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

Christian Hess

Dept. Inorganic Chemistry, Fritz Haber Institute, Berlin
• 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

\[
\begin{align*}
\text{propene} & \quad 350 \pm 50^\circ C \quad + O_2 \quad - H_2O \\
\text{acrolein} & \quad 270^\circ C \quad + \frac{1}{2} O_2 \\
\text{acrylic acid} & \quad Y \leq 87\%
\end{align*}
\]

Mo-Bi-O\textsubscript{x} \quad \text{Mo-V-W-O\textsubscript{x}} \quad \text{high costs: (US$ 420/t)}

Alternative process: Direct oxidation of propane

\[
\begin{align*}
\text{propane} & \quad 400^\circ C \quad + 2 O_2 \quad - 2 H_2O \\
\text{acrylic acid} & \quad Y \approx 50\%
\end{align*}
\]

Mo\textsubscript{0.1-V0.3-Te0.23-Nb0.125O\textsubscript{x}} \quad \text{low costs: (US$ 200/t)}

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

• 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
Synthesis of vanadia supported on silica SBA-15

\[ \text{Si-OH} \rightarrow \text{functionalization} \rightarrow \text{ion exchange} \rightarrow \text{calcination} \rightarrow \text{Novel method to anchor TM oxides on mesoporous supports} \]

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

Visible Raman characterization of $V_xO_y$/SBA-15

Raman allows for sensitive detection of $V=O$ in crystalline $V_2O_5$
DRIFTS characterization during synthesis

C-H bending vibrations

90% KBr, 15 min

$\Rightarrow$ DRIFTS data demonstrates the presence of Si-propyl chain

C1s XP spectra during synthesis of $V_xO_y$/SBA-15

Detailed information on framework structure

⇒ Detailed information on framework structure


N1s XP spectra during synthesis of $V_xO_y$/SBA-15

APTMS-SBA-15

Quantitative surface composition of intermediates

$\text{NH}_3^+$

$\text{NH}_2$

$\text{Si}(-\text{O})_{3}$

$\text{Si}(-\text{O})_{3}$

$\text{Si}(-\text{O})_{3}$

$\text{Si}(-\text{O})_{3}$

$\text{Si}(-\text{O})_{3}$

$\text{Si}(-\text{O})_{3}$

Quantitative surface composition of intermediates

$\frac{\text{C(C-C)}}{\text{N}} = 3.07$

$\Rightarrow$ no C impurity!
• 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

$C_3H_8/O_2/N_2 = 2.8/6.3/90.0$

- Conversion of propane (%)
- Selectivity for propene (%)

$C_3H_8 \rightarrow H_2C=CH-CH_3$

3 wt% V/SBA-15

500°C
### Selective oxidation of propane: Effect of steam

C\(_3\)H\(_8\) → H\(_2\)C=CH-COOH

\(\text{CO}_x\) (degradation products)

1200 h\(^{-1}\), 0.5 ml, C\(_3\)H\(_8\)/O\(_2\)/N\(_2\)/H\(_2\)O = 2.8/6.3/50.8/40

<table>
<thead>
<tr>
<th>400°C</th>
<th>C(_3)H(_8) Conversion (%)</th>
<th>Time on stream (min)</th>
<th>Selectivity (%) AA</th>
<th>C(_3)H(_6)</th>
<th>AcetAc</th>
<th>CO(_x)</th>
<th>Yield of AA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>0</td>
<td>165</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3.3 wt% V/SBA-15</td>
<td>8</td>
<td>165</td>
<td>84</td>
<td>10</td>
<td>2</td>
<td>4</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>345</td>
<td>86</td>
<td>13</td>
<td>1</td>
<td>0</td>
<td>4.5</td>
</tr>
</tbody>
</table>

⇒ Highly dispersed vanadia shows high selectivity towards AA

Selective oxidation of propane over $V_xO_y$/SBA-15

Mesoporous structure is largely conserved!

\[ A = 491 \text{ m}^2/\text{g} \]

\[ A = 288 \text{ m}^2/\text{g} \]
• 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
dehydrated

\[ \text{V}_2\text{O}_5 \cdot 1.2\ \text{H}_2\text{O} \]

\[ \text{OH} \]

\[ \text{O} \]

\[ \text{Si} \]

\[ \text{O} \]

\[ \text{Si} \]

\[ \text{O} \]

\[ \text{Si} \]

\[ \Rightarrow \text{Dehydration dramatically changes surface vanadia structure} \]

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

2.7 wt% V (0.7 V/nm$^2$)

$\Rightarrow$ Bridged nitrates imply presence of dimeric/polymeric vanadia

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

$\Rightarrow$ XPS reveals strong positive BE shift for silica supported $V_xO_y$
Effect of water on dispersion of $V_xO_y$/SBA-15

**V loading in V$_x$O$_y$/SBA-15: XPS vs. bulk**

- **Graph**: A graph showing the correlation between V/Si (XPS) and V/Si (ICP) for dehydrated and hydrated V$_x$O$_y$/SBA-15 samples. The presence of V$_2$O$_5$ is indicated.

- **Legend**:
  - Red circles: dehydrated samples.
  - Blue circles: hydrated samples.

**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**

- **In situ UV-Vis (fibre)**
  - Outlet gas
  - Sample, surface (8x12 mm²)
  - Inlet gas

- **In situ Raman (fibre)**
  - 488/514/632 nm
  - 1 bar, flow ~40 ml/min

- **Furnace**

**Modified ESCA setup – quasi in situ XPS**
Direct correlation of structure and dispersion

**UV-Vis**

- V$_2$O$_5$/SBA-15: 0.8 V/nm$^2$
- 350°C
- RT O$_2$/He

**XPS**

- Binding Energy (eV)
- V$_2$P$_{3/2}$

**Raman**

- Wavelength (nm)
- Absorbance
- Raman shift (cm$^{-1}$)
- Raman intensity

Other model approaches: $V_xO_y$/SBA-15/SiO$_2$/Si

Order microrods of silica SBA-15 using Si templates

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

Fritz Haber Institute, Berlin:
Rita Herbert
Ute Wild
Dr. Ceco Venkov
Dr. Friederike Jentoft
Members of the Department of Inorganic Chemistry
Prof. Dr. Robert Schlögl

Combicat, Kuala Lumpur:
Dr. Ming Hoong Looi

MPI of Microstructure Physics, Halle:
Dr. Xin Chen
Dr. Martin Steinhart