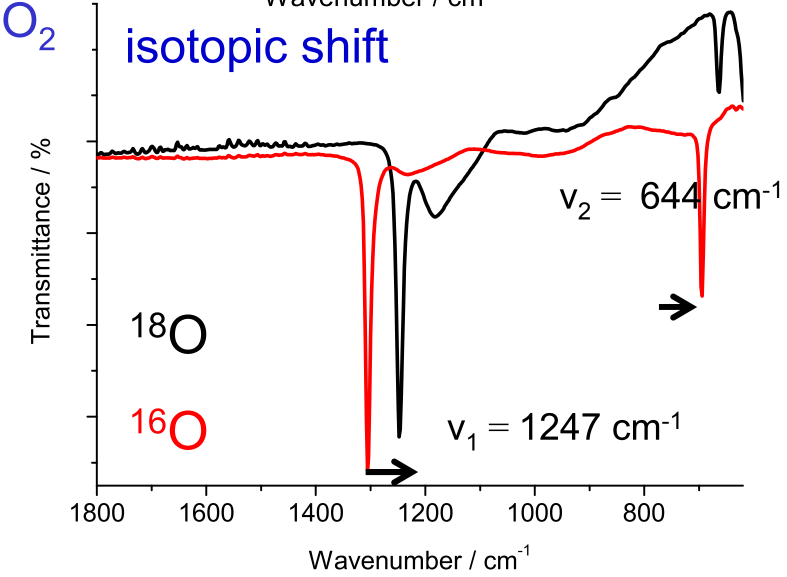
2 sharp phonons (FWHM 12 cm^{-1})

high structural order of SiO_2 film

no interference with V=O

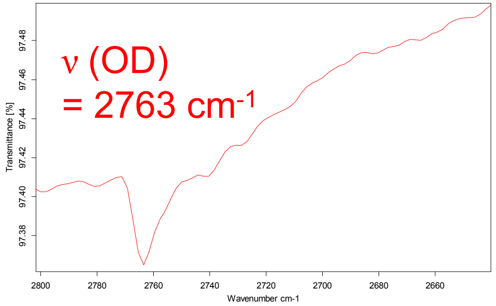
$^{18}O_2$

isotopic shift



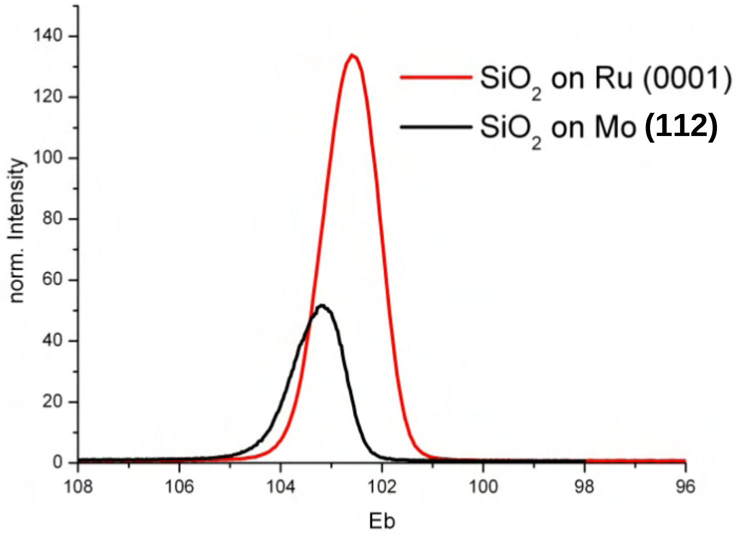
$$\frac{\nu_1(^{18}O)}{\nu_1(^{16}O)} = \frac{\nu_2(^{18}O)}{\nu_2(^{16}O)} = 0{,}957 \sim \sqrt{\frac{\mu(Si{-}^{16}O-Si)}{\mu(Si{-}^{18}O-Si)}}$$

hydroxylation with $D_2O(s) \rightarrow \nu$ (OD)



hydroxyl groups as potential anchoring sites

estimation of SiO_2/Ru film thickness



2.5 x monolayer intensity on Mo(112)
(~ 3 Å)

- ➢ calibration on Si 2p XPS intensity

  ~ 2.5 x ML

- ➢ attenuation of Ru 3d signal

  (IEMFP from S. Tanuma, Surf. Int. Anal., 29,165,1993)

  5 - 10 Å

- ➢ attenuation of O 1s signal O prec. Ru

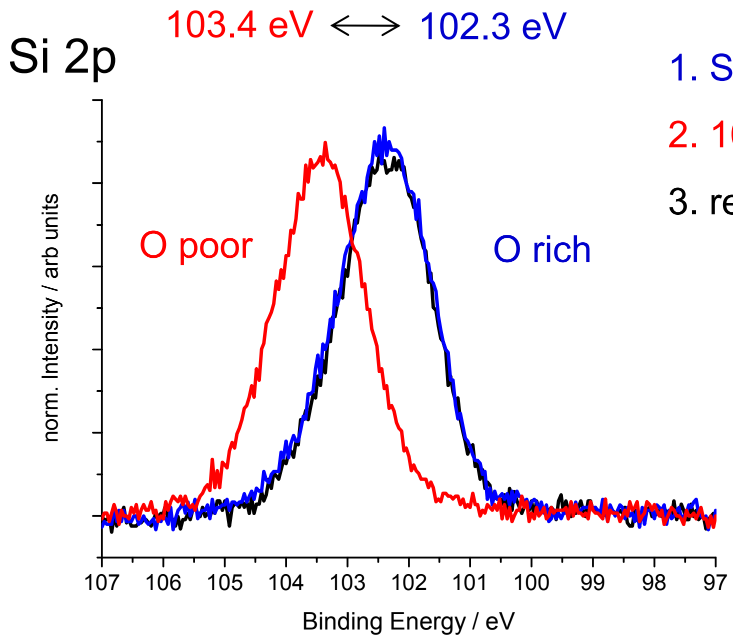
  ~ 5 Å

- ➢ attenuation of Ru 3d signal at grazing emission

  ~ 10 Å

⟶ ≥ 2 layers of SiO_2 on Ru(0001)

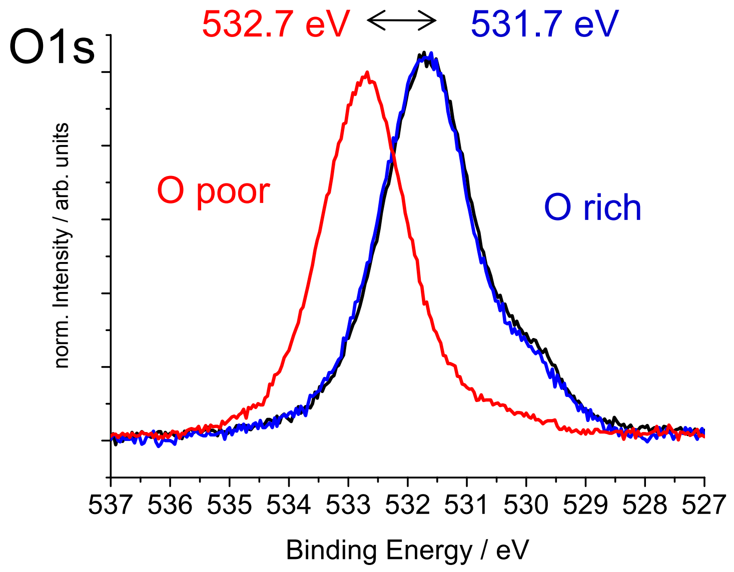
reversible shift



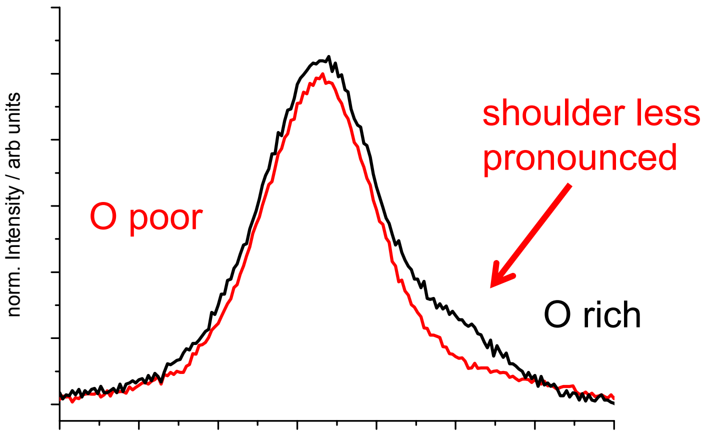
1. SiO_2 as prepared
2. 1000 K in UHV
3. reox. at 1025 K

reversible binding energy shift (>1 eV)

no changes in IR/LEED spectra

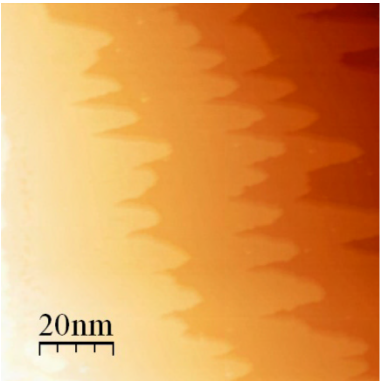


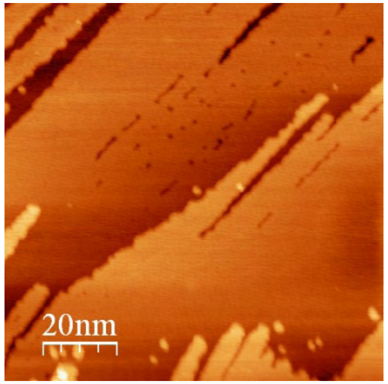
shift “O poor” → on top of “O rich”

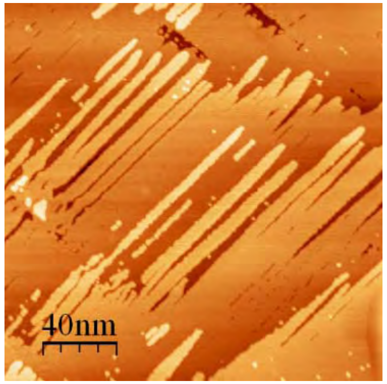


→ oxygen from Ru/SiO_2 interface ?

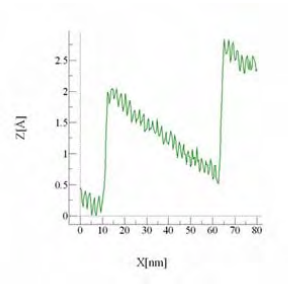
STM

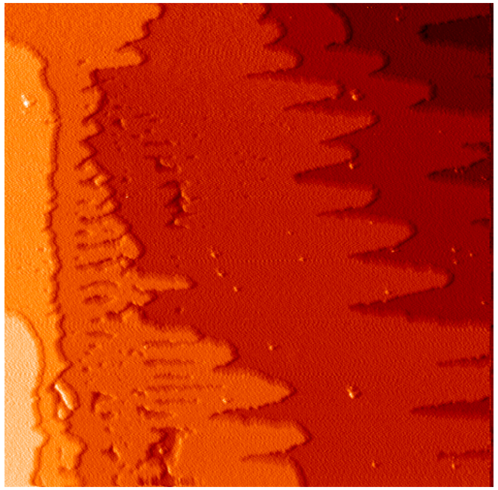






step ↨ 2 ± 0,2 Å





STM reveals relatively uniform and flat SiO_2 film on Ru(0001)

curved step edges and long stripes

destruction during scanning ($U_T > 4V$)

→ weak interaction between SiO_2 layers/substrate

no atomic resolution yet

summary part A

Key observations:

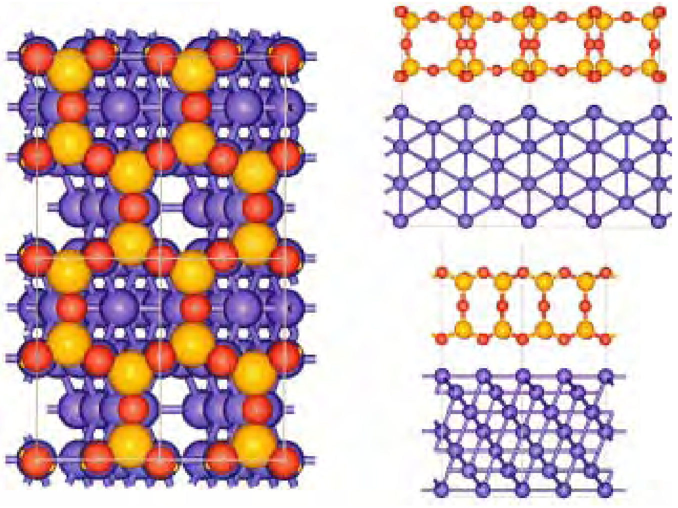
LEED: p(2x2) Ru, crystalline

XPS: Si: only Si (4+); O: SiO_2 and Ru-O state, thickness ≥ 2ML

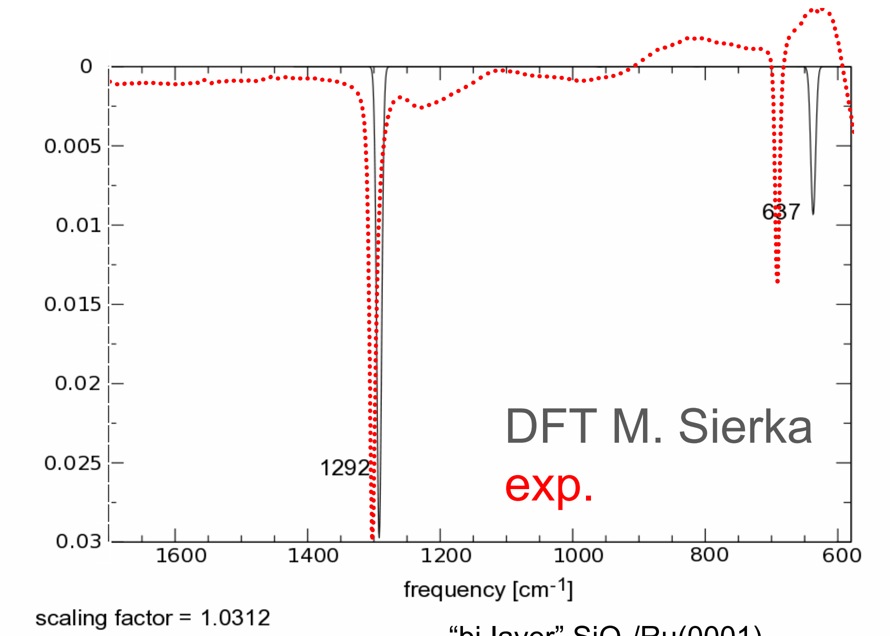
IRAS: 1300 cm^{-1}, 690 cm^{-1}, sharp

STM: flat terraces, weak interaction between SiO_2 layers (and/or) Ru substrate

recent DFT calculations by M. Sierka on “bi-layer” SiO_2 model



“bi-layer” SiO_2/Mo(112)



“bi-layer” SiO_2/Ru(0001)

B. Vanadia on SiO_2/Ru(0001)

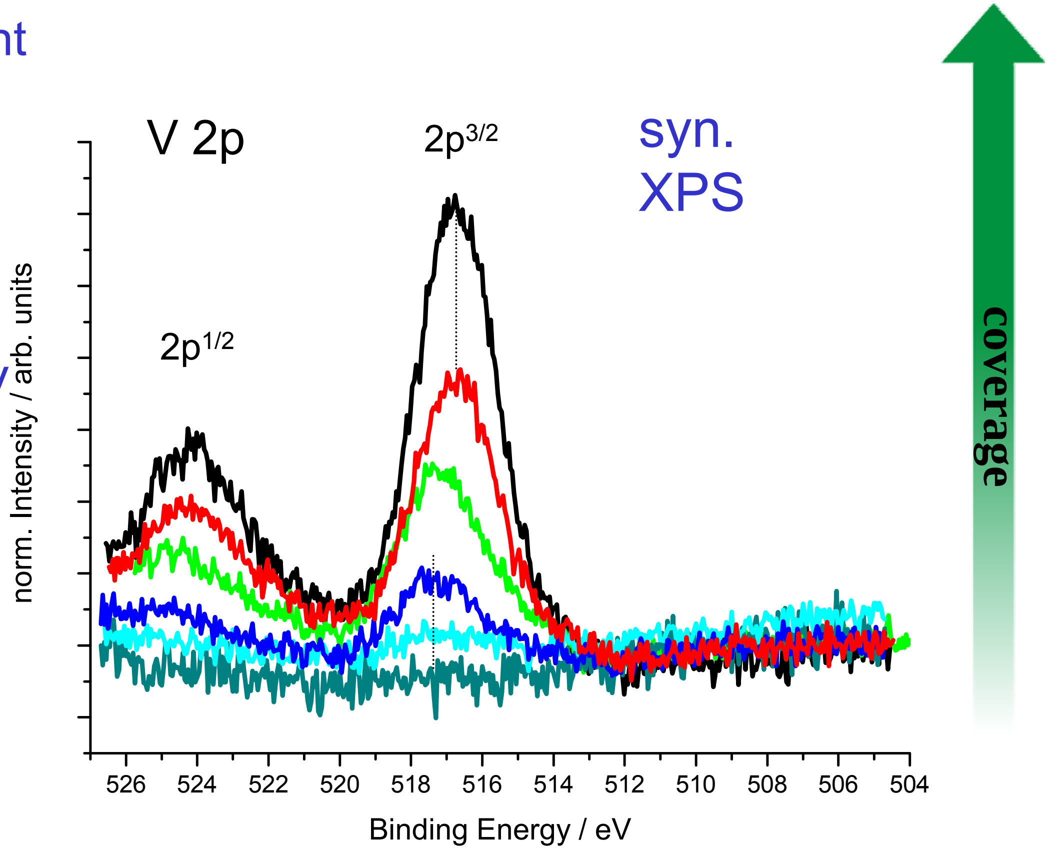
preparation: PVD of V in O_2 ambient (~10^{-6} mbar) at T_s ~100 K

→ E_B(V $2p^{3/2}$) at ~ 517 eV
→ V in oxidation state +5

E_B shifts from 517,3 eV to 516,7 eV with increasing dose

→ similar to VO_x on CeO_2

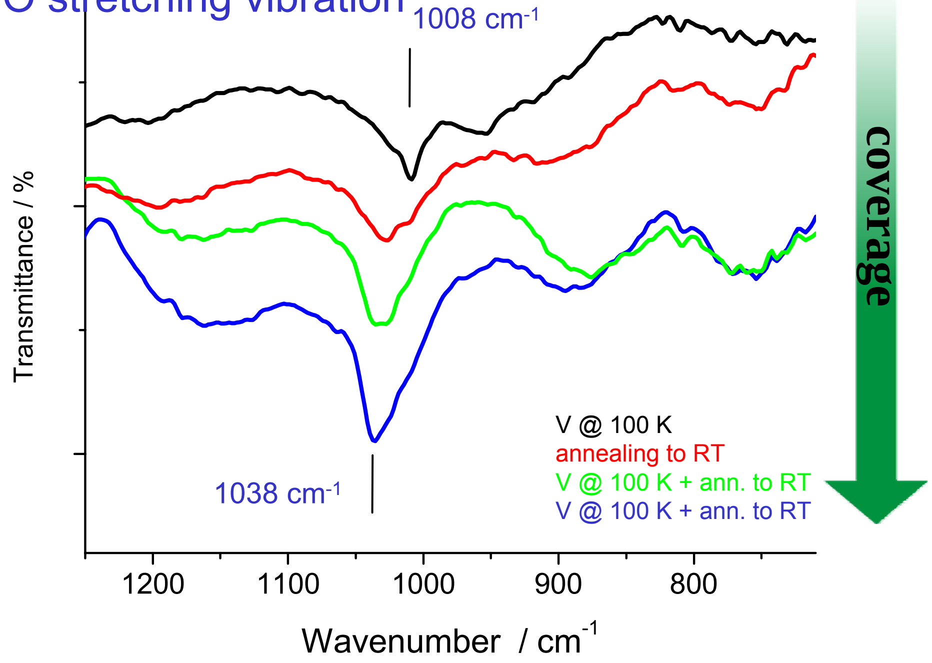
→ aggregation of V clusters

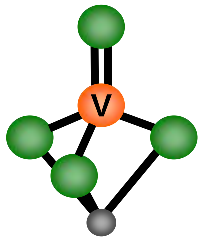


↔ VO_x on monolayer SiO_2/Mo(112) significant lower E_B (→ V in +3/+4) coverage

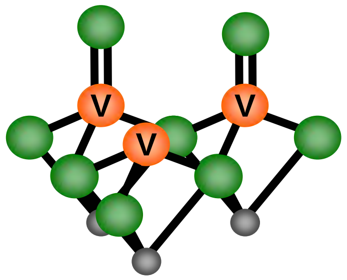
IRAS

V=O stretching vibration





monomeric VO_x



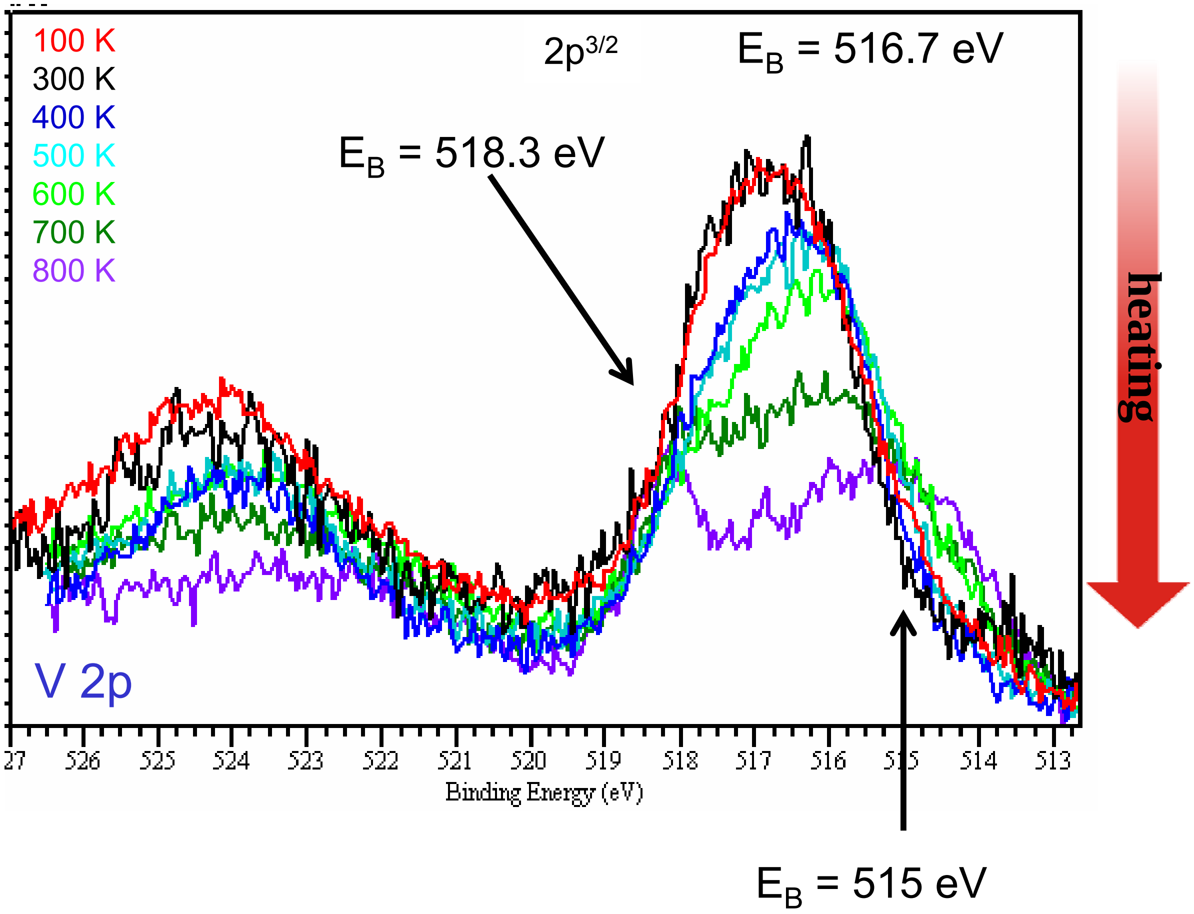
polymeric VO_x

vanadyl (V=O) stretching vibration shifts from 1008 cm^{-1} to 1038 cm^{-1}
→ coalescence of VO_x monomers to polymeric VO_x
→ dipole coupling between neighboring V=O groups

comparable behavior to vanadia on CeO_2

Baron et al., Angew. Chem. 2009, 121, 8150

thermal stability of VO_X/SiO_2 in UHV



V 2p peak shifts to lower E_B
→ $E_B(V\ 2p^{3/2})$ ~ 515 eV

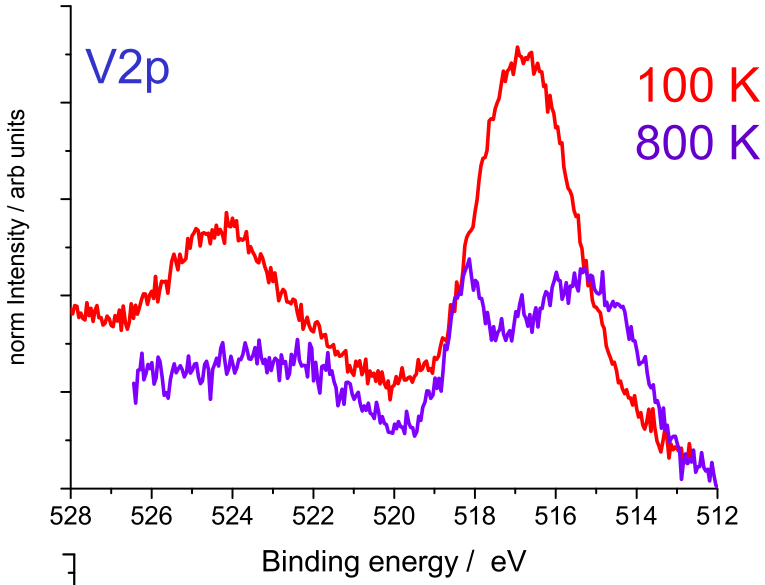
- reduction of V^{5+} to V^{3+}

decrease in intensity

- aggregation, segregation
- Vanadia silicate?

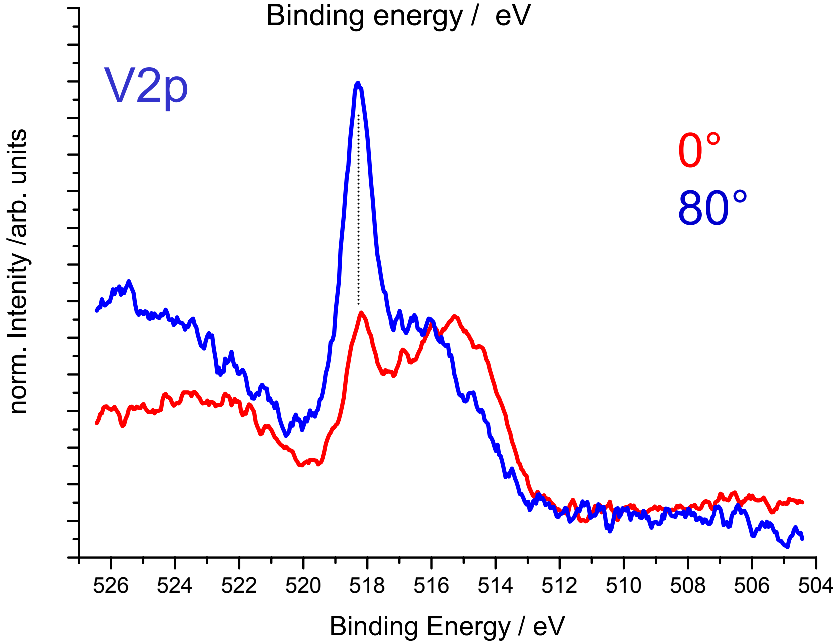
shoulder /peak at E_B = 518.3 eV gets more pronounced after heating to higher temperatures

thermal stability



unusual high E_B (518.3 eV) for V 2p peak

- ➢ small particles (final state effects)
- ➢ V (5+) in special environment



518.3 eV state increases in intensity at grazing emission

- ➢ V with E_B= 518.3 eV is surface species (= on top of VO_x or vanadia silicate

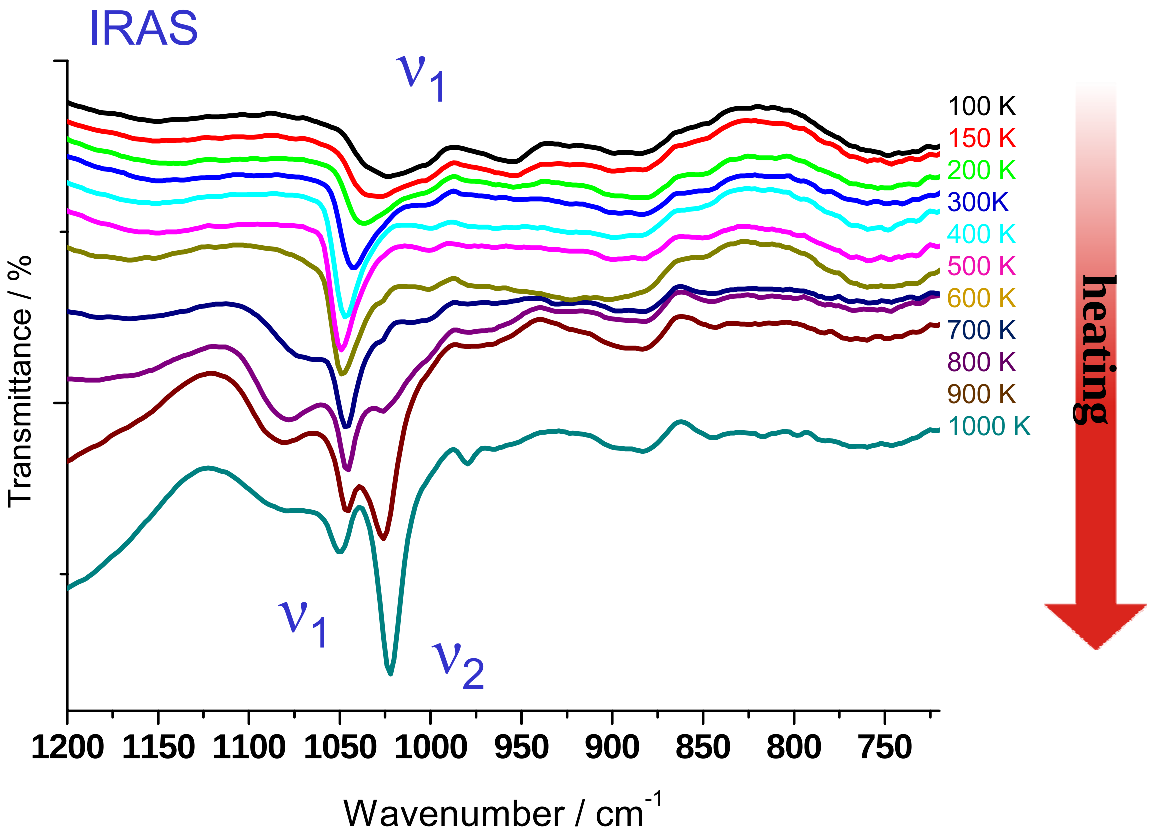
thermal stability

thermal stability of VO_X on SiO_2 : V=O stretching vibration

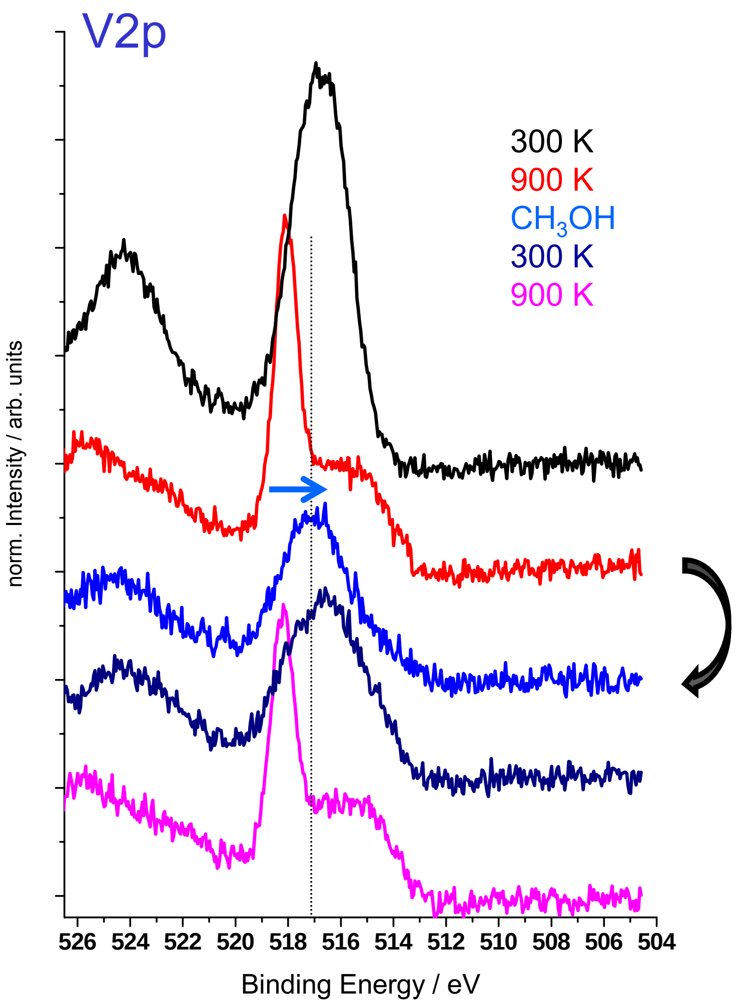
shift of ν_1 from 1020 cm^{-1} to 1048 cm^{-1}
➢ coalescence of small VO_x clusters to polymeric vanadyls

800 K onset of peak ν_2 at 1026 cm^{-1} , shift of ν_2 to 1022 cm^{-1} (1000 K)

➢ formation of new VO_X/SiO_2 phase (E_b 518.3 eV)



thermal stability + reactivity



5 L CH_3OH
at 100 K

1. VO_X evap. at 100K, annealed to 300 K
2. heating to 900 K in UHV formation of V phase with E_B 518.3 eV
3. dosing CH_3OH at 100 K
→ reduction of V phase back to E_B= 517.2 eV
4. heating to 300 K; shift to 516,6 eV desorption of CH_3OH
5. heating to 900 K
→ formation of V phase again

reversible redox. of new V phase due to heating ↔ CH_3OH cycles

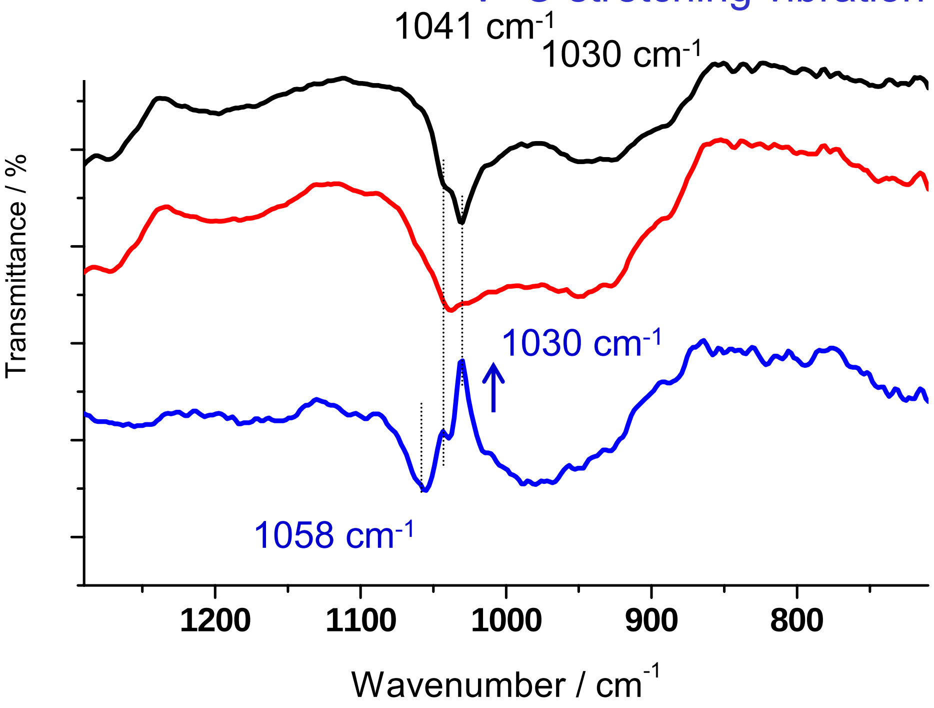
IRAS

V=O stretching vibration

a) VO_x on SiO_2 at 300 K

b) 0.5 L CH_3OH at 300 K

c) ratio: b/a



CH_3OH adsorption

<u>before</u> CH_3OH exposure:

➢ two V=O components at 1030 and 1041 cm^{-1} (shoulder)

<u>after</u> CH_3OH exposure:

➢ new peak at 1058 cm^{-1} → v(C-O) str. from CH_3O-/CH_3OH

➢ 1030 cm^{-1} strongly reduced → interaction between these (oligomeric) V=O and CH_3OH

➢ polymeric V=O (1041 cm^{-1}) inactive

➢ XPS: no changes, V remains in +5 state (↔ VO_x on Ceria V +3)

Summary

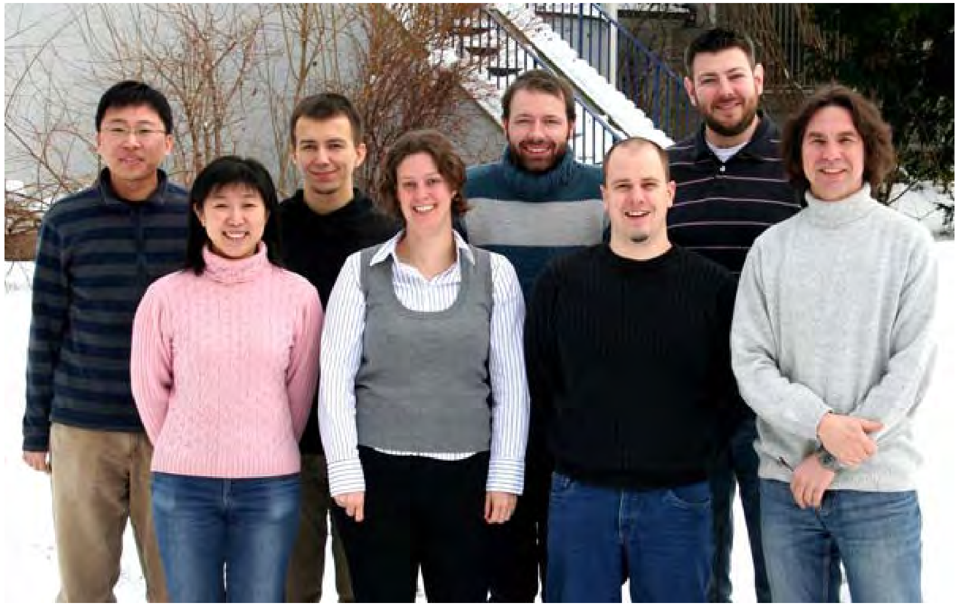
- preparation of “thick” ordered silica film on Ru(0001)
    - bi-layer (“sandwich”) model
- structural studies of Vanadia/SiO_2 species
    - monomeric -> oligomeric (polymeric) V=O species
    - formation of V=O terminated mixed oxide phase at HT

Outlook

- atomic structure of silica film (+ DFT)
- morphology of VO_x on silica (LT STM, AFM)
- structure of “mixed” oxide phase (vanadia silicate?)
- reactivity of VO_x/SiO_2 systems towards CH_3OH as compared to VO_x/CeO_2 (TPD)

Thank you for your attention!

Question and/or comments?



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The Workforce

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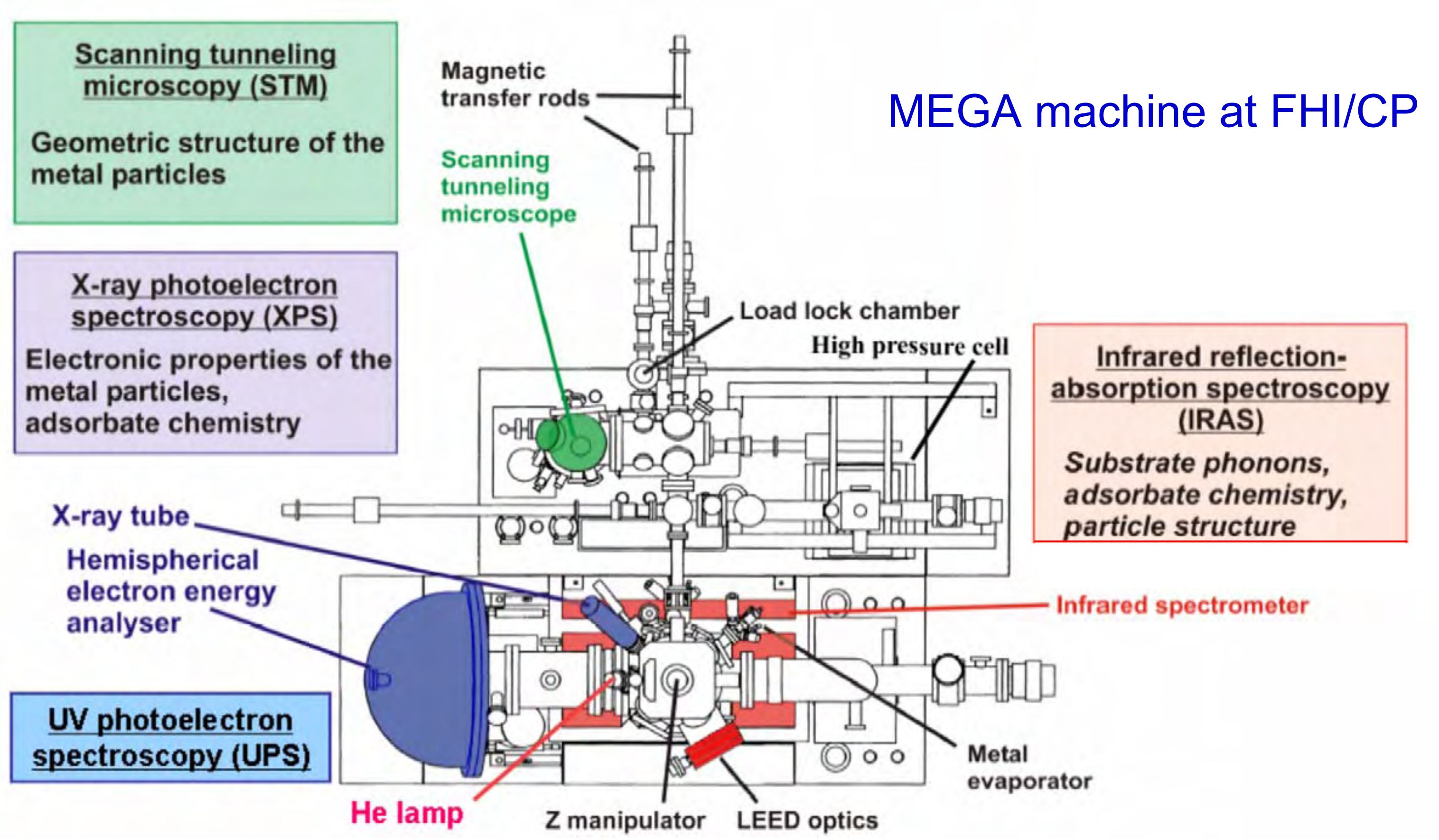
Osman Karslioglu

} BESSY

MEGA machine at FHI/CP



<u>Scanning tunneling microscopy (STM)</u>

Geometric structure of the metal particles

<u>X-ray photoelectron spectroscopy (XPS)</u>

Electronic properties of the metal particles, adsorbate chemistry

<u>UV photoelectron spectroscopy (UPS)</u>

<u>Infrared reflection-absorption spectroscopy (IRAS)</u>

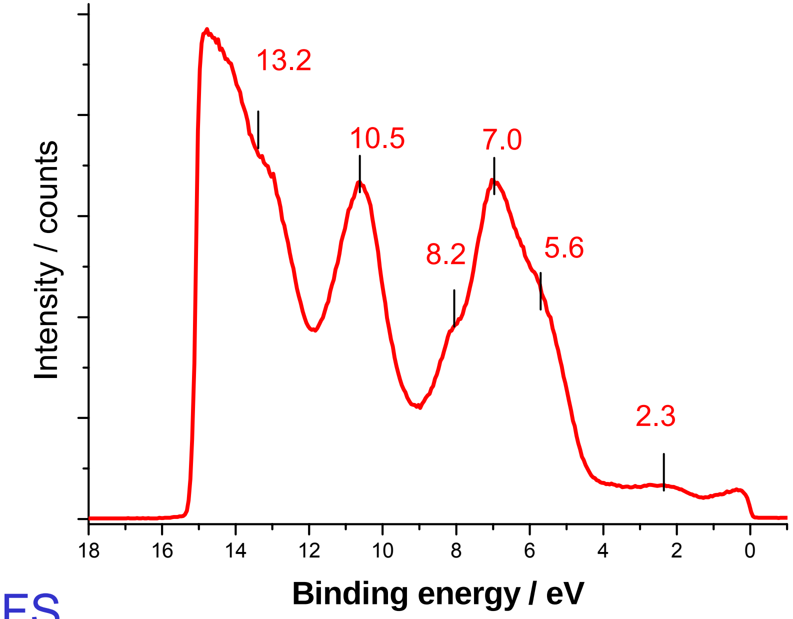
Substrate phonons, adsorbate chemistry, particle structure

complementary techniques in same UHV system

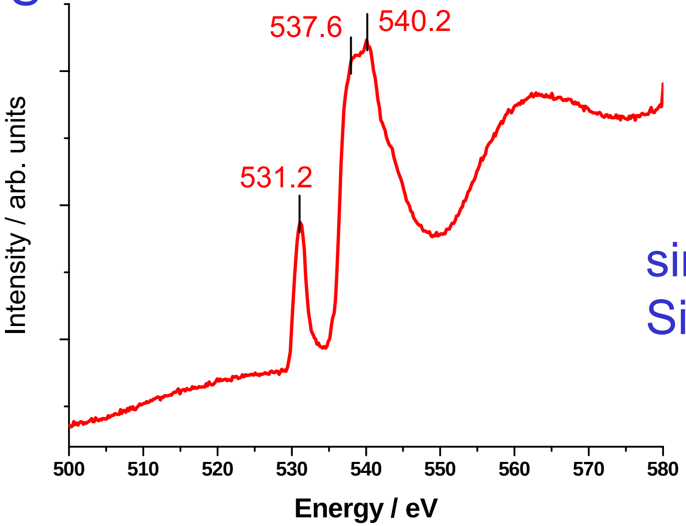
additional measurements at BESSY II
→ better resolution and more surface sensitive XPS + NEXAFS

UPS/NEXAFS

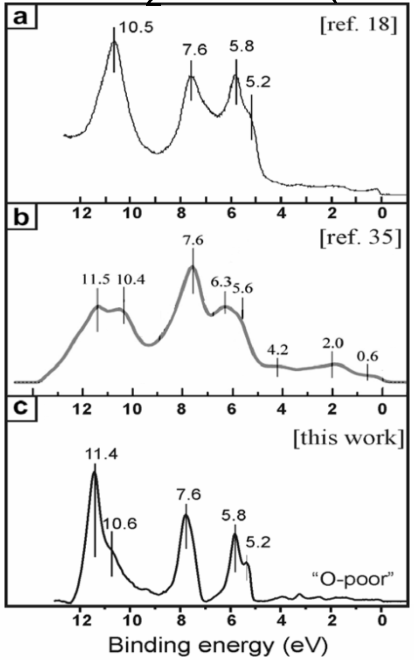
UPS

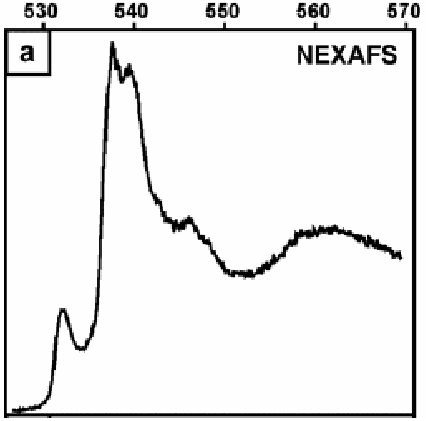


NEXAFS



ML SiO_2 on Mo (112)





similar to monolayer SiO_2 on Mo(112)

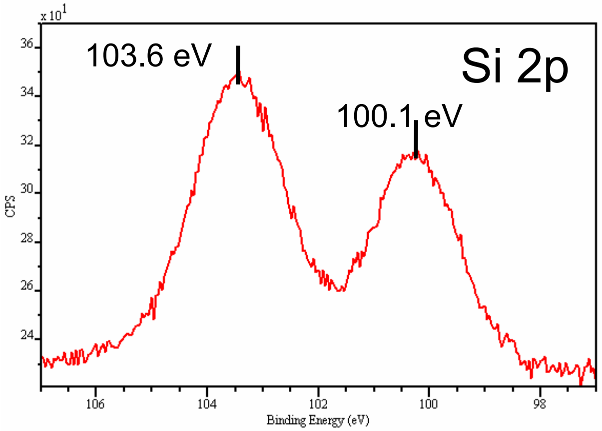
Kaya et al., Surface Science (2007), 601, 4849–4861

SiO_2 on Ru(0001): Preparation

A. preparation of SiO_2 on Ru(0001)

- 1. Step: PVD of Si in O_2 ambient (~$2*10^{-7}$ mbar) at 633 K on O precovered Ru(0001)

XPS

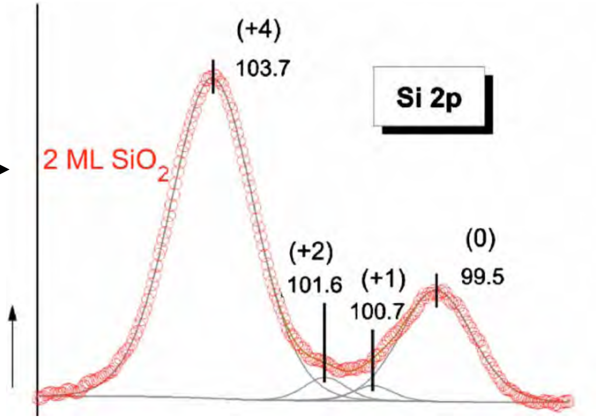


E_B (Si 2p) at 103.6 eV (+4)

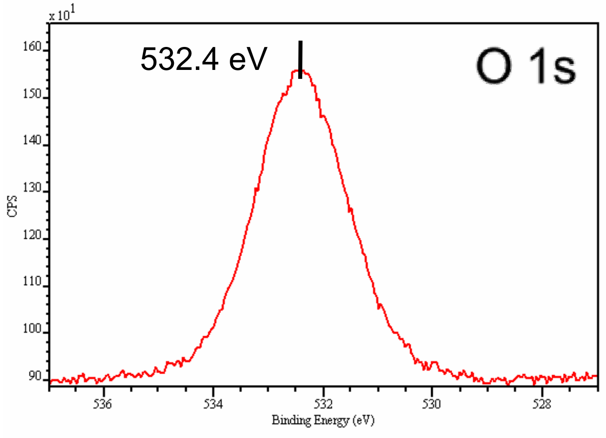
and 100.1 eV (+0/+1)

↔

2ML SiO_2 on Mo(112)



Stacchiola et al., App. Phy. Lett. 92, 011911(2008)

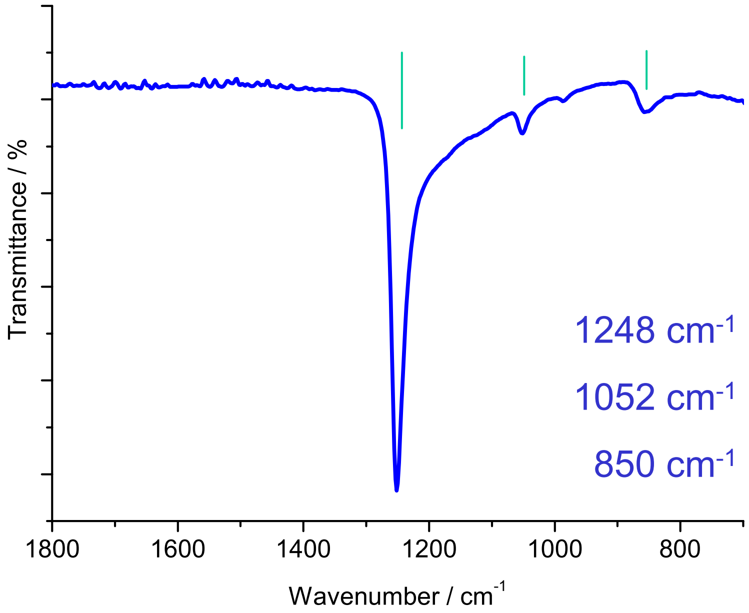


E_B (O1s) = 532.4 eV

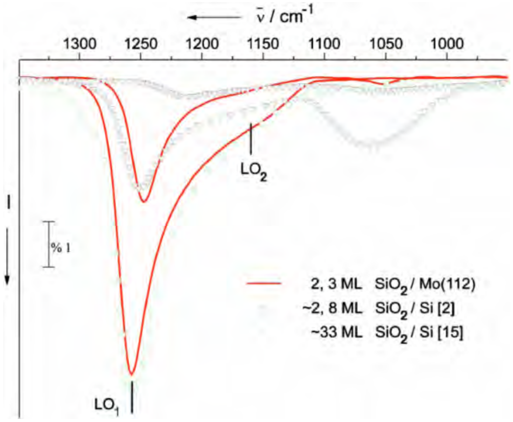
- Si not fully oxidized
- inhomogeneous SiO_x film

IRAS & LEED

IRAS



2 ML SiO_2 on Mo(112)

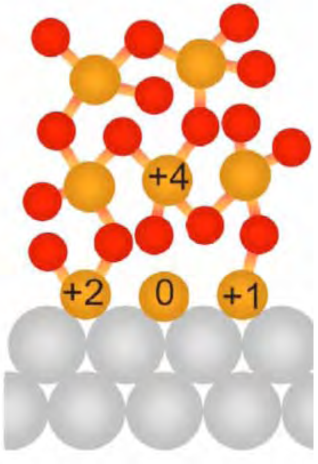


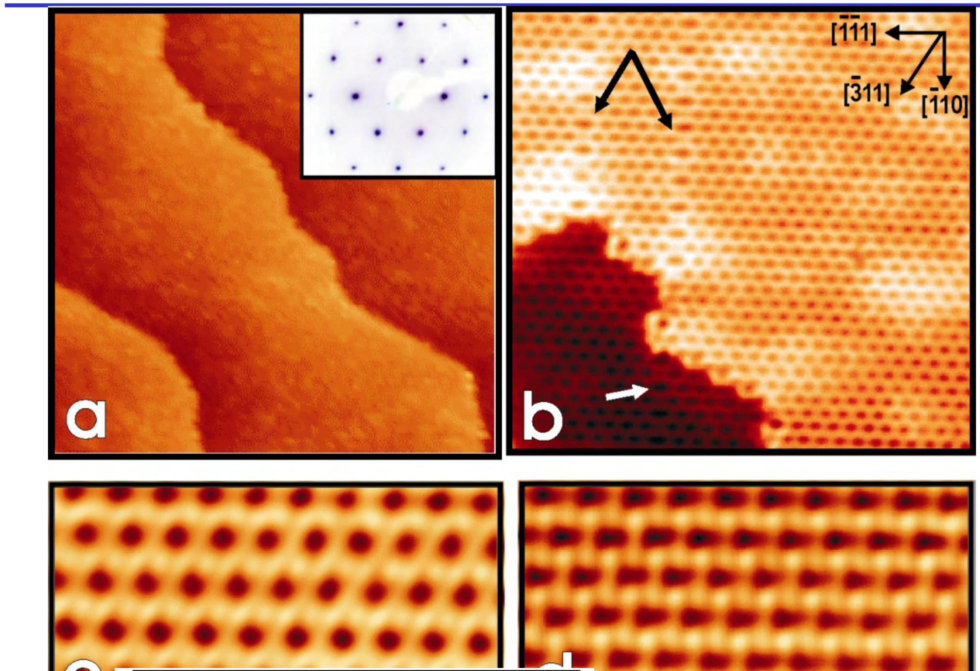
Stacchiola et al., App. Phy. Lett. 92, 011911(2008)

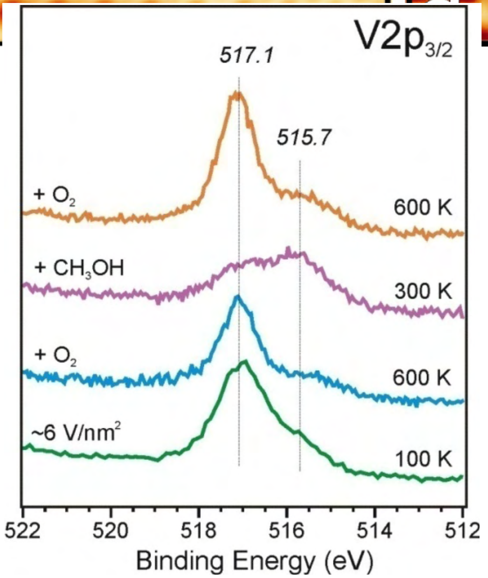
LEED

no LEED pattern

- ➢ film not crystalline
- ➢ amorphes SiO_x

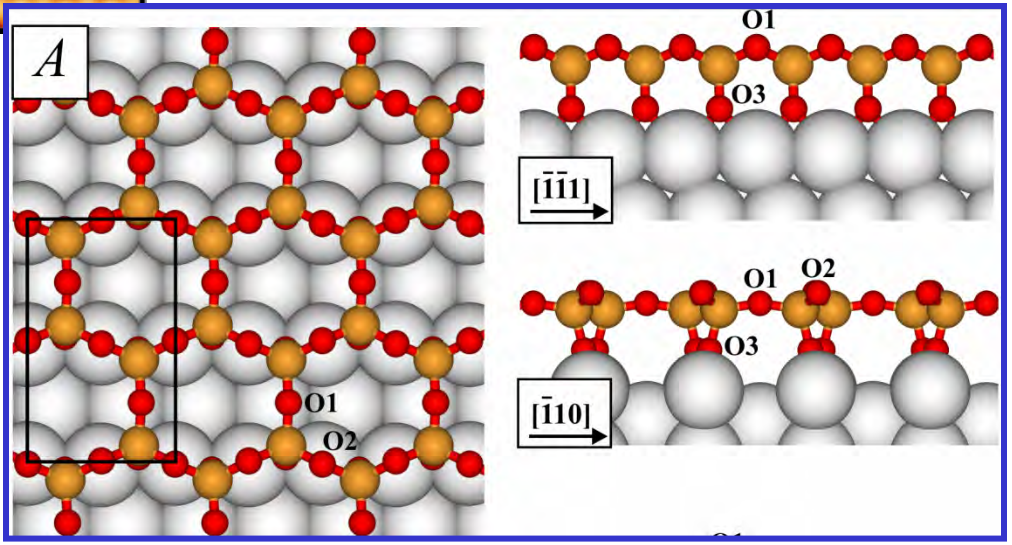




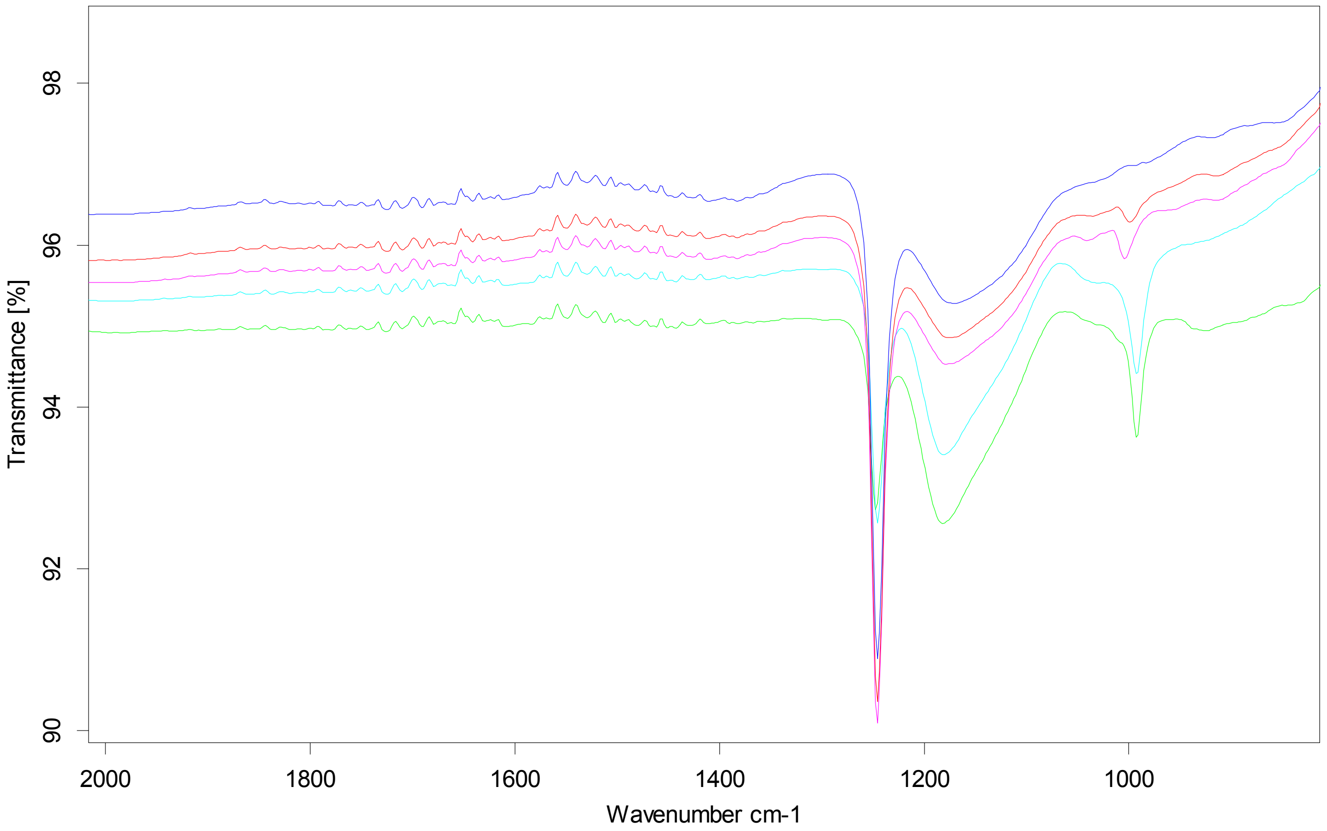


Two dimensional network of corner sharing SiO_4 tetrahedra on Mo(112)

J. Weissenrieder, S. Kaya, J.-L. Lu, H.-J. Gao, S. Shaikhutidnov, H.-J. Freund, M. Sierka, T. Todorova, J. Sauer, Phys. Rev. Lett. 95 (2005) 076103



Teilprojekt B1 (Shaikhutdinov/Freund)



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W:\IRData\2010\jan10\012609.0	Ru(0001)	sample form	26/01/2010

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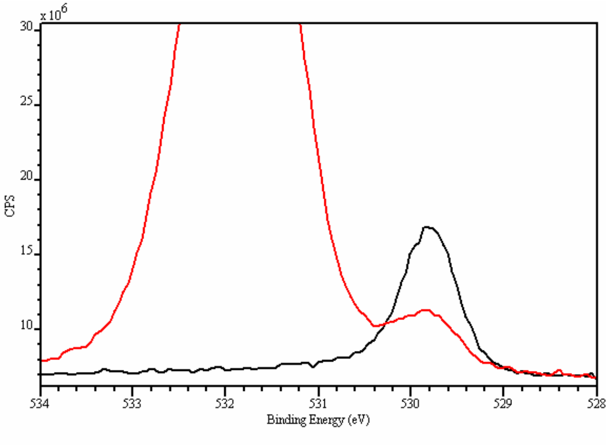
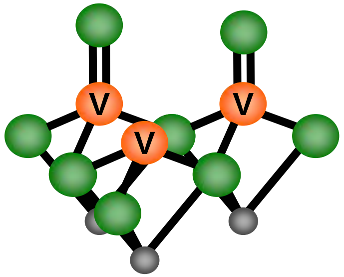
SiO_2 (^{18}O)
V at cold
500 K
900 K
1100 K

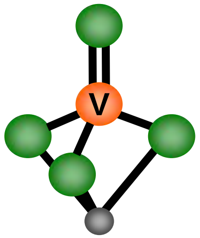
999 cm^{-1}
1006 cm^{-1}
992 cm^{-1}
993 cm^{-1}

Teilprojekt B1 (Shaikhutdinov/Freund)

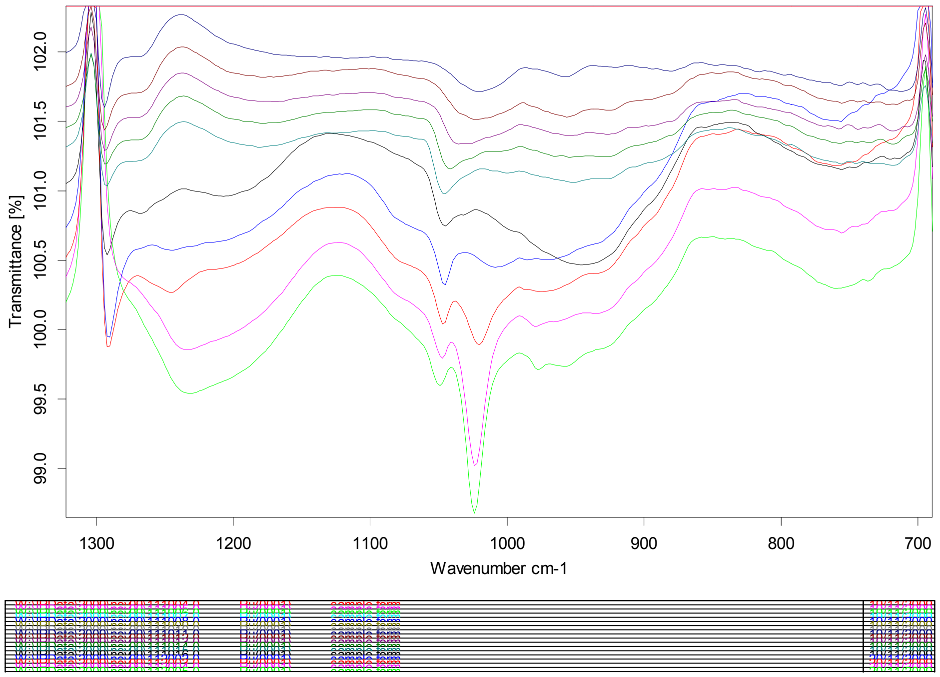


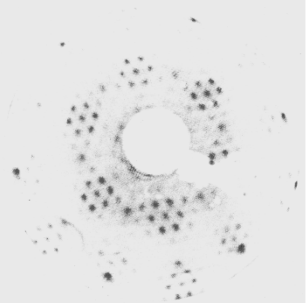


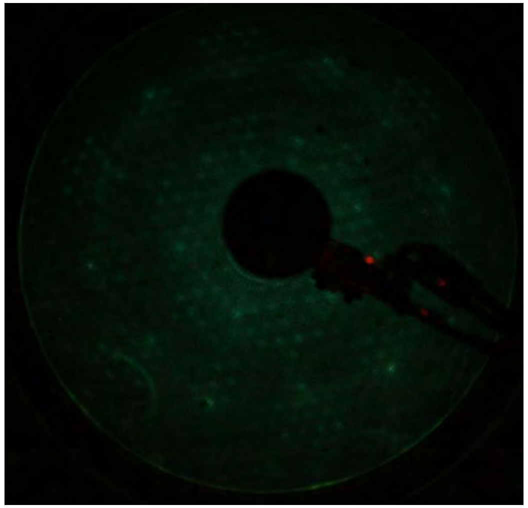
Polymeric VO_x

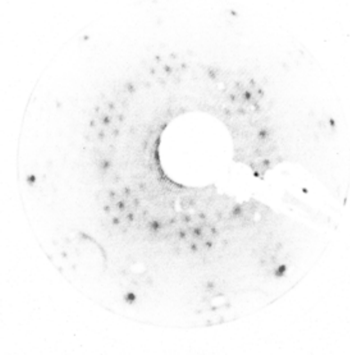


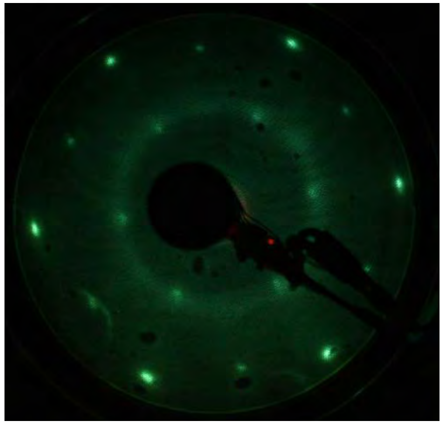
Monomeric VO_x

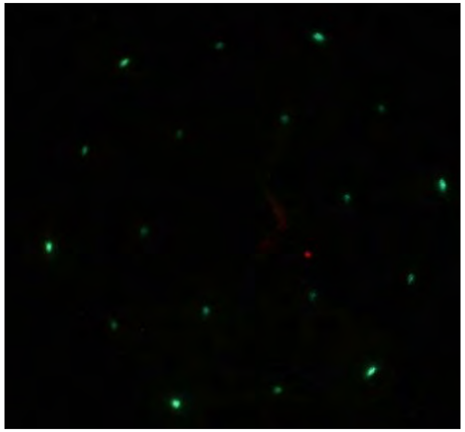












Teilprojekt B1 (Shaikhutdinov/Freund)