B2/B6: VxOy (TixOy) in SBA 15:

Synthesis
Structure
ODH of propane
Who did the work

Reactivity group:  A. Trunschke
    G. Tzolova-Müller
    J. Kröhnert
    T. Wolfram
    B. Frank

G. Weinberg & W. Zhang, A. Klein-Hoffmann
G. Lorenz & M. Hashagen & D. Brennecke
F. Girgsdies & E. Kitzelmann
M. Haevecker

R. Schlögl

• **FU**: K. Dinse

• **TU**: Schomäcker group:
  A. Dinse, C. Carrero
Targets

• Synthesize families of title catalysts in reproducible and large quantities.
• Characterize geometric and electronic structures.
• Share with K. Dinse for in-depth electronic structure analysis by EPR.
• Share with R. Schomäcker for kinetic testing.
• Compare with other systems in C3 ODH.
• Identify generic data for comparison with theory.
<table>
<thead>
<tr>
<th>sample</th>
<th>% wt Ti/V set</th>
<th>% wt Ti from EDX / XRF</th>
<th>% wt Ti from EDX / XRF</th>
<th>BET surface / m²/g (16.2nm²/N₂)</th>
<th>S(micropore) [m²/g]</th>
<th>XRD</th>
<th>S(micro)/S(BET)</th>
<th>DFT (equ.) pore size d₀ [nm]</th>
<th>a₀ [nm]</th>
<th>wall thickness [nm]</th>
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<td>0/0</td>
<td>0/0</td>
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<td>“3.4“/ 3.45</td>
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<td>10.97</td>
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<td>10.96</td>
<td>3.65</td>
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<td>3/4</td>
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<td>3.9</td>
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<td>10.94</td>
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<td>3.6</td>
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<td>13.0</td>
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<td>39</td>
<td>Peak 22.6°</td>
<td>“19.5%”</td>
<td>Macro pore</td>
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</table>
Structural integrity
Vanadía localiza preferentemente en microporos
Titania localiza en partes massivas de las paredes
V en Ti localiza substancialmente en Ti
Integridad del sistema de poros mantenida
Crystallización de oxídeos fácilmente detectada (no mostrada)
OH groups and acid-base chemistry

V reacts with all OH groups available (micropores!)

Ti adds more OH groups to the system

Metal loading creates acidity.
Ti-bonded OH weakly acidic.
V-bonded OH strongly acidic.
Structure and the metal species

Titania forms tetrahedral distorted species at all loadings (NEXAFS).
Vanadia oligomerizes with increasing loading to a mixture of species (NEXAFS, K.Hermann).
The combination of V+Ti suppresses the structural dynamics of V and leads to mixed oligomers.
Structure of the metal species

77 K, 0.04 mbar

Hadjijanov, Applied Catalysis A: General 188 (1999) 355-360

Anchoring of V on Ti but no coverage: Non-planar arrangement, micropore location of V.

SBA-15, #7495, 0.044 mbar
8Ti/SBA-15, #7622, 0.044 mbar
4V/8Ti/SBA-15, #7624, 0.040 mbar
4V/3Ti/SBA-15, #7620, 0.041 mbar
0.8V/3Ti/SBA-15, #7606, 0.047 mbar
4V/SBA-15, #7815, 0.042 mbar

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The system is structurally stable at very low loading but becomes gradually dynamical at higher loading.
Selectivity-conversion trajectories for 2%VOx/SBA15 and 13 VOx/SBA15 catalyst. \( \text{C}_3\text{H}_8/\text{O}_2/\text{N}_2 = 17.2/8.6/34.3. \) Catalysts mass = 300 and 30 mg Flows = 20-100 cc/min.
Multiple reaction pathways: “simple” reaction network?

Different loadings (differing species distributions) exhibit in the details of their conversion-selectivity profiles substantial differences:

mulitiple sites in action

The “noise” in some catalytic data arises from the species interconversion (structural dynamics) with time constants of the catalysis experiments.
Selectivity fixed at 2% of conversion for VOx/SBA15 catalysts at 460 and 500°C. C3H8/O2/N2 = 17.2/8.6/34.3 Catalyst mass = 30–300mg. Flows = 20 – 100 ml/min.
CO/CO$_2$ ratio (a) TOF (b) and activation energy (c) as a function of the vanadium loading. $C_3H_8/O_2/N_2 = 17.2/8.6/34.3$ Catalyst mass = 30 – 300 mg.
Flows = 20 – 100 ml/min.
Catalysts: VODx/Ti/SBA15

"Grading" of catalysts depends much on conditions!

C₃H₈/O₂/N₂ = 17.2/8.6/34.3. Catalysts mass = 300 and 30 mg. Flows = 20-100 cc/min
Electronic structure and reactivity

In-situ UV-Vis reveals similar initial electronic structure of the V species:

In feed a differentiation occurs reflecting the presence of the Ti species.
Structural dynamics

The catalyst becomes more selective when the species at 392 nm (larger V-O-V arrays (RAMAN)) disappear; the reducibility (d-d-transitions) remains limited. In NEXAFS spriting of V on Ti is detected, the average oxygen coordination changes.
Reaction rate constants for C3 ODH

A model-free time law:

Reaction orders

0-0.33 for n

0.60-1.0 for m

Propene selectivity S

Propane conversion X

Time on stream / h
A reaction network
Results and future activities

• V is dynamical.
  – Static diluted and static crystalline are not desired.
  – Rapid dynamics is detrimental.
  – Redox dynamics requires an optimum.

• Multiple active sites for different reactions: kinetic parameters are intermixed.

• Beware of tof!

• Ti (mixed species) suppresses polymeric species and its mobility.

• Gas phase chemistry?

• CO\textsubscript{x} chemistry.

• Kinetics of temporal changes.

• Complete Ti/V matrix.

• Create Ce/V matrix.
Structure of the metal species

UV-Vis and RAMAN are differently sensitive to the aggregation and coordination of the metal species.
Process under severe conditions

Water has a different effects on several site types: overall site blocking but beneficial for selectivity.

#7964, C\textsubscript{3}H\textsubscript{8}/O\textsubscript{2}/H\textsubscript{2}O/N\textsubscript{2}=3/6/z/(91-z) vol\%, GHSV=1200 h\textsuperscript{-1}, 450°C

\[8V/SBA\text{ 15}\]