Conductivity of supported VO$_x$ catalysts:

Impedance spectroscopy, oxygen vacancy formation enthalpy and correlation to catalytic properties

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B6 C. Carrero (Catalytic Testing)
C11 R. Mitdank (Oxidation State of V$_x$O$_y$)
Overview

SFB 4th period:

Poly B,

**Redox state**
XRD, SEM, TEM (B2), RBS (C11)
ASAXS (HZB)

**Volume Properties**
thermal (XRD)
mechanical
electrical (impedance, DC, RBS, UV-Vis, XRD, microscopy)

1. Introduction
2. Impedance spectroscopy
3. Results
   1. Determination of $\Delta H_f$
   2. Oxygen vacancies and catalytic properties
4. Conclusion and Outlook
Percolation needed for Conductivity via VxOy?

Support
Assumed
non conducting

Poly B
B2, amorphous on SBA

B6 amorphous,
Dinse
TiO2, SiO2, alpha, kappa Al2O3, CeO2, ZrO2

B7, crystalline

Crystals

Single Sites

Polymers

O
V

O
O

-V-O-V-

O1
O2
O3
1. Introduction

\[ \Delta H_{f,O} \leftrightarrow E_{a,\text{propane}} \leftrightarrow X_{\text{propane}} \]

- **gas**
  - \( \text{CH}_3\text{-CH}_2\text{-CH}_3 \)
  - \( \text{CH}_2=\text{CH-CH}_3 \)
  - \( \text{H}_2\text{O} \)
- **surface**
  - \( \text{O M O M} \)
  - \( \text{2e}^- \)
  - \( \text{MO M O} \)
- **catalyst**
  - \( \text{MO M O} \)
  - \( \text{O}_2 \)
- **bulk**

The diagram illustrates the reaction and energy changes involved in the conversion of propane to other compounds, showing the roles of gas, surface, catalyst, and bulk in the process.
2. Impedance Spectroscopy - Setup

Frequency Generator and Analyzer:

- **Frequency range**: 10 µHz to 3 MHz
- **AC-amplitude range**: 1 mV to 1 V
- **Impedance range**: 1 mOhm to 1G Ohm (± 2%)
DC experiments exhibit often polarization effects

AC methods give possibility to determine influences on overall conductivity

Apply an electrical stimulus and observe the response (current or voltage)

Different mechanisms show different time relaxation times $\tau$ and can therefore be resolved

- polarization
- electrode reaction
- different charge carriers
- bulk / grain boundary mechanism

2. Impedance Spectroscopy - Method

Different regions of sample characterized by R and C often placed in parallel characteristic relaxation time of each RC element given by product of R and C

\[ \tau = RC \]

\[ \omega_{\text{max}} RC = 1 \]

Frequency scan resolves the different relaxation times:
Distribution of relaxation time. B: bulk, GB grain boundary

John T. S. Irvine et al., Advanced Materials 2 (1990) 132
2. Impedance Spectroscopy - Method

\[(R_1C_1)_p - (R_2C_2)_p\]

Data + model \rightarrow Results for \(R_1, C_1, R_2, C_2\)

CNRLS fit
3. Results - Determination of $\Delta H_f$

\[ 2V^x + O^x_O \xrightarrow{\text{reduction}} 2V^' + \cup^* + \frac{1}{2}O_2 \]

\[ [V^'V] = (2K)^{\frac{1}{3}} \cdot P_{O_2}^{-\frac{1}{6}} \]

\[ \sigma = K_2 \cdot \exp\left(-\left(\frac{\Delta H_f^0}{3kT} + \frac{\Delta E_m}{kT}\right)\right) \cdot P_{O_2}^{-\frac{1}{6}} \]

\[ \Delta E^* = \frac{\Delta H_f^0}{3} + \Delta E \]

\[ \Delta H_f^0 = 1.23 \pm 0.03 \text{ eV} = 119 \pm 3 \text{ kJmol}^{-1} \]

Reduction: $V_2O_5$ in oxygen
HT XRD
UV-vis
RBS

M. Harth et al., IJMR (2010) submitted
3. Results - Determination of $\Delta H_f$

\[ 2V^x + O^x_O \xrightarrow{\text{reduction}} 2V^x + \text{\textit{U}O} + 1/2 O_2 \]

\[ [V^x] = (2K)^{1/3} \cdot P^{-7/6}_{O_2} \]

\[ \sigma = K_2 \cdot \exp\left(-\left(\Delta H_f^0 / 3kT + \Delta E_m / kT\right)\right) \cdot P^{-7/6}_{O_2} \]

\[ \Delta E^* = \Delta H_f^0 / 3 + \Delta E \]

\[ \Delta H_f^0 = 1.23 \pm 0.03 \text{ eV} = 119 \pm 3 \text{ kJmol}^{-1} \]

Reduction: $V_2O_5$ in oxygen

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3. Supported Catalysts: Conductivity and Propane Conversion

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<th>$T_s$</th>
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<td>$V_2O_5$</td>
<td>690 °C</td>
<td>369 °C</td>
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Surface diffusion
~ $\frac{1}{2} T_s$ (K)

Volume diffusion
~ $\frac{2}{3} T_s$ (K)
3. Supported Catalysts: Conductivity and Propane Conversion

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3. Supported Catalysts: Conductivity and Propane Conversion

Si70V30, O2

![Graph showing conductivity and propane conversion vs. temperature]
3. Supported Catalysts: Conductivity and Propane Conversion

\[ \ln \sigma \] vs. \[ T \text{ [°C]} \]

\[ X(C_3H_8) \text{ [%]} \]

Zr70V30, O2

Supported Catalysts: Conductivity and Propane Conversion
3. Supported Catalysts: Conductivity and Propane Conversion

AI70V30, O2

![Graph showing conductivity and propane conversion](image)
3. Supported Catalysts: Conductivity and Propane Conversion

Ti70V30, O2

Ti70V30 different activation energy at high temperature:
Phase transitions to rutile
3. Supported Catalysts: Conductivity and Propane Conversion

Mg70V30 starts to transform into different spinel phases
3. Supported Catalysts: Correlation to Catalytic Properties

![Graph showing the correlation between catalysts and catalytic properties.

- Bars represent ΔH_B [kJ mol⁻¹] for various catalysts.
- Error bars indicate the uncertainty.
- Catalysts include Ti70V30, Zr70V30, Si70V30, V100, y-Al70V30, Mg70V30, and a-Al70V30.

- ΔH_B values range from 0 to 350 [kJ mol⁻¹].
- E_a,propane values range from 0 to 350 [kJ mol⁻¹].]
3. Supported Catalysts: Correlation to Catalytic Properties

![Graph showing the correlation between catalysts and catalytic properties with data from T. Allersma et al., J. Chem. Phys. 46 (1967) 154]
3. Supported Catalysts: Correlation to Catalytic Properties

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Catalytic testing in cooperation with B6
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Catalytic testing in cooperation with B6
3. Supported Catalysts: Correlation to Catalytic Properties

![Graph showing phase transitions and activation energies for different catalysts.]

3. Supported Catalysts: Correlation to Catalytic Properties

preliminary results: y-Al70V30

\[ \ln \sigma = 1.08 \pm 0.03 \text{ eV} \]
3. Supported Catalysts: Correlation to Catalytic Properties

Preliminary results: y-Al70V30
3. Supported Catalysts: Correlation to Catalytic Properties

Preliminary results: y-Al70V30

- \( \ln \sigma \) vs. \( T \) [°C]

- \( \text{O}_2 \)
- \( \text{N}_2 \) heating

1,08 ± 0,03 eV
3. Supported Catalysts: Correlation to Catalytic Properties

\[ \Delta H_f, O \leftrightarrow E_{a, propane} \]
4. Conclusion and outlook

Correlation looks promising but certain improvements necessary

- sample influence
  - phase transition → sample treatment
  - homogeneity → new preparation method
  - lower loading for stronger support effect

- other steps in catalytic reaction, like H-transfer
  - kinetic studies on conductivity samples

- in-situ experiments necessary
  - set-up constructed
  - experiments this year
4. Conclusion and outlook

Sample holder

Heated gas outlet
Metal shielding
Small sample chamber

electrodes

furnace
4. Conclusion and outlook

- Processing
  - Material
    - Real Micro Structure
      - Redox State
      - Wetting, Distribution
    - Reaction Condition
      - Electrical Properties
        - ΔE
        - ΔH
    - Catalytic Properties
Thank you for your attention
<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta H_B$ [kJ/mol]</th>
<th>$\Delta H_B$ [eV]</th>
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<tbody>
<tr>
<td>Ti70V30</td>
<td>53 ± 6</td>
<td>0,55 ± 0,06</td>
</tr>
<tr>
<td>Zr70V30</td>
<td>82 ± 9</td>
<td>0,85 ± 0,1</td>
</tr>
<tr>
<td>Si70V30</td>
<td>107 ± 7</td>
<td>1,11 ± 0,08</td>
</tr>
<tr>
<td>V100</td>
<td>119 ± 4</td>
<td>1,23 ± 0,04</td>
</tr>
<tr>
<td>y-Al70V30</td>
<td>138</td>
<td>1,43</td>
</tr>
<tr>
<td>Mg70V30</td>
<td>156 ± 9</td>
<td>1,62 ± 0,09</td>
</tr>
<tr>
<td>a-Al70V30</td>
<td>287 ± 34</td>
<td>3,00 ± 0,4</td>
</tr>
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