Recent activities in TP C6:

Adsorption, diffusion, and reaction at MoO_3 and V_2O_5 substrate

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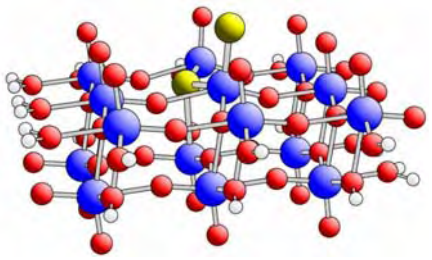
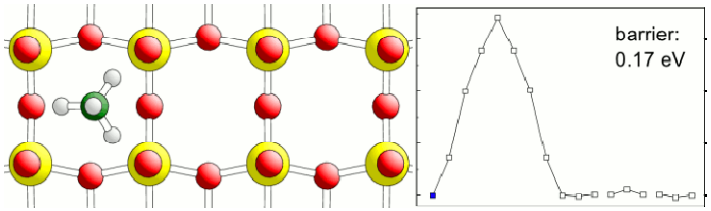
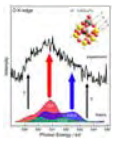






TP C6 Introduction

- **Personnel**

  - Matteo Cavalleri (Postdoc), NEXAFS
    → Wiley (phys. stat. solidi), since March 2009
  - Xuerong Shi (PhD student), adsorption, reactions
    → Key State Lab. of Coal Conversion, Taiyuan (PR China), since Jan. 2010
  - Mathis Gruber (IMPRS PhD student), adsorption, reaction, NEXAFS (learning), until 2011
  - Murat Mesta (PhD student), NEXAFS (starting), relativistic effects, until 2013
  - NN (Sfb 546 PostDoc), NEXAFS, searching since Jan. 2010

  Any suggestions? Please tell me quickly, time is running!

TP C6 Introduction

- **Subjects considered**

  - **Adsorption, diffusion, substitution, vacancies, spectroscopy**
  - **Extended substrates : V_2O_5, MoO_3, MoS_2, Mo_2C**
  - **Adsorbates : H, NH_x , CO, NO, H_2O, O, S**
  - **Small particles : V_xO_y, Mo_xO_y, (NEXAFS)**

- **Publications 2009 -2010**

  - **Refereed journals : 5 apprd., 1 in print, 1 submt., 1 in prep.**
  - **Proceedings : 1 apprd.**

Specific subjects

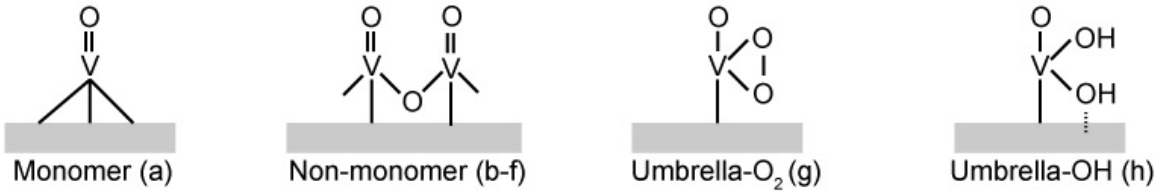
- **Discrimination between V_xO_y particles at SBA-15 SiO_2 using O 1s NEXAFS (collaboration with TP B2)**
  - **most recent: confirmation of theoretical spectra [1] , improved resolution in experiment [2]**

[1] M. Cavalleri et al., J. Catal. 262, 215 (2009).

[2] M. Häveckeret al., Phys. Stat. Solidi (b) 246, 1459 (2009).

O 1s NEXAFS for V_xO_y / SiO_2 , Introduction

- **Structure / type of reactive VO_x species at catalyst support, monomeric vs. non-monomeric VO_x**

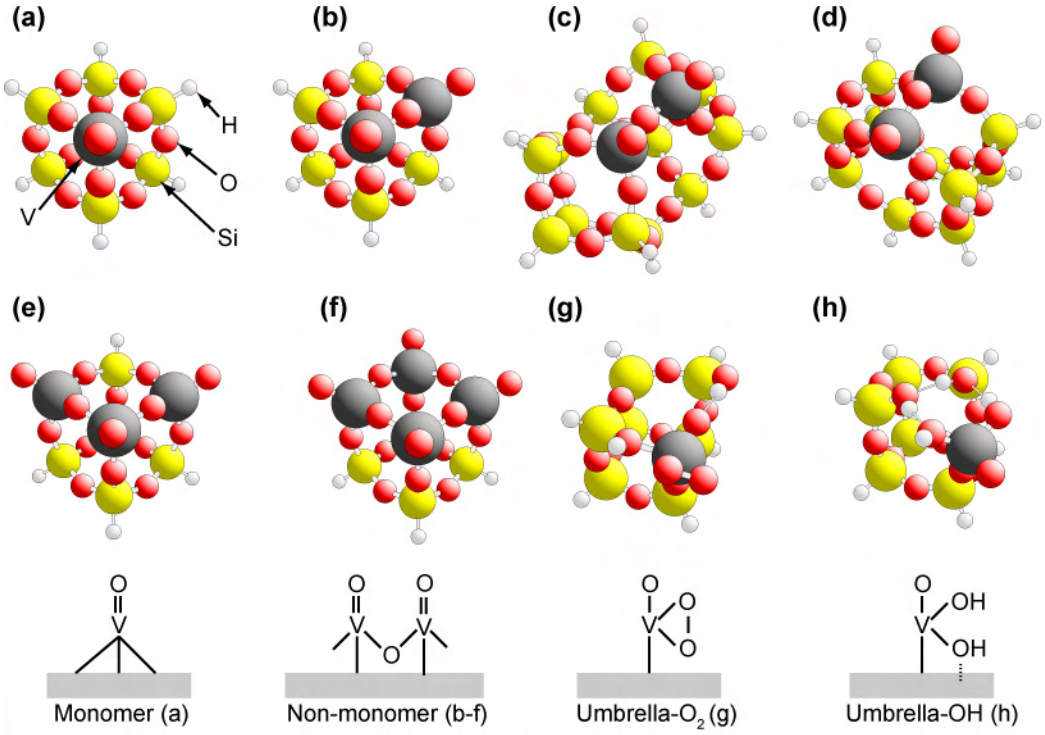


- **Model system (B2) :**
  - **small VO_x particles on SBA-15 SiO_2 support,**
  - **determine structural details of VO_x**
- **Analysis of different oxygen species inside VO_x and at support interface**
- **Discrimination of V=O, V-O-V, V-O-Si, Si-O-Si bonds in NEXAFS spectra**

O 1s NEXAFS for V_xO_y / SiO_2 , Theoretical Details

- **Model clusters**
  - from vibrational studies (A4) [1,2]
  - hydrogen termination at periphery
  - clusters $VSi_7O_{13}H_7$, $V_2Si_6O_{14}H_6$, …

- **Electronic structure**
  - DFT, GGA (RPBE) functional, StoBe
  - Slater's TP method for O 1s excitations
  - atom resolved NEXAFS spectra



[1] N. Magg et al., J. Catal. 226, 88 (2004)

[2] J. Döbler, M. Pritzsche, and J. Sauer, in preparation.

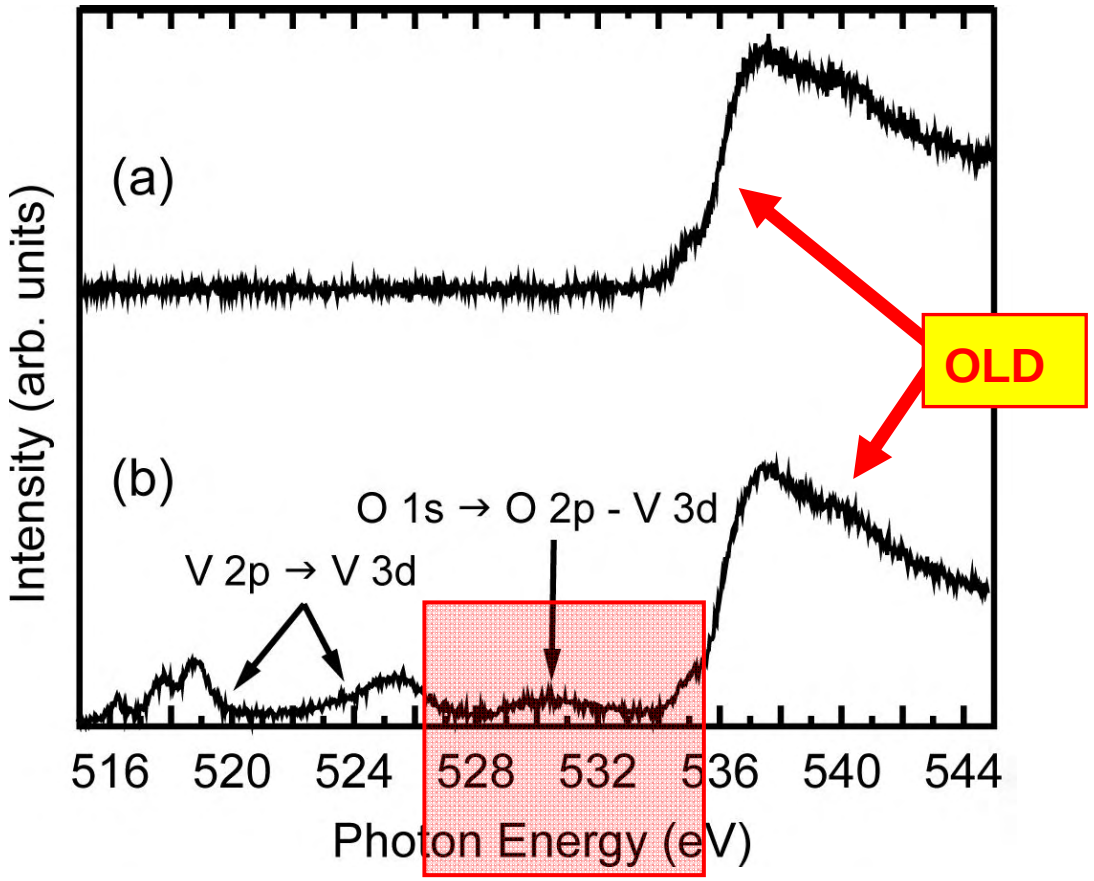
O 1s NEXAFS for V_xO_y / SiO_2 , Exp. NEXAFS Spectra [1]

- **NEXAFS measurements (B2 [1])**

  - **(a) clean SBA-15**
  - **(b) SBA-15 + V_xO_y (2.7% V weight loading)**

  Excitation regions

  - **V 2p → 3d**
  - **O 1s → O 2p – V 3d**

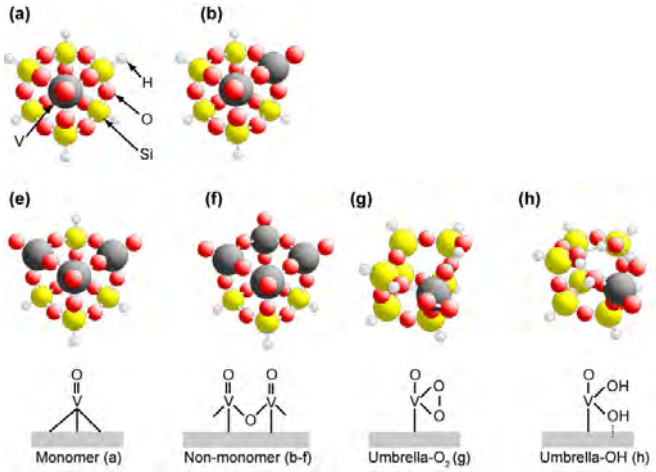


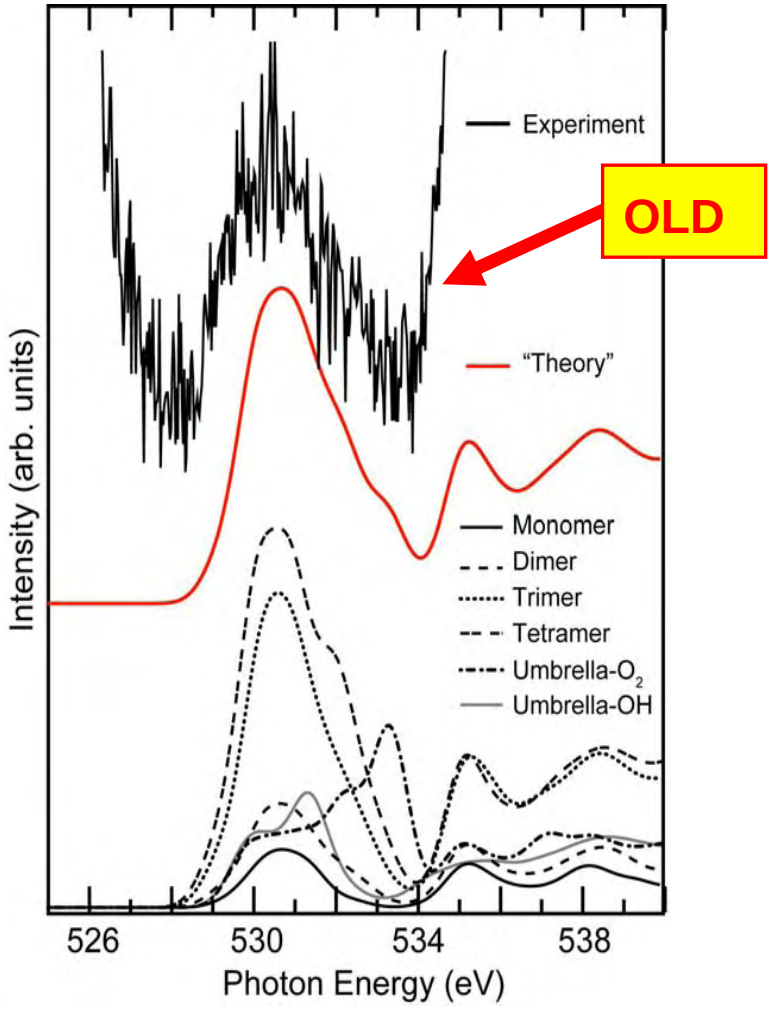
- **broad asymmetric oxygen peak at about 528 – 534 eV**

[1] M. Häveckeret al., Phys. Stat. Solidi (b) 246, 1459 (2009).

O 1s NEXAFS for V_xO_y / SiO_2 , Theory vs. Experiment [1, 2]

- **Comparison with experiment [1]**
  - all $V_xSi_yO_zH_w$ clusters considered , total NEXAFS spectra [2]
  - higher non-monomers, umbrella type V_xO_y contribute to peak asymmetry





- **non-monomeric V_xO_y must exist at SBA-15 surface**

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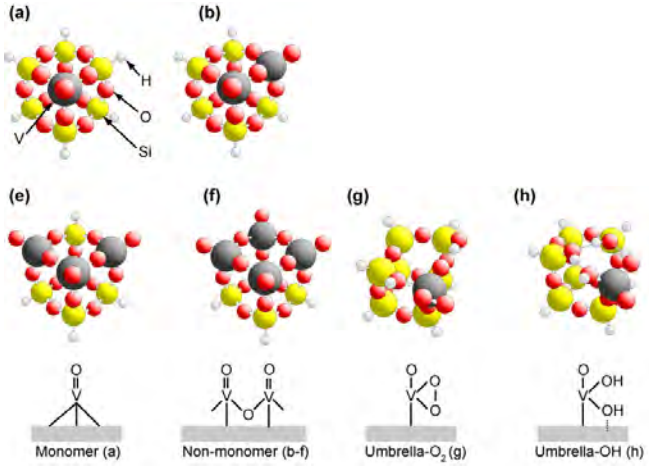

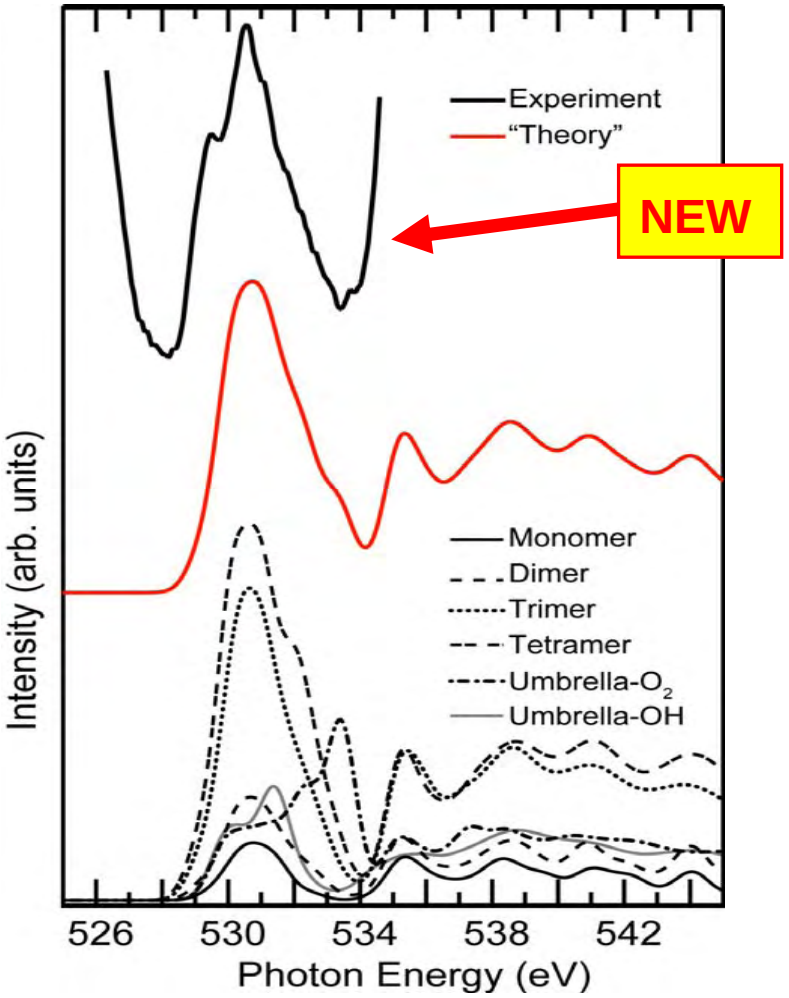

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Specific subjects

- NH_x (de)hydrogenation at $V_2O_5(010)$
  - NH_4 formation at OH groups (Bronstedt sites), NH_4 diffusion
  - NH_x binding at oxygen vacancies (Lewis sites)
  - H binding, diffusion,
  - surface OH + OH reaction to form H_2O + O , H_2O desorption

- Selective Catalytic reduction (SCR) of NO_x with NH_3
  - reaction schemes with OH groups (Bronstedt sites)
  - reaction schemes near oxygen vacancies (Lewis sites)

NH_x at $V_2O_5(010)$, Introduction

- Use of vanadia based catalysts in ammoxidation reactions

  example: selective catalytic reduction (SCR) of NO_x with NH_3

  $$4\ NH_3 + 4\ NO + O_2 \rightarrow 4\ N_2 + 6\ H_2O$$

  $$4\ NH_3 + 2\ NO_2 + O_2 \rightarrow 3\ N_2 + 6\ H_2O$$

- NH_x reactions (dehydrogenation, hydrogenation)

  $$NH_x \rightarrow NH_{x-1} + H_{ads} \quad , \quad x = 1 - 3$$

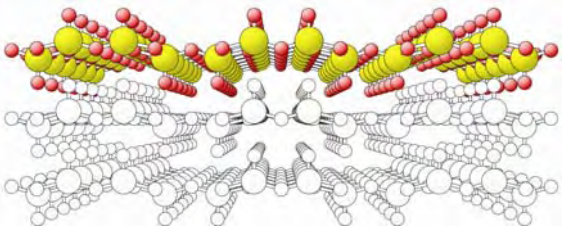
  $$NH_x + H_{ads} \rightarrow NH_{x+1}$$

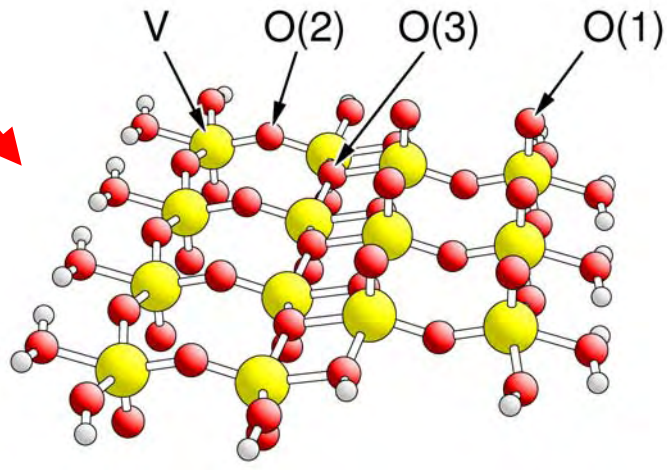
- Adsorption / desorption of NH_x, N, H

- Diffusion of NH_x, N, H at surface

NH_x at $V_2O_5(010)$, Theoretical Details

- **Substrate clusters for $V_2O_5(010)$**
  - 1- / 2-layer sections, start from exp. geometry
  - hydrogen termination at periphery (embedding)
  - clusters $V_{12}O_{40}H_{20}$, $V_{14}O_{42}H_{14}$, $V_{14}O_{46}H_{22}$, …
  - adsorbates added (H, NH_x, NO)
  - O removed from O(1-3) sites

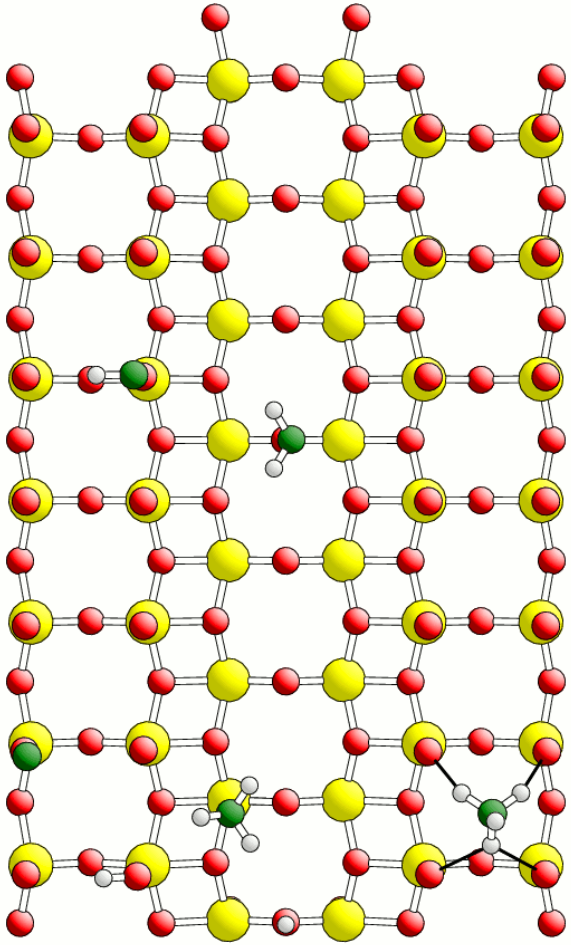




- **Electronic structure**
  - DFT, GGA (RPBE) functional, StoBe
  - equilibrium geometries
  - transition states, barriers (NEB)

NH_x at $V_2O_5(010)$, Adsorption sites, Energetics

- **Adsorption sites**



- **Adsorption energies E_{ads} [eV]**

  from total energy differences

	O(1)	O(2)	O(3)	V
H	-2.64	-2.79	-2.51	--
N	-1.54	-1.09	-0.49	--
NH	-0.95	-0.76	-0.06	--
NH_2	-0.46	-0.73	-0.16	-0.12
NH_3	-0.11	→ V	-0.18	-0.26
NH_4	-3.90	-3.57	-3.27	-3.37

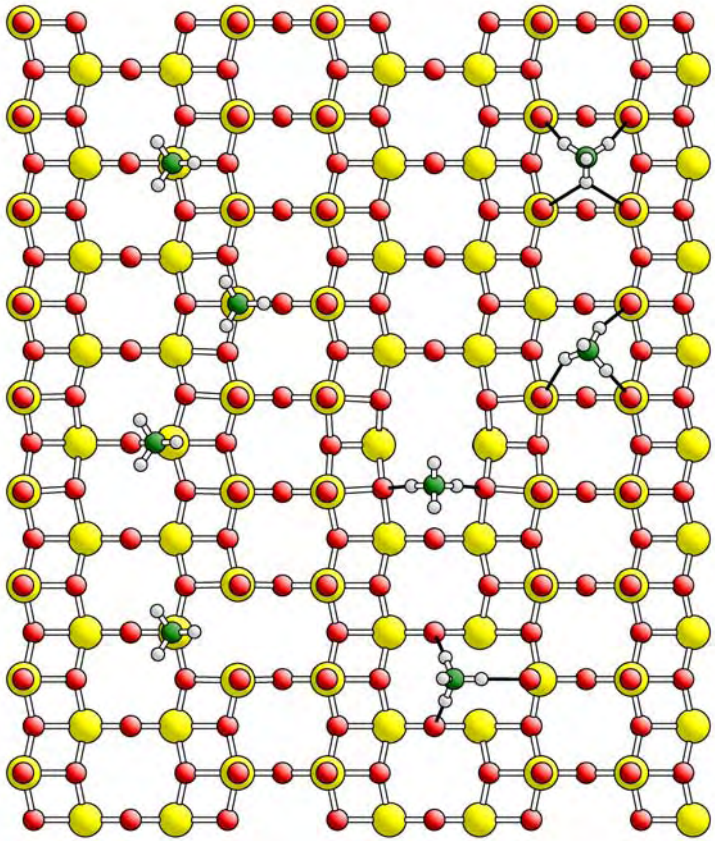
→ NH_3 bound quite weakly

→ NH_4, H bound quite strongly

NH_x at $V_2O_5(010)$, Adsorption sites, Energetics

- **Adsorption (vacancy) sites**

  NH_3, NH_4



- **Adsorption energies E_{ads} [eV]**

  from total energy differences

  vacancy clusters

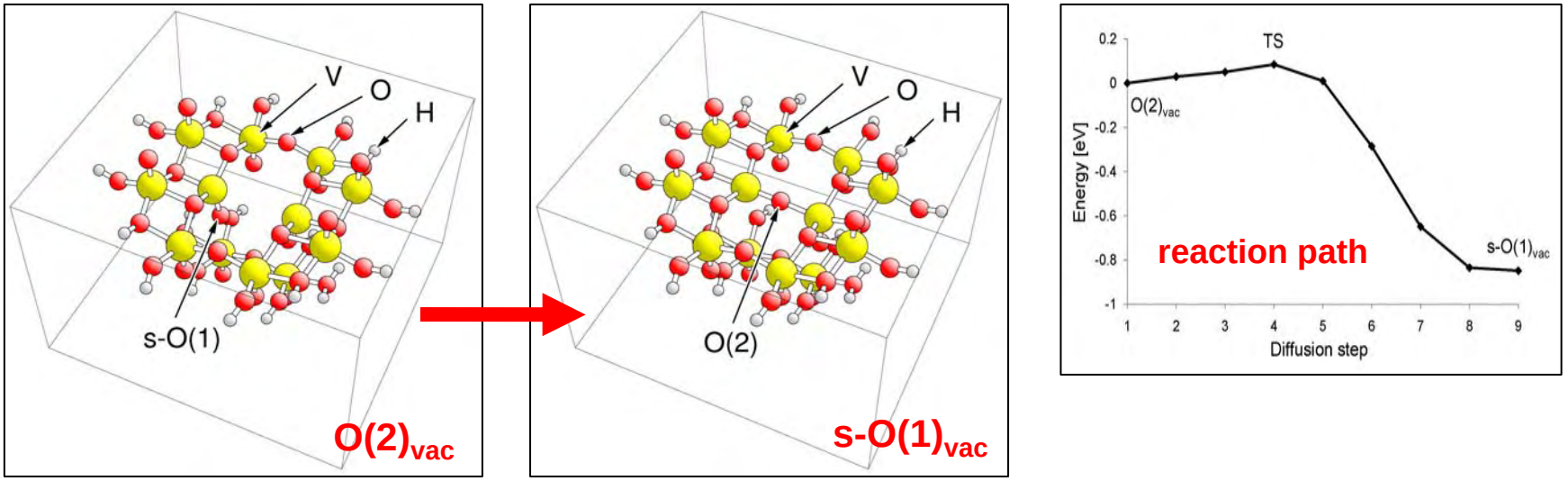
	$O(1)_{vac}$	$O(2)_{vac}$	$O(3)_{vac}$	$s\text{-}O(1)_{vac}$
H	-1.40	-2.60	-2.60	-2.10
N	-2.20	-4.10	-3.80	-2.70
NH	-3.20	-4.90	-4.60	-3.60
NH_2	-2.20	-3.90	-2.90	-2.80
NH_3	-0.90	→ $s\text{-}O(1)_{vac}$	-0.30	-1.20
NH_4	-3.30	-2.80	-3.30	-2.80

→ **Binding stronger near O vacancy**

→ **NH_3 bound near sub-surface $s\text{-}O(1)_{vac}$**

$V_2O_5(010)$, sub-surface oxygen vacancy

- **Vacancy exchange**



- **Diffusion process**

  oxygen :

  s-O(1) → O(2)

  O vacancies :

  $O(2)_{vac}$ → $s\text{-}O(1)_{vac}$

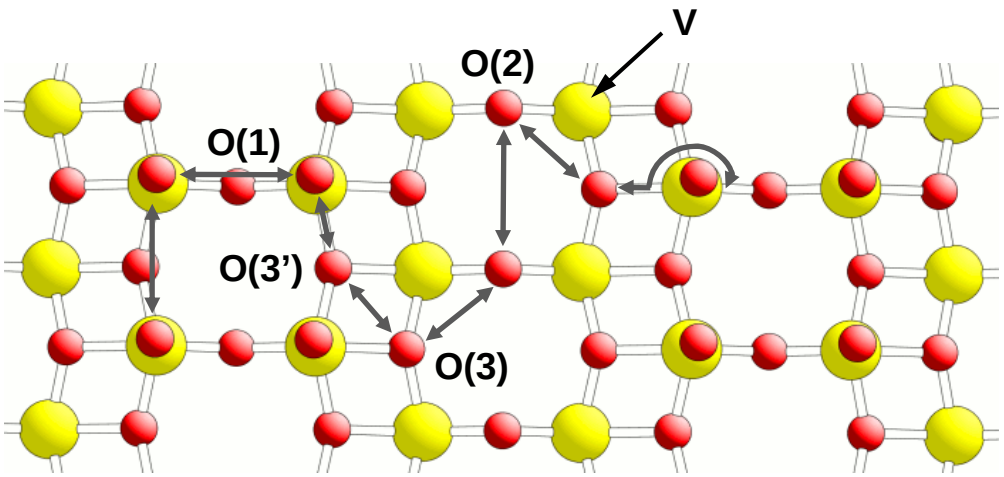
→ **$s\text{-}O(1)_{vac}$ more stable than $O(2)_{vac}$**

→ **small diffusion barrier, 0.1 eV**

→ **importance for reactions ?**

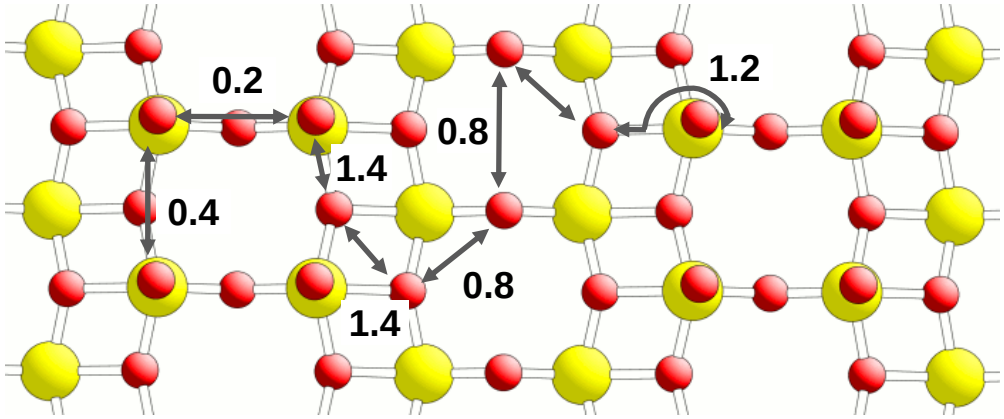
NH_x at $V_2O_5(010)$, Hydrogen diffusion

- Reactant **diffusion** at surface important for reaction, example hydrogen
- Diffusion **paths**, **barriers** from nudged elastic band (**NEB**) calculations
- H **hops** between O sites, **OH** "**diffusion**"



NH_x at V_2O_5(010) , Hydrogen diffusion

- Reactant diffusion at surface important for reaction, example hydrogen
- Diffusion paths, barriers from nudged elastic band (NEB) calculations
- H hops between O sites, OH "diffusion"



(Barriers in eV)

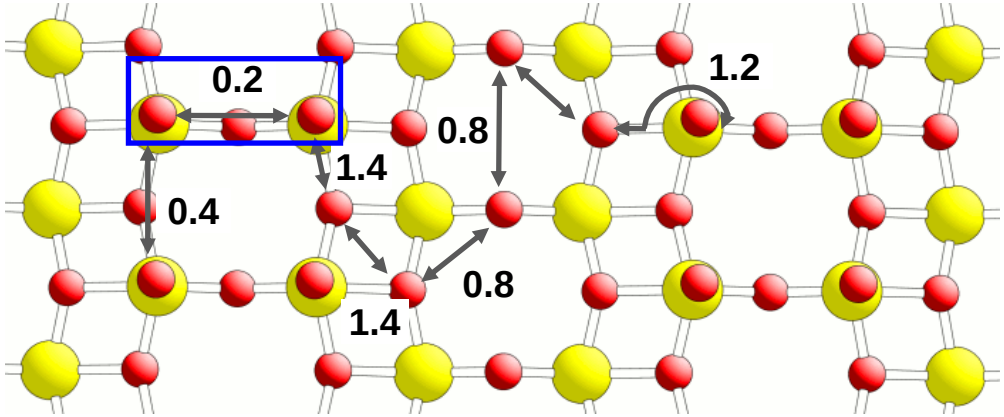
→ Low barriers :

O(1) / O(1) : 0.2 / 0.4 eV

O(2) / O(2) : 0.8 eV

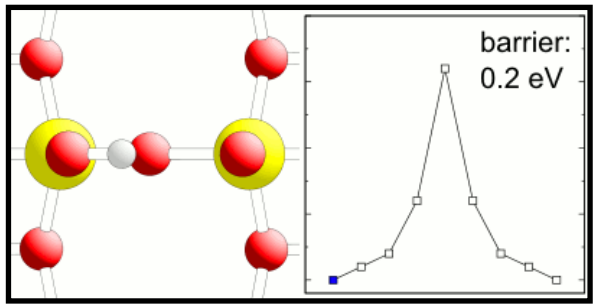
NH_x at V_2O_5(010) , Hydrogen diffusion

- Reactant **diffusion** at surface important for reaction, example hydrogen
- Diffusion **paths**, **barriers** from nudged elastic band (**NEB**) calculations
- H **hops** between O sites, **OH** "**diffusion**"



(Barriers in eV)

H diffusion O(1) / O(1)

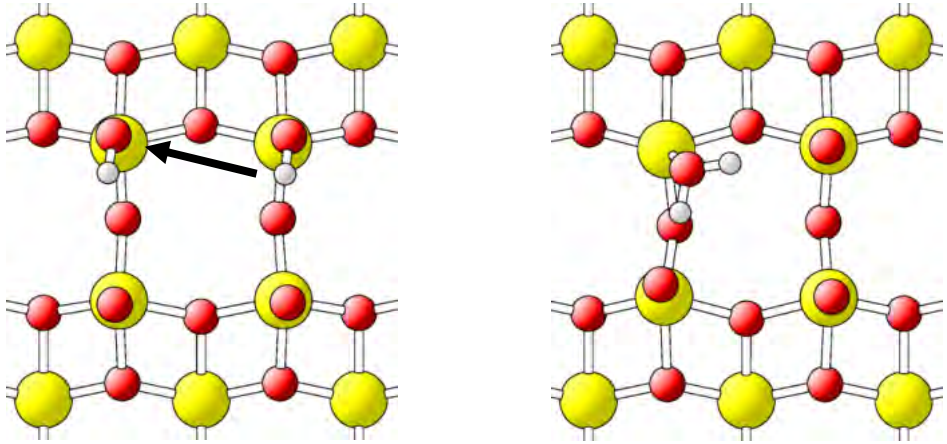


animation

→ Mobile oxygen facilitates O-H bond breaking / making

NH_x at $V_2O_5(010)$, Hydrogen reaction

- Hydrogen **diffusion** at surface may lead to adjacent surface OH
- **Reaction** of surface OH : V=OH + V=OH → V-H_2O + V=O
  Surface H_2O formed (barrier = 0.3 eV)
- Surface H_2O **weakly** bound (0.4 eV) → **easy** desorption
  oxygen vacancy filled by gas phase O_2



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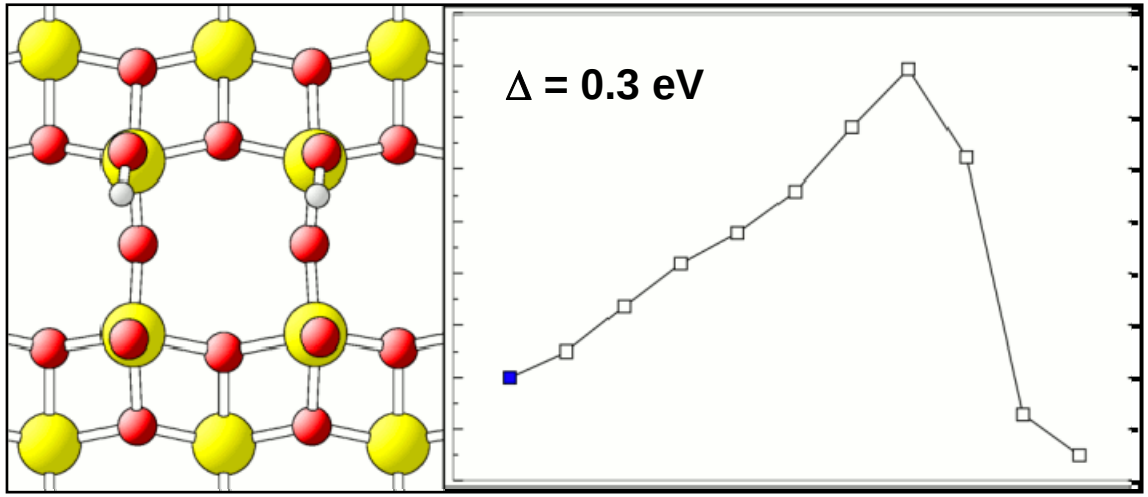


→ Mobile oxygen facilitates reaction

SCR of NO_x with NH_3 at V_2O_5(010)

- Use of vanadia based catalysts in ammoxidation reactions

  Selective Catalytic Reduction (SCR) of NO_x with NH_3

$$4\,NH_3 + 4\,NO + O_2 \rightarrow 4\,N_2 + 6\,H_2O$$

$$4\,NH_3 + 2\,NO_2 + O_2 \rightarrow 3\,N_2 + 6\,H_2O$$

- Reaction schemes near OH groups (Bronstedt sites) [1]
- Reaction schemes near oxygen vacancies (Lewis sites) [1]
- Initial testing steps, conclusive results → Schmöckwitz 2011

[1] S. Soyer, A. Uzun, S. Senkan , and I. Onal, Catal. Today ***118*** *(2006) 268.*

SCR of NO_x with NH_3 at V_2O_5(010)

$4\,NH_3 + 2\,NO_2 + O_2 \rightarrow 3\,N_2 + 6\,H_2O$

Scheme 1: NH_3 adsorbs near OH group, NH_4^+ formation [1]

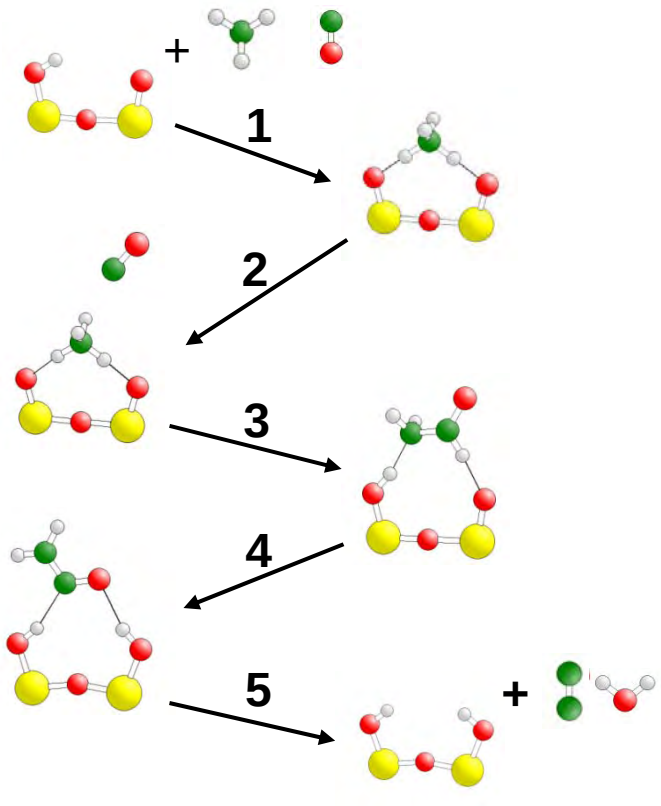
1: $V{=}OH + NH_3 + NO \rightarrow V{=}O\text{-}NH_4^+ + NO$

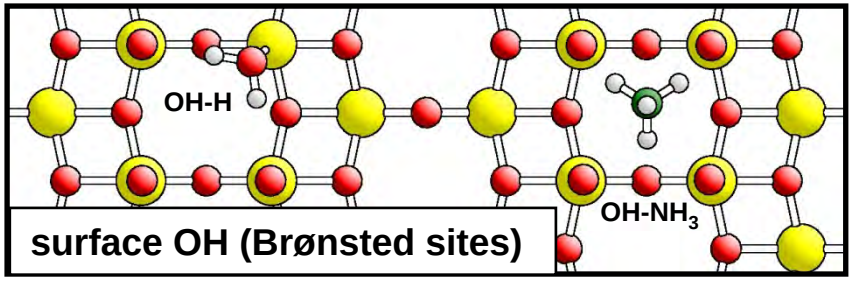
2: $V{=}O\text{-}NH_4^+ + NO \rightarrow V{=}O\text{-}NH_4^+\text{-}NO$

3: $V{=}O\text{-}NH_4^+\text{-}NO \rightarrow V{=}OH\text{-}NH_2NOH$

4: $V{=}OH\text{-}NH_2NOH \rightarrow 2 * V{=}OH\text{-}NH_2NO$

5: $2 * V{=}OH\text{-}NH_2NO \rightarrow V{=}OH + V{=}OH + N_2 + H_2O$





*[1] S. Soyer, A. Uzun, S. Senkan , and I. Onal, Catal. Today **118** (2006) 268.*

SCR of NO_x with NH_3 at V_2O_5(010)

$4\ NH_3 + 2\ NO_2 + O_2 \rightarrow 3\ N_2 + 6\ H_2O$

Scheme 2: NH_3 adsorbs near O(1) vacancy [1] (= reduced metal center, Lewis site)

1a: $V + NH_3 + NO \rightarrow V\text{-}NH_3 + NO$

2a: $V\text{-}NH_3 + NO \rightarrow V\text{-}NH_3\text{-}NO$

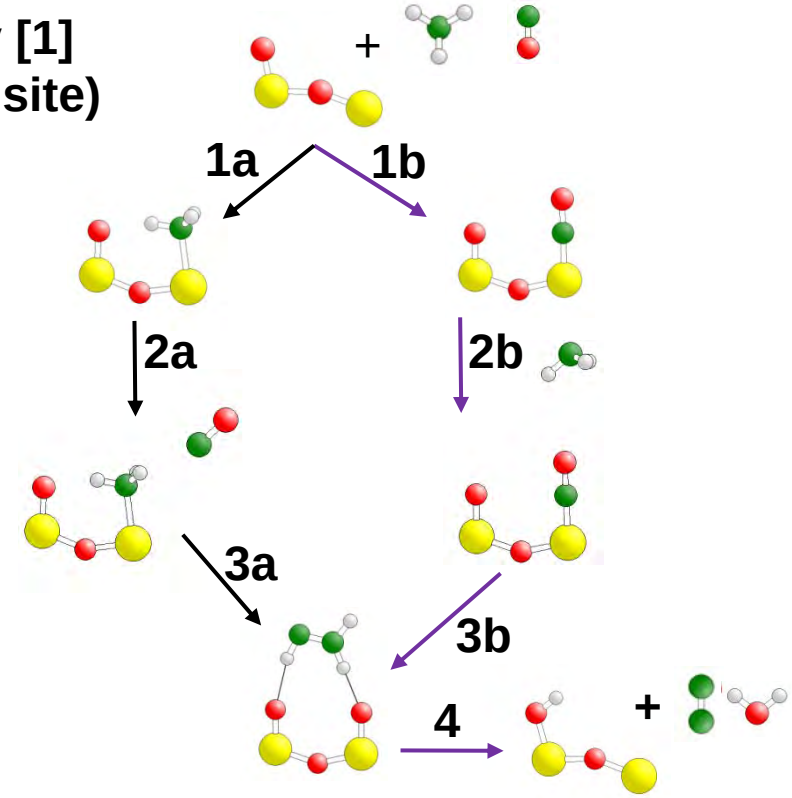
3a: $V\text{-}NH_3\text{-}NO \rightarrow V{=}O\text{-}NH_2NH$

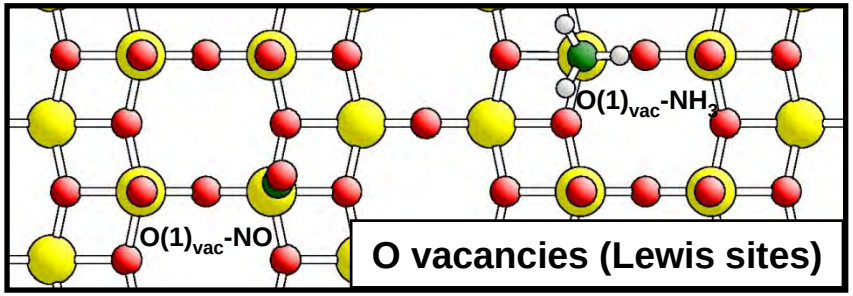
1b: $V + NH_3 + NO \rightarrow V\text{-}NO + NH_3$

2b: $V\text{-}NO + NH_3 \rightarrow V\text{-}NO\text{-}NH_3$

3b: $V\text{-}NO\text{-}NH_3 \rightarrow V{=}O\text{-}NH_2NH$

4: $V{=}O\text{-}NH_2NH \rightarrow V + V{=}OH + N_2 + H_2O$





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Other subjects

- $MoO_3(010)$ [1] (MoS_2 oxidation)
  - sulfidation vs. sulfur adsorption
  - importance of hydrogen

- Molecular vs. dissociative CO and NO adsorption at $Mo_2C(0001)$ [2])
  - preferred adsorption, sites and energetics

➡ Private discussions

[1] X. Shi, J. Wang und K. Hermann, J. Phys. Chem. C, (2010), in print.

[2] X. Shi, J. Wang und K. Hermann, J. Phys. Chem. C, (2010), submitted.