Recent activities in TP C6: Adsorption, diffusion, and reaction at MoO$_3$ and V$_2$O$_5$ 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$_2$O$_5$, MoO$_3$, MoS$_2$, Mo$_2$C
  - Adsorbates: H, NH$_x$, CO, NO, H$_2$O, O, S
  - Small particles: V$_x$O$_y$, Mo$_x$O$_y$, (NEXAFS)

- Publications 2009 -2010
  - Refereed journals: 5 apprd., 1 in print, 1 submt., 1 in prep.
  - Proceedings: 1 apprd.
Specific subjects

• **Discrimination** between $V_x O_y$ 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]

**O 1s NEXAFS for V$_x$O$_y$ / SiO$_2$, Introduction**

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

  ![Diagram showing different VO$_x$ configurations](image)

  - **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 $V_{Si_7}O_{13}H_7$, $V_{2Si_6}O_{14}H_6$, ...

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

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
- $V\,2p \rightarrow 3d$
- $O\,1s \rightarrow O\,2p - V\,3d$

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

Comparison with experiment [1]
- all \( V_xS_i_yO_zH_w \) clusters considered, total NEXAFS spectra [2]
- higher non-monomers, umbrella type \( V_xO_y \) contribute to peak asymmetry

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

non-monomeric \( V_xO_y \) must exist at SBA-15 surface

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

Specific subjects

• \( \text{NH}_x \) (de)hydrogenation at \( \text{V}_2\text{O}_5(010) \)
  - \( \text{NH}_4 \) formation at OH groups (Bronstedt sites), \( \text{NH}_4 \) diffusion
  - \( \text{NH}_x \) binding at oxygen vacancies (Lewis sites)
  - H binding, diffusion,
  - surface OH + OH reaction to form \( \text{H}_2\text{O} + \text{O} \), \( \text{H}_2\text{O} \) desorption

• Selective Catalytic reduction (SCR) of \( \text{NO}_x \) with \( \text{NH}_3 \)
  - reaction schemes with OH groups (Bronstedt sites)
  - reaction schemes near oxygen vacancies (Lewis sites)
**NH\textsubscript{x} at V\textsubscript{2}O\textsubscript{5}(010), Introduction**

- Use of vanadia based catalysts in **ammoxidation** reactions

  **example**: selective catalytic reduction (SCR) of NO\textsubscript{x} with NH\textsubscript{3}

  \[
  4 \text{NH}_3 + 4 \text{NO} + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O}
  \]

  \[
  4 \text{NH}_3 + 2 \text{NO}_2 + \text{O}_2 \rightarrow 3 \text{N}_2 + 6 \text{H}_2\text{O}
  \]

- **NH\textsubscript{x} reactions** (dehydrogenation, hydrogenation)

  \[
  \text{NH}_x \rightarrow \text{NH}_{x-1} + \text{H}_{\text{ads}}, \quad x = 1 - 3
  \]

  \[
  \text{NH}_x + \text{H}_{\text{ads}} \rightarrow \text{NH}_{x+1}
  \]

- **Adsorption / desorption** of NH\textsubscript{x}, N, H

- **Diffusion** of NH\textsubscript{x}, N, H at surface
Substrate clusters for $V_2O_5(010)$
- 1- / 2-layer sections, start from exp. geometry
- hydrogen termination at periphery (embedding)
- clusters $V_{12}O_{40}H_{20}, V_{14}O_{42}H_{14}, V_{14}O_{46}H_{22}, \ldots$
- 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\textsubscript{x} at V\textsubscript{2}O\textsubscript{5}(010), Adsorption sites, Energetics

- **Adsorption sites**

- **Adsorption energies** $E_{\text{ads}}$ [eV] from total energy differences

<table>
<thead>
<tr>
<th></th>
<th>O(1)</th>
<th>O(2)</th>
<th>O(3)</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-2.64</td>
<td>-2.79</td>
<td>-2.51</td>
<td>--</td>
</tr>
<tr>
<td>N</td>
<td>-1.54</td>
<td>-1.09</td>
<td>-0.49</td>
<td>--</td>
</tr>
<tr>
<td>NH</td>
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<td>-0.76</td>
<td>-0.06</td>
<td>--</td>
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<tr>
<td>NH\textsubscript{2}</td>
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<td>-0.73</td>
<td>-0.16</td>
<td>-0.12</td>
</tr>
<tr>
<td>NH\textsubscript{3}</td>
<td>-0.11</td>
<td>V</td>
<td>-0.18</td>
<td>-0.26</td>
</tr>
<tr>
<td>NH\textsubscript{4}</td>
<td>-3.90</td>
<td>-3.57</td>
<td>-3.27</td>
<td>-3.37</td>
</tr>
</tbody>
</table>

- $\text{NH}_3$ bound quite weakly
- $\text{NH}_4$, H bound quite strongly
**NH$_x$ at V$_2$O$_5$(010), Adsorption sites, Energetics**

- **Adsorption (vacancy) sites**
  - NH$_3$, NH$_4$

- **Adsorption energies $E_{ads}$ [eV]**
  from total energy differences
  vacancy clusters

<table>
<thead>
<tr>
<th></th>
<th>O(1)$_{vac}$</th>
<th>O(2)$_{vac}$</th>
<th>O(3)$_{vac}$</th>
<th>s-O(1)$_{vac}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-1.40</td>
<td>-2.60</td>
<td>-2.60</td>
<td>-2.10</td>
</tr>
<tr>
<td>N</td>
<td>-2.20</td>
<td>-4.10</td>
<td>-3.80</td>
<td>-2.70</td>
</tr>
<tr>
<td>NH</td>
<td>-3.20</td>
<td>-4.90</td>
<td>-4.60</td>
<td>-3.60</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>-2.20</td>
<td>-3.90</td>
<td>-2.90</td>
<td>-2.80</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>-0.90</td>
<td>s-O(1)$_{vac}$</td>
<td>-0.30</td>
<td>-1.20</td>
</tr>
<tr>
<td>NH$_4$</td>
<td>-3.30</td>
<td>-2.80</td>
<td>-3.30</td>
<td>-2.80</td>
</tr>
</tbody>
</table>

→ Binding *stronger* near O vacancy
→ NH$_3$ bound near sub-surface s-O(1)$_{vac}$
\( V_2O_5(010) \), sub-surface oxygen vacancy

- **Vacancy exchange**

- **Diffusion process**
  - Oxygen: \( s-O(1) \rightarrow O(2) \)
  - O vacancies: \( O(2)_{\text{vac}} \rightarrow s-O(1)_{\text{vac}} \)

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

  small diffusion barrier, 0.1 eV

  importance for reactions?
$\text{NH}_x$ 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\textsubscript{x} at V\textsubscript{2}O\textsubscript{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”

![Diagram of diffusion paths and barriers](image)

Low barriers:
- O(1) / O(1): 0.2 / 0.4 eV
- O(2) / O(2): 0.8 eV
NH$_x$ at V$_2$O$_5$(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”

Mobile oxygen facilitates O-H bond breaking / making
**NH\textsubscript{x} at V\textsubscript{2}O\textsubscript{5}(010), Hydrogen reaction**

- Hydrogen **diffusion** at surface may lead to adjacent surface OH
- **Reaction** of surface OH: \( V=OH + V=OH \rightarrow V-H_2O + V=O \)
  - Surface H\textsubscript{2}O formed (barrier = 0.3 eV)
- Surface H\textsubscript{2}O **weakly** bound (0.4 eV) \( \rightarrow \) **easy** desorption
  - Oxygen vacancy filled by gas phase O\textsubscript{2}
NH$_x$ at V$_2$O$_5$(010), Hydrogen reaction

- Hydrogen **diffusion** at surface may lead to adjacent surface OH

- **Reaction** of surface OH: $V=OH + V=OH \rightarrow V-H_2O + V=O$
  
  Surface H$_2$O formed (barrier = 0.3 eV)

- Surface H$_2$O **weakly** bound (0.4 eV) $\rightarrow$ easy desorption

  oxygen vacancy filled by gas phase O$_2$
SCR of $\text{NO}_x$ with $\text{NH}_3$ at $\text{V}_2\text{O}_5(010)$

- Use of vanadia based catalysts in **ammonoxidation** reactions

Selective Catalytic Reduction (**SCR**) of $\text{NO}_x$ with $\text{NH}_3$

\[
4 \text{NH}_3 + 4 \text{NO} + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O}
\]

\[
4 \text{NH}_3 + 2 \text{NO}_2 + \text{O}_2 \rightarrow 3 \text{N}_2 + 6 \text{H}_2\text{O}
\]

- **Reaction** schemes near $\text{OH}$ groups (**Bronstedt** sites) [1]

- **Reaction** schemes near oxygen **vacancies** (**Lewis** sites) [1]

- **Initial testing steps, conclusive results** \(\rightarrow\) Schmöckwitz 2011

**SCR of NO\textsubscript{x} with NH\textsubscript{3} at V\textsubscript{2}O\textsubscript{5}(010)**

\[ 4 \text{NH}_3 + 2 \text{NO}_2 + \text{O}_2 \rightarrow 3 \text{N}_2 + 6 \text{H}_2\text{O} \]

**Scheme 1:** NH\textsubscript{3} adsorbs near OH group, NH\textsubscript{4}\textsuperscript{+} formation [1]

1: \( \text{V}=\text{OH} + \text{NH}_3 + \text{NO} \rightarrow \text{V}=\text{O-NH}_4^+ + \text{NO} \)

2: \( \text{V}=\text{O-NH}_4^+ + \text{NO} \rightarrow \text{V}=\text{O-NH}_4^+\text{-NO} \)

3: \( \text{V}=\text{O-NH}_4^+\text{-NO} \rightarrow \text{V}=\text{OH-NH}_2\text{NOH} \)

4: \( \text{V}=\text{OH-NH}_2\text{NOH} \rightarrow 2 \times \text{V}=\text{OH-NH}_2\text{NO} \)

5: \( 2 \times \text{V}=\text{OH-NH}_2\text{NO} \rightarrow \text{V}=\text{OH} + \text{V}=\text{OH} + \text{N}_2 + \text{H}_2\text{O} \)

**SCR of NO\textsubscript{x} with NH\textsubscript{3} at V\textsubscript{2}O\textsubscript{5}(010)**

\[ 4 \text{NH}_3 + 2 \text{NO}_2 + \text{O}_2 \rightarrow 3 \text{N}_2 + 6 \text{H}_2\text{O} \]

**Scheme 2:** NH\textsubscript{3} adsorbs near O(1) vacancy [1]

(= reduced metal center, Lewis site)

1a: V + NH\textsubscript{3} + NO \rightarrow V-NH\textsubscript{3} + NO

2a: V-NH\textsubscript{3} + NO \rightarrow V-NH\textsubscript{3}-NO

3a: V-NH\textsubscript{3}-NO \rightarrow V=O-NH\textsubscript{2}NH

1b: V + NH\textsubscript{3} + NO \rightarrow V-NO + NH\textsubscript{3}

2b: V-NO + NH\textsubscript{3} \rightarrow V-NO-NH\textsubscript{3}

3b: V-NO-NH\textsubscript{3} \rightarrow V=O-NH\textsubscript{2}NH

4: V=O-NH\textsubscript{2}NH \rightarrow V + V=OH + N\textsubscript{2} + H\textsubscript{2}O

Other subjects

• \( \text{MoO}_3(010) \) [1] (MoS$_2$ oxidation)
  - sulfidation vs. sulfur adsorption
  - importance of hydrogen

• Molecular vs. dissociative CO and NO adsorption at \( \text{Mo}_2\text{C}(0001) \) [2]
  - preferred adsorption, sites and energetics

→ Private discussions
