Microcalorimetry beyond Adsorption: Basics and Applications in Heterogeneous Catalysis

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Lecture Series: Modern Methods in Heterogeneous Catalysis;
10:45 - 12:15
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   - CO$_2$ ads. on CeO$_2$ at 40°C
   - O$_2$ adsorption on supported CeO$_2$ at 200°C
   - Ethanol adsorption on VO$_x$/$\gamma$-Al$_2$O$_3$ at 40°C
   - Propane & ethane ads. on MoVTeNb oxide, V/SBA15, MoV oxide and P/oCNT at 40°C
   - Propylene adsorption on MoO$_x$/SBA-15 at $T_{reaction}$=50°C
   - 1-Hexyne ads. on CeO$_2$/TiO$_2$ at $T_{reaction}$=80°C
   - CO on IrOx at $T_{reaction}$= r.t.
   - CO on Ni/MgAl oxide at 30°C
Introduction

- adsorption steps, surface reaction processes, and desorption steps

- 1st step in the catalytic cycle: activation of the reacting molecules by adsorption (strength of chemisorption bond can effect the activation energy)

- adsorption phenomena (bond strength between adsorbate and surface) play an important role in heterogeneous catalysis

For a detailed understanding of complex reaction networks we need:

- thermodynamic data of high accuracy
- information about the nature of the catalyst surface

- quantitatively study the adsorption, activation, and reaction phenomena close to the reaction parameters
- simulate reactants-induced responses of the surface

- since perhaps only a minor fraction of all surface atoms form active centers

Ads. Isothermal Microcalorimetry / Microcalorimetry beyond Ads.

direct method to determine number, strength and energy distribution of the adsorption sites

- key to the effective use of adsorptive microcalorimetry is the careful choice of probe molecules and adsorption temperature to study
surface sites

careful choice of probe molecules and the adsorption temperature

metal oxide catalysts provide **acid/base** properties

Brønsted acid sites: transfer of $H^+$ from OH to Adsorbate

Lewis acid sites: coordination to an electron-deficient metal atom $Me^{n+}$

**oxygen vacancy:** $O^{2-}$

metall cations under participation of oxygen: $Me_x O_y$

strong basic $NH_3$ at 80°C weak basic CO at RT, 77 K acidic CO$_2$ at RT

Focus

use of probe molecules such as educt, intermediate, product or molecules closely related to the reactants is an elegant method to study the surface sites relevant for catalytic reaction

$T_{\text{adsorption}} < T_{\text{reaction}}$ → study of the pure ads. process or the activation of the reactant

$T_{\text{adsorption}} = T_{\text{reaction}}$ → study of the surface chemical events during the reaction
Introduction

Simplified energy diagram

Exothermic process, gas phase

Activation barrier

Gas state

Adsorbed state

Product state

Catalyst surface

Deficient Phase $\alpha$

reactivated

active state

Adaptive state

Deactivated Phase $\beta$

Phase $\alpha$

dynamics

active site formation

Deactivated Phase $\beta$

CO$_2$ ads. chemisorption on CeO$_2$ for DEACON reaction

MoV oxide catalyst in oxidative dehydrogenation of alkanes

Ir-based catalysts for the oxygen evolution reaction at r.t.

Vanadium Oxide-based and Metal-free Catalysts in the ODH of Ethane and Propane

Ni based catalysts for the dry reforming of methane

Propylene Metathesis over MoOx/SBA-15

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   - Ethanol adsorption on VOₓ/γ-Al₂O₃ at 40°C
   - Propane ads. On MoVTeNb oxide at 40°C
   - Propylene adsorption on MoOₓ/SBA-15 at T_{reaction}=50°C
   - 1-Hexyne ads. on CeO₂/TiO₂ at T_{reaction}=80°C
Adsorptive microcalorimetric setup

Tian-Calvet calorimeter of SETARAM

**Sample cell (static, dynamic)**

Reference cell  
Sample cell  
Cell chamber  
Isolation  
Electronics / Real Time  
Heating  
Thermopile, Heat flow detector  
Calorimetric Element  
Thermocouple  
Body  

**Catalyst bed**

Volumetric-Barometric System

**Calorimetric Element**

\[
\sum n_{ads} \quad vs \quad p_{eq}, \quad mmol \cdot g^{-1}
\]

\[
q_{diff} = \frac{\Delta H_{ads}}{n_{ads}}, \quad kJ/mol
\]

**Pressure gauge dosing system**

\[
q_{diff} \quad vs \quad n_{ads}, \quad kJ/mol
\]

\[
K = K_0 \exp \left(\frac{\Delta H_{ads}}{RT}\right), \quad hPa^{-1}
\]
Adsorptive microcalorimetric setup

**HT1000 (rt-1000°C),**
**MS 70 (rt-100°C)**
**BT 2.15 (200°C–77K)**

**Tian-Calvet calorimeter of SETARAM**
combined with a custom-designed high vacuum and gas dosing apparatus.

**The history of modern calorimetry began at the University of Provence in Marseilles.**

Tian described his compensation microcalorimeter for the first time in 1922, when he and his colleague COTTE used it to study the metabolism of insects. He brought further improvements to this thermocouple instrument in 1924 and 1926.

**Prof. Albert Tian**

CALVET introduced the differential setup (1948) and a rational construction of the **two twinned calorimetric elements**, transforming Tian's apparatus into a true laboratory instrument that today is commercialized by Setaram.

**Prof. Edouard Calvet** (1895–1966)
Low Temperature Calorimeter (from -196°C to 200°C)
Setaram BT 2.15

- Combination of LT-Calorimetry and LT-FTIR
  CO, CO$_2$, CH$_4$ ..... ads. on e.g. Cu catalysts, Ni-catalysts, MgO
**in-situ DSC setup** (Differential scanning calorimetry)
Setaram instrument SENSYS EVO.

- Direct measurement of reaction enthalpy
- Precise product analysis

- Calvet calorimetric element
- 3D sensor totally surrounds the catalyst
**in-situ DSC setup** *(Differential scanning calorimetry)*

Setaram instrument SENSYS EVO.

Dr. Andrey Tarasov

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**Simplified energy diagram**

- **Exothermic process, gas phase**
  - Activation barrier
  - $E_{eq(A)}$
  - $E_{app}$
  - $\Delta H^\#$
  - Gas state
  - $\Delta H_{ads}^A$
  - Adsorbed state
  - Product state
  - $\Delta H_{ads}^B$

- **Catalyst surface**
  - Deficient Phase $\alpha$
  - active state
  - $\Delta H^\#$
  - adaptive state
  - $\Delta H_{relx}$
  - reactivated
  - Phase $\alpha$
  - Deactivated
  - Phase $\beta$

**Transformation of gas phase molecules**
- Information about reaction kinetics
- Simulation of different conditions *in situ*

---

**Transformation in solid state**
- Redox dynamics
- Thermochemistry of defects formation

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Experimental procedure

**Activation:**
UHV (10⁻⁸hPa), gases (H₂, O₂ ......), rt - 600°C

**Reaction:**
Calorimeter cell can used as a flow-type reactor. Catalyst is used in the selected reaction until stady-state performance, rt - 600°C


**Transfer**
of the sample cell into the calorimeter and degassing/equilibration at T_ads.

**Adsorptive microcalorimetric experiment:**
Stepwise adsorption, desorption and re-adsorption of the selected probe molecule at the selected temperature.
Adsorption Calorimetry - Standard procedure

• The probe molecule must be introduced **stepwise** at **constant temperature**, the pressure is increased slowly.

• For each adsorption step, the **adsorbed amount** must be determined (isotherm).

• For each adsorption step, the **evolved heat** must be determined (integral heat of adsorption).

• The **differential heat** ($\Delta H_{\text{ads}}$) can then be determined by dividing the evolved heat through the number of molecules adsorbed in a particular step.
### Introduction

<table>
<thead>
<tr>
<th>Type of interaction and heat of adsorption (negative enthalpy of adsorption)</th>
<th>Physisorption</th>
<th>Chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>van der Waals force</td>
<td>$0 &lt; \Delta_pH &lt; 50 \text{ kJ/mol}$</td>
<td>chemical bonding, electron transfer</td>
</tr>
<tr>
<td>Noble gases, CH$_4$, N$_2$</td>
<td>Dipole-dipole interaction</td>
<td>$60 &lt; \Delta_cH &lt; 400 \text{ kJ/mol}$</td>
</tr>
<tr>
<td>20 – 25 kJ/mol</td>
<td>H$_2$O, NH$_3$</td>
<td>CO on metals (Pt, Pd)</td>
</tr>
<tr>
<td>Dissociative adsorption</td>
<td>(O$_2$, H$_2$ on Pt, H$_2$O on oxides)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reversibility</th>
<th>reversible</th>
<th>reversible, irreversible or partially irreversible</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed</td>
<td>fast</td>
<td>can be slow (e.g. activated adsorption, dissociative adsorption)</td>
</tr>
<tr>
<td>Coverage</td>
<td>non-specific and weak</td>
<td>specific (chemisorbed molecule blocks surface sites)</td>
</tr>
<tr>
<td></td>
<td>multilayers possible</td>
<td>monolayer only</td>
</tr>
</tbody>
</table>
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   - Evolved adsorption heat
   - Differential heats of adsorption

4. Volumetric-Barometric System
   - calibration & measurement of adsorbed amount

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   - CO on IrOx at $T_{reaction}=r.t.$
   - CO on Ni/MgAl oxide at 30°C
The Calorimetric Element

Calorimetric Element
The Calorimetric Element

- The sample cell is placed into a calorimeter element

3D Calvet heat flow sensor

- The cell is totally surrounded by a thermopile made of more than 400 conductive thermocouples in series

- Thermopile has 2 functions:
  1. heat transfer
  2. signal generation
The heat produced by the adsorption/activation/reaction of a dosed probe molecule on/with the catalyst surface is consumed by 2 processes:

1. Increase of the temperature of the sample cell
2. Once there is a temperature gradient between cell and surrounding block, heat flow through the thermopile
The calorimetric block consists of a sample cell and a reference cell.

The reference cell compensate external temperature fluctuations and it provides a good stability of the baseline.

Measurement of the temperature difference $\Delta \theta$

The heat-flow detector gives an electrical signal “$U$” which is proportional to the heat transferred per time unit.

Setup according to Tian and Calvet

Power balance, measuring signal and the Tian equation

The power $P$ [W] necessary to heat the cell by $d\theta$ is proportional to the heat capacity $C$ [J/K] of the cell

$$ P = C \frac{d\theta}{dt} $$

The heat flow $\Phi$ [power] is proportional to the temperature gradient $\Delta \theta$ between cell and block and to the thermal conductivity $G$ [W/K]

$$ \Phi = G (\theta_{cell} - \theta_{block}) = G \Delta \theta $$

Total thermal power of calorimetric element

$$ P_{total} = P + \Phi = C \frac{d\theta}{dt} + G \Delta \theta $$

The electrical signal is proportional to the temperature difference; (proportionality factor $g=f$ (number and type of the thermocouple))

$$ U = g \Delta \theta $$

The relation between power and electrical signal is then

$$ P_{total} = \frac{C}{g} \frac{dU}{dt} + \frac{G}{g} U $$

$G$ [W/K] is constant and if $C$ [J/K] can be considered constant, then $C/G$ is a constant with units of time

$$ \tau = \frac{C}{G} $$

The Tian equation shows that the power is not proportional to the temperature difference, the power is delayed with respect to the signal $U$ produced by the cell

$$ P_{total} = \frac{G}{g} \left( U + \tau \frac{dU}{dt} \right) $$
Evolved Heat & Differential Heat of Adsorption

- If heat is released in the cell for a limited period of time, e.g. through adsorption, then an **electrical signal** $U$ with an exponential decrease is obtained.

- The integral under the curve is proportional to the evolved heat

\[
Q_{\text{int}} = \frac{G}{g} \int U \, dt = fA
\]

$A$: area under curve [Vs]

$f$: calibration factor [J/(Vs)]

The heat signal of the calorimeter can be calibrated by:

- using an Ohm resistance which produces a certain amount of heat

\[
Q_{\text{Ohm resistance}} = U*I*t
\]

$f = Q_{\text{Ohm resistance}} / A_{\text{ohm resistance}}$ [Ws/Vs]

- chemical reaction

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**Heat signal calibration at 40°C**

Calibration source:
Variation of voltage, current and time

<table>
<thead>
<tr>
<th>Voltage U [V]</th>
<th>Current I [mA]</th>
<th>time t [s]</th>
<th>Q introduced =U⋅I⋅t [mWs, mJ]</th>
<th>Q integral [Vs]</th>
<th>f = \frac{Q_{\text{introduced}}}{Q_{\text{integral}} [mJ/Vs]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0528</td>
<td>3</td>
<td>3</td>
<td>27.48</td>
<td>45.544</td>
<td>1657.64</td>
</tr>
<tr>
<td>3.0527</td>
<td>3</td>
<td>6</td>
<td>54.95</td>
<td>91.143</td>
<td>1658.69</td>
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<tr>
<td>10.1733</td>
<td>10</td>
<td>10</td>
<td>1017.33</td>
<td>1692.075</td>
<td>1663.25</td>
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<tr>
<td>3.0563</td>
<td>3</td>
<td>1</td>
<td>9.16</td>
<td>14.978</td>
<td>1635.30</td>
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</tr>
</tbody>
</table>

\( f_{40°C} = 1659 \)
Heat signal calibration, time constant \( \tau \) at 50°C

<table>
<thead>
<tr>
<th>Voltage ( U ) [V]</th>
<th>Current ( I ) [mA]</th>
<th>time ( t ) [s]</th>
<th>( Q ) introduced ( = U \cdot I \cdot t ) [mWs, mJ]</th>
<th>( Q ) integral [Vs]</th>
<th>( f ) = ( \frac{Q\text{ introduced}}{Q\text{ integral}} ) [mJ/Vs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.18</td>
<td>10</td>
<td>3</td>
<td>305.4</td>
<td>511.077</td>
<td>1673.47</td>
</tr>
<tr>
<td>2.03</td>
<td>2</td>
<td>5</td>
<td>20.30</td>
<td>34.631</td>
<td>1705.96</td>
</tr>
<tr>
<td>3.07</td>
<td>3</td>
<td>10</td>
<td>92.10</td>
<td>152.98</td>
<td>1661.02</td>
</tr>
<tr>
<td>10.17</td>
<td>10</td>
<td>3</td>
<td>305.10</td>
<td>514.63</td>
<td>1686.76</td>
</tr>
</tbody>
</table>

\( f_{50°C} = 1674 \)

\( \tau = 322 \text{s} \)

\( \tau = 333 \text{s} \)

\( \tau_{\text{calorimeter,50°C}} = 300 - 350 \text{s} \)

\( \tau = \frac{C \text{ heat capacity [J/K]}}{G \text{ thermal conductivity [W/K]}} = \text{const.} \)

\( U = U_0 + A \cdot \exp \left( -\frac{t - t_0}{\tau} \right) \)
Evolved Heat &
Differential Heat of Adsorption

\[ Q_{\text{int}} = \frac{G}{g} \int U \, dt = fA \]

A: area under curve [Vs]
f: calibration factor [J/(Vs)]

úaDifferential heats of adsorption as a function of coverage can be determined:

\[ q_{\text{diff}} = \left( \frac{\delta Q_{\text{int}}}{\delta n} \right)_{T,V,p(\text{equ.})} \]

Calculation of the adsorbed amount

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   - Propylene adsorption on MoO$_x$/SBA-15 at $T_{\text{reaction}}=50^\circ$C
   - 1-Hexyne ads. on CeO$_2$/TiO$_2$ at $T_{\text{reaction}}=80^\circ$C
Measurement of the adsorbed amount

- Adsorption via stepwise dosing of probe molecule into the sample cell
- $Q_{\text{int}}$, $p$, $T$ are measured
- $q_{\text{diff}} = \Delta H_{\text{cond}} \rightarrow$ saturation of the surface
- The probe molecule is distributed into three partitions: gas phase, wall adsorption, sample adsorption

$V_{\text{dos}}$, $V_{\text{cal}}$, $n_{\text{introduced}}$

Calibration isotherm $n_{\text{inner wall + gas}} = f(p_{\text{equ.}})$

Adsorbed amount on the surface of the catalyst

Volumetric-barometric system

Pressure gauge dosing system

$V_{\text{Dos}}$

Cell volume

Reference cell

$P_{\text{eq}}$

Sample cell + catalyst

$Q_{\text{int}}$

$T = \text{constant}$
Volumetric-Barometric System

Front view

Top view
The Dosing Volume \( V_{Dos} \)

\[ \text{pressure gauge dosing system} \]

- \( p, T \) can be easily measured
- \( V \) needs to be determined

Volume Calibration

An unknown volume of any shape can then be determined through expansion from gas (an ideal gas that does not stick much to the walls) from one volume to the other and pressure measurement before and after the equilibration.
Calibrating the Dosing Volume

- Fill $V_{\text{cal}}$ and $V_{\text{Dos}}$, same pressure
- Close valve between $V_{\text{cal}}$ and $V_{\text{Dos}}$
- Set pressure in $V_{\text{dos}}$ to $p_{\text{Dos}}$
- Open valve, equilibrate

**Dosing Volume $V_{\text{Dos}}$**

**Calibration Volume $V_{\text{cal}} = 74.39 \text{ml}$**
Calibrating the Dosing Volume

pressure gauge dosing system

- Initial situation:
  \[ nRT = p_{Cal}V_{Cal} + p_{Dos}V_{Dos} \]

- After opening valve:
  \[ nRT = p_{fin}(V_{Cal} + V_{Dos}) \]

- \( n, T \) are constant

\[ V_{Dos} = \frac{p_{Cal} - p_{fin}}{p_{fin} - p_{Dos}}V_{Cal} \]
### Example Data

**Propane at 40°C**

*Project: $V_xO_y$/SBA15 for ODH of propane*

<table>
<thead>
<tr>
<th>Nr</th>
<th>$p_{Cal}$ [mbar]</th>
<th>$p_{Dos}$ [mbar]</th>
<th>$p_{fin}$ [mbar]</th>
<th>$V(Dos)$ [ml]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>before</td>
<td>before</td>
<td>after equilibration</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>5,314</td>
<td>9,467</td>
<td>8,683</td>
<td>137</td>
</tr>
<tr>
<td>2</td>
<td>8,683</td>
<td>7,648</td>
<td>7,843</td>
<td>137</td>
</tr>
<tr>
<td>3</td>
<td>7,638</td>
<td>6,341</td>
<td>6,585</td>
<td>137</td>
</tr>
<tr>
<td>4</td>
<td>6,585</td>
<td>4,768</td>
<td>5,111</td>
<td>137</td>
</tr>
<tr>
<td>5</td>
<td>5,111</td>
<td>4,712</td>
<td>4,787</td>
<td>137</td>
</tr>
<tr>
<td>6</td>
<td>4,786</td>
<td>3,197</td>
<td>3,496</td>
<td>137</td>
</tr>
<tr>
<td>7</td>
<td>3,469</td>
<td>2,701</td>
<td>2,846</td>
<td>136</td>
</tr>
</tbody>
</table>

*It is important that the entire system is at the same constant temperature!*

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Determining the Dosed Amount \( n_{int, i} \)

\[
n_{int, i} = \frac{(p_{Dos, bef} - p_{Dos, aft})V_{Dos}}{RT}
\]

vacuum → pressure gauge dosing system

gas in

Sample cell static, dynamic

Sample holder

L = 70 mm
\( \varnothing = 15 \text{ mm} \)

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Total number of molecules accumulated in cell

\[ n_{SC,tot,i} = \sum_{i} n_{int,i} = n_{SC,tot,i-1} + n_{int,i} \]

i.e. the sum of

- the number of molecules already in the cell
- the number of molecules introduced in the \( i^{th} \) step
Empty Cell: The Wall Adsorption

- Molecules are in the gas phase but also adsorbed on the inner wall surface.
- Only the gas phase molecules contribute to the measured pressure.
- The number of molecules adsorbed on the walls depends on the pressure.
  → wall adsorption isotherm.
- Measure the pressure in the cell as a function of the total number of molecules introduced into the cell

- Without wall adsorption and without sample, the relation between pressure and number of molecules in the sample cell would be given by the ideal gas law

\[ p_{SC,i} = \frac{n_{SC,tot,i}RT}{V_{SC}} \]
With wall adsorption and with or without a sample, the relation between number of molecules in the gas phase + on the walls and the pressure can be written as a polynomial expression:

\[ n_{SC,w+g,i} = a(p_{SC,i}) - b(p_{SC,i})^2 + c(p_{SC,i})^3 - d(p_{SC,i})^4 \ldots \]

Without a sample, the coefficients can be determined:

\[ n_{SC,w+g,i} = n_{SC,tot,i} \]
### Example Blank Measurement

<table>
<thead>
<tr>
<th>Nr</th>
<th>( p_{\text{Dos,bef}} )/mbar</th>
<th>( p_{\text{Dos,aft}} )/mbar</th>
<th>( p_{\text{SC,i}} )/mbar</th>
<th>( n_{\text{int,i}} )/( \mu \text{mol} )</th>
<th>( n_{\text{SC,tot,i}} )/( \mu \text{mol} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9,682</td>
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<td>1,870</td>
<td>0,97</td>
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<tr>
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<tr>
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<td>6,487</td>
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<tr>
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</table>

**Isobutane at 40°C**

without catalyst

(\textit{Project:} isomerisation of \( n \)-butane to isobutane over sulf. ZrO₂)

\[
\begin{align*}
n_{\text{int,}i} &= \frac{(p_{\text{Dos,bef}} - p_{\text{Dos,aft}}) V_{\text{Dos}}}{RT} \\
n_{\text{SC,tot,}i} &= \sum_{i} n_{\text{int,}i} = n_{\text{SC,tot,}i-1} + n_{\text{int,}i}
\end{align*}
\]
Correction for Wall Adsorption

- The adsorption of isobutane on the walls is insignificant

\[ n_{w+g(He)} = 8 \times 10^{-5}p_{SC}^3 + 0.0146p_{SC}^2 + 9.3348p_{SC} \]
\[ R^2 = 1 \]

Isobutane \( @ 40^\circ C \)

\[ n_{w(He)} \sim 0 \mu \text{mol} \]

\( He \ @ 40^\circ C \) (does not stick to the walls)
The adsorption of e.g. \( \text{C}_2\text{H}_5\text{OH} \), \( \text{NH}_3 \), \( \text{CH}_3\text{OH} \) on the walls is significant.
Correction for Wall Adsorption

\[ n_{g,(\text{He})} = 8E-05x^3 + 0.0146x^2 + 9.3348x \quad R^2 = 1 \]

\[ n_{w+g,(\text{NH}_3)} = -0.289p_{\text{SC}}^2 + 13.248p_{\text{SC}} + 19.585 \quad R^2 = 0.9991 \]

\[ n_{w+g,(\text{NH}_3)} = -1047p_{\text{SC}}^2 + 245.69p_{\text{SC}} + 3.5634 \quad R^2 = 0.9498 \]

Saturation of the inner wall
Calulation of Adsorbed Amount

- Total number of molecules in sample cell after the $i^{\text{th}}$ step

$$n_{SC,\text{tot},i} = n_{\text{ads,\text{tot},i}} + n_{SC,\text{w+g},i}$$

- Total number of molecules in sample cell after the $(i+1)^{\text{th}}$ step

$$n_{SC,\text{tot},i+1} = n_{\text{ads,\text{tot},i}} + n_{SC,\text{w+g},i} + n_{\text{ads},i+1} + n_{SC,\text{w+g},i+1}$$

- The difference in number of molecules between $i^{\text{th}}$ and $(i+1)^{\text{th}}$ step is the number of molecules introduced in the $(i+1)^{\text{th}}$ step
Calculation of Adsorbed Amount

- The number of molecules adsorbed in the \((i+1)^{th}\) step is then

\[
  n_{ads,i+1} = n_{int,i+1} + n_{SC,w+g,i} - n_{SC,w+g,i+1}
\]

- The total number of molecules adsorbed after \((i+1)\) steps is

\[
  n_{ads,tot,i+1} = n_{ads,tot,i} + n_{ads,i+1}
\]

Isobutane adsorption on different activated sulf. ZrO$_2$ at 40°C.

(Project: isomerisation of n-butane to isobutane over sulf. ZrO$_2$
1. Introduction

2. Adsorptive microcalorimetric setup

3. Power balance of Tian-Calvet calorimeter & Evolved adsorption heat & Differential heats of adsorption

4. Volumetric-Barometric System calibration & measurement of adsorbed amount

5. Obtained physical quantities & evaluation criteria of the calorimetric results

6. Applications of microcalorimetry in heterogeneous catalysis
   - H₂ and CO adsorption on 2%Pt/Al₂O₃ at 40°C
   - NH₃ adsorption on pure-phase MoVTeNb oxide at 80°C
   - CO₂ ads. on CeO₂ at 40°C
   - O₂ adsorption on supported CeO₂ at 200°C
   - Ethanol adsorption on VOₓ/γ-Al₂O₃ at 40°C
   - Propane ads. on MoVTeNb oxide at 40°C
   - Propylene adsorption on MoOₓ/SBA-15 at Treaction=50°C
   - 1-Hexyne ads. on CeO₂/TiO₂ at Treaction=80°C
Obtained physical quantities & evaluation criteria of the calorimetric result

Adsorption Isotherm  \( n_{ads} = f \left( p_{equ.} \right) \)

\( n_{ads} \) (total): overall adsorbed amount under an equilibrium pressure of 95 mbar
\( n_{ads} \) (irrev.): chemisorbed amount

Sabine Wrabetz, Electronic Structure and Adsorption, Dept. of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany
Analysis of the Adsorption Isotherm

**Langmuir model:** The enthalpy of adsorption $\Delta a H$ per site is constant with coverage $\Theta$

- **Langmuir model for dissociative adsorption**
  
  \[
  \theta_H = \frac{n_{ads}}{n_m} = \frac{\sqrt{pH_2 K_{ads}}}{1 + \sqrt{pH_2 K_{ads}}}
  \]
  
  e.g., dissociative ads. of $H_2$ on Pt supported on $Al_2O_3$ at 40°C
  
  - **Higher order Langmuir model**
    
    \[
    N_{ads} = \frac{N_{mono} (Kp)^{\frac{1}{n}}}{1 + (Kp)^{\frac{1}{n}}}
    \]
    
    e.g., activated ads. of n-butane (educt) on sulf. ZrO$_2$ at 40°C $< T_{reaction} = 60°C$
    
  
  - **Langmuir model**
    
    \[
    \theta = \frac{Kp}{1 + Kp}
    \]

**Freundlich isotherm:** The enthalpy of adsorption $\Delta a H$ per site decreases exponential with coverage $\Theta$

\[
N_{ads} = \frac{1}{1 + A p^n}
\]

**Tempkin isotherm:** The enthalpy of adsorption $\Delta a H$ per site decreases linear with coverage $\Theta$

\[
\theta = \frac{RT}{q_{ads}^{(\theta=0)} - q_{ads}^{(\theta=1)}} \ln \left( 1 + \frac{p}{p^*} \exp \frac{q_{ads}^{(\theta=0)}}{RT} \frac{q_{ads}^{(\theta=1)}}{RT} \right)
\]

- e.g., propane adsorption (313 K) on the oxygen surface groups of CNT and $B_2O_3$–CNT catalysts used in ODH of propane
  
  [B. Frank, S. Wrabetz et al., ChemPhysChem 2011, 12, 2709 – 2713]

- CO Adsorption on supported Gold nanoparticle catalysts
  
Analysis of the Adsorption Isotherm

Adsorption Isotherm of propane on 10%V/SBA15 catalyst active in oxidation of propane

Higher order Langmuir model
1st order Langmuir model
Freundlich model

Δ_aH (q_diff) = 40kJ/mol = const

Analysis of adsorption isotherm of propane on 10%V/SBA15 catalyst active in oxidation of propane

Specific surface area = N_{mono} * Avogadro constant * S_{1:1, assumed} * cross-section area 39Å² for propane

[A. L. McClellan et.al., J. of Colloid and Interface Science, 23 (1967) 577]

\[ N_{ads} = \frac{N_{mono}(Kp)^{\frac{1}{n}}}{1 + (Kp)^{\frac{1}{n}}} \]

n = 1 non-activated ads.
n > 1 activated ads.

<table>
<thead>
<tr>
<th>10%V/SBA15 dehydration temperature</th>
<th>N_{mono} µmol * g⁻¹</th>
<th>n</th>
<th>R²</th>
<th>S_{propane} m²*g⁻¹</th>
<th>BET S_{N2} m²*g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>373 K</td>
<td>0.9 (2)</td>
<td>1.20 (2)</td>
<td>0.99983</td>
<td>226 (10)</td>
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<tr>
<td>573 K</td>
<td>1.3 (4)</td>
<td>1.22 (2)</td>
<td>0.99982</td>
<td>304 (10)</td>
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<tr>
<td>673 K</td>
<td>1.2 (3)</td>
<td>1.22 (2)</td>
<td>0.99905</td>
<td>290 (10)</td>
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</table>
Analysis of the Adsorption Isotherm

Propane adsorption on **pure-phase M1** catalyst (MoVTeNb oxide #6059) active in selective oxidation of propane

![Adsorption Isotherm @ 40°C](image)

Delta aH \( q_{diff} \) @ 40°C \( \sim 58 \text{ kJ/mol} = \text{const} \)

Specific surface area = \( N_{\text{mono}} \times \text{Avogadro constant} \times S_{1:1, \text{assumed}} \times \text{cross-section area} \sim 39 \text{ Å}^2 \) for propane

[ A. L. McClellan et al., J. of Colloid and Interface Science, 23 (1967) 577

<table>
<thead>
<tr>
<th>Catalyst (ID)</th>
<th>( N_{\text{mono}} ) μmol *g(^{-1})</th>
<th>( R^2 )</th>
<th>( S_{\text{propane}} ) m(^2)*g(^{-1})</th>
<th>( A_{\text{propane}} ) ( \sim 39 \text{ Å}^2 )</th>
<th>( A_{\text{N}_2} ) = ( 16.2 \text{ Å}^2 )</th>
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</thead>
<tbody>
<tr>
<td>M1 (5630)</td>
<td>34.9 (2)</td>
<td>0.99951</td>
<td>8.2 (1)</td>
<td>6.6</td>
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</tr>
<tr>
<td>M1 (6059)</td>
<td>48.5 (8)</td>
<td>0.99991</td>
<td>11.3 (1)</td>
<td>8.8</td>
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<tr>
<td>M1 (5737)</td>
<td>42.3 (8)</td>
<td>0.99986</td>
<td>9.9 (1)</td>
<td>13.4</td>
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</tr>
</tbody>
</table>

\( N_{\text{ads}} \) - coverage with certain equilibrium pressure
\( N_{\text{mono}} \) - monolayer coverage
\( p \) - equilibrium pressure
\( n \) - adsorption order
\( K/A \) - adsorption equilibrium constant
\( R^2 \) - adsorption equilibrium constant
\( S \) - stoichiometry
Obtained physical quantities & evaluation criteria of the calorimetric result

Classical Calorimetric Curve

Initial differential heat
Slope: heterogeneously distributed and energetically different adsorption sites

Plateau: homogeneously distributed and energetically uniform adsorption sites

Completion of monolayer

High diff. heats & heat oscillation:
dynamic ads. process
chemisorption-oxidation-reaction

Amount of adsorbed propane on phase-pure MoVTeNb\#6059 / mmol/m²

Amount of adsorbed propane on CNT at 313 K [mmol/g]

Amount of ads. O₂ on Pd\textsubscript{PVA}/N-CNT at T\textsubscript{react.}=80°C / µmol/g
Evaluation criteria of the calorimetric result

Integral heat signal of adsorption and desorption
stepwise adsorption of propane on MoVTeNb oxide at 40°C

\[ \Sigma + q_{\text{integral (ads.)}} = 7892 \text{ mJ} \]

- \[ q_{\text{integral (des.)}} = 6560 \text{ mJ} \]

\[ \Sigma q_{\text{int (ads.)}} > q_{\text{int (des.)}} \rightarrow \text{partially irreversible ads.}; \text{ activated ads. process} \]

\[ \Sigma q_{\text{int (ads.)}} < q_{\text{int (des.)}} \rightarrow \text{instability of the catalyst in the presence of probe molecule} \]

\[ \Sigma q_{\text{int (ads.)}} = q_{\text{int (des.)}} \rightarrow \text{reversible ads. process} \]

Background of the thermo signal during the stepwise adsorption
stepwise n-butane ads. on sulf. ZrO₂ at 40°C < 60°C = T_{\text{reaction}}

Heat signal deviates from the base-line
→ Adsorption process is accompanied by secondary processes
e.g. during n-butane ads. a partial isomerization of n-butane to isobutane in the calorimeter cell was observed.
Evaluation criteria of the calorimetric result

**Determination of the time constant** $\tau$ **of the integral heat signal**

$$y = y_0 + A \cdot \exp\left(-\frac{x - x_0}{\tau}\right)$$

- $R = 1 \, \text{k}\Omega \rightarrow 27.45 \, \text{mJ}$
- $\tau_{\text{(calorimeter+cell, 40°C)}} \sim 265 \, \text{s}$

**Shape of the integral heat signal**

- **O$_2$ adsorption on 2\%Pd/N-CNT473K at 353K=T$_{\text{reaction}}$**
  - $0.039 \, \mu\text{mol/g oxygen}$
  - $K(t) = 377 \, \text{s}$
  - Response time / $0.4 \, \text{h}$

- **2 \mu\text{mol/g oxygen}**
  - $K(t) = 998 \, \text{s}$
  - Response time / $0.7 \, \text{h}$

- **14 \mu\text{mol/g oxygen}**
  - $K(t) = 998 \, \text{s}$
  - Response time / $10.3 \, \text{h}$

**5.9 \mu\text{mol/g propylene adsorbed on MoVTeNb at 313 K}**
- $\tau = 287 \, \text{s} \sim \tau_{\text{cal+cell}}$
- quasi pure ads. process

**4.8 \mu\text{mol/g methanol adsorbed on } \gamma\text{Al}_2\text{O}_3 \text{ at 313 K}**
- $\tau = 722 \, \text{s} > \tau_{\text{cal+cell}}$
- ads. + reaction

- $\gamma\text{Al}_2\text{O}_3$, Methanol-Ads, 40grd, 3. Ads.-Step
  - $(A+B*\exp(-(x-C)/D), A=0.5438~, B=0.0249~, C=9237.80~, D=722.458~)$

- $5.9 \, \mu\text{mol/g propylene} \rightarrow 4.8 \, \mu\text{mol/g methanol}$

- $\gamma\text{Al}_2\text{O}_3$ at 313 K
  - $\tau = 287 \, \text{s} \sim \tau_{\text{cal+cell}}$
  - quasi pure ads. process

- $\gamma\text{Al}_2\text{O}_3$ at 313 K
  - $\tau = 722 \, \text{s} > \tau_{\text{cal+cell}}$
  - ads. + reaction

- **At low coverage**
  - quasi pure dissociative oxygen chemisorption on Pd

- **At higher coverage**
  - oxygen chemisorption is accompanied by secondary processes

Sabine Wrabetz, Electronic Structure and Adsorption, Dept. of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany
Applications of microcalorimetry in heterogeneous catalysis

Specific surface area of Pt:
- \( H_2 \) and CO ads. on 2%Pt/\( \text{Al}_2\text{O}_3 \) at 40°C

Titration of acid or basic surface sites:
- \( \text{NH}_3 \) ads. on pure-phase MoVTeNb oxide at 80°C
- \( \text{NH}_3 \) ads. on H-ZSM5 at 80°C; Validation of the TP-surface chemical probe reaction of n-propylamin
- CO\(_2\) ads. on CeO\(_2\) at 40°C

Investigation of the oxidation process:
- O\(_2\) ads. on supported CeO\(_2\) at 200°C

Study of catalytic relevant sites via calorimetry close to the reaction conditions:
- Ethanol ads. on \( \text{VO}_x/\gamma-\text{Al}_2\text{O}_3 \) at 40°C
- Propane ads. on MoVTeNb oxide at 40°C
- Propane and EB adsorption on the oCNT

Study of catalytic relevant sites via calorimetry under reaction conditions:
- Propylene chemisorption on \( \text{MoO}_x/\text{SBA-15} \) at \( T_{\text{reaction}}=50°C \)
- O\(_2\) ads. on Ag for ethylene epoxidation at \( T_{\text{reaction}}=230\) °C
- 1-Hexyne chemisorption on \( \text{CeO}_2/\text{TiO}_2 \) at \( T_{\text{reaction}}=80°C \)
- CO chemisorption on Ir based catalysts for OER at r.t.

Reactants induced dynamic responses of catalyst surface:
- CO chemisorption cycles (30°C) on Ni/MgAl oxide catalyst for dry reforming of methane (DRM)
- propane and ethane ads./des. cycles on MoV oxide at 40°C

Estimation of the enthalpy of formation of the transition state (activation barrier):
- ethane & ethylene and propane & propylene ads. on the Vanadium oxide-based and Metal-free catalysts for ODH
Applications of microcalorimetry in heterogeneous catalysis

VALIDATION

H₂ chemisorption on 2 wt.% Pt₇₆H₂-673K-2h /Al₂O₃ at 40°C

Reference Material from Quantachrome

Active Metal Surface Area = 1.146 m² g⁻¹
H₂ adsorption on Pt₃₋₆₇₃K⁻²h /Al₂O₃ Quantachrome at 40°C

Heat plateau: homogeneously distributed and energetically uniform adsorption sites

\[ q_{diff} = 215 \text{ kJ/mol} \] : chemisorption! \[ \Delta_c H = 215 \text{ kJ/mol} \]

Hydrogen is dissociative adsorbed on platinum

\[ H_2 + Pt + Pt \rightarrow Pt-H + Pt-H \quad \Delta_c H = 266 \text{ kJ/mol} \]

H₂ adsorption on Pt/Al₂O₃ Quantachrome at 40°C

\[
\theta_H = \frac{n_{ads}}{n_m} = \frac{\sqrt{p_{H2}K_{ads}}}{1 + \sqrt{p_{H2}K_{ads}}}
\]

\[
n_{ads} \left(1 + \sqrt{p_{H2}} \sqrt{K_{ads}}\right) = n_m \sqrt{p_{H2}} \sqrt{K_{ads}}
\]

\[
\frac{1}{n_m \sqrt{K_{ads}}} + \frac{1}{n_m \sqrt{p_{H2}}} = \frac{\sqrt{p_{H2}}}{n_{ads}}
\]

| Linearization | 
|---|---|---|---|---|---|
| \(p_{H2}\) (mbar) | \(10^{-6}\) | \(6 \cdot 10^{-4}\) | \(1.2 \cdot 10^{-3}\) | \(6.69 \cdot 10^{-2}\) | \(2.09 \cdot 10^{-1}\) | \(3.05 \cdot 10^{-1}\) |
| \(n_{ads}\) (mmol·g⁻¹) | \(1.208 \cdot 10^{-2}\) | \(1.555 \cdot 10^{-2}\) | \(1.956 \cdot 10^{-2}\) | \(2.264 \cdot 10^{-2}\) | \(2.366 \cdot 10^{-2}\) | \(2.387 \cdot 10^{-2}\) |
| \(\frac{\sqrt{p_{H2}}}{\sqrt{mbar}}\) | \(10^{-3}\) | \(24.5 \cdot 10^{-3}\) | \(34.6 \cdot 10^{-3}\) | \(259 \cdot 10^{-3}\) | \(457 \cdot 10^{-3}\) | \(552 \cdot 10^{-3}\) |
| \(\frac{n_{ads}}{\sqrt{mbar} \cdot g}\) (mmol) | 0.083 | 1.58 | 1.77 | 11.44 | 19.32 | 23.13 |

\[
\frac{1}{n_m} = 42 \frac{g}{mmol} \Rightarrow n_m = 24 \cdot 10^{-3} \frac{mmol}{g}
\]

\[
\frac{1}{n_m \sqrt{K_{ads}}} = 0.4 \frac{\sqrt{mbar} \cdot g}{mmol} \Rightarrow K_{ads} = \left(\frac{1 \cdot g \cdot mmol}{24 \cdot 10^{-3} mmol \cdot 0.4 \sqrt{mbar} \cdot g}\right)^2
\]

\[
\Rightarrow K_{ads} = 10851 \text{ mbar}^{-1}
\]

Specific surface area of Pt \(m^2_{Pt} / g_{cat}\)

Sabine Wrabetz, Electronic Structure and Adsorption, Dept. of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany
Specific surface area of Pt $m^2_{Pt}/g_{cat}$

$$S_{Pt} = \frac{n_m \cdot \text{Avogadro constant}}{\text{Surface sites density} \cdot \Gamma_{\text{fcc lattice, Pt}}}$$

$$S_{Pt} = \frac{24 \cdot 10^{-6} \text{ mol} \cdot 6.022 \cdot 10^{23} \text{ particles} \cdot \text{cm}^2}{g \cdot 1.5 \cdot 10^{15} \text{ atoms} \cdot \text{mol}}$$

$$S_{Pt} = 9667 \text{ cm}^2/g \approx 1 \text{ m}^2/g$$

Final Results

Kinetic parameters determined for the $H_2$ ads. on $\text{Pt/Al}_2\text{O}_3$

- $n_{\text{mono}} = 24 \cdot 10^{-6} \text{ mol} \cdot g^{-1}$
- $K_{\text{ads}} = 10851 \text{ mbar}^{-1}$
- $\Delta H_{\text{ads.}} = 215 \pm 4 \text{ kJ} \cdot \text{mol}^{-1}$
- $S_{Pt} \approx 1.0 \text{ m}^2 \cdot g^{-1}$

Sabine Wrabetz, Electronic Structure and Adsorption, Dept. of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany
Applications of microcalorimetry in heterogeneous catalysis

CO adsorption on $\text{Pt}^{H_2-673K-2h}_{/\text{Al}_2\text{O}_3}$ Quantachrome at 40°C
CO adsorption on Pt\textsubscript{H2-673K-2h/Al\textsubscript{2}O\textsubscript{3}} \textit{Quantachrome} at 40°C

**Heat plateau:** homogeneously distributed and \textbf{energetically uniform} adsorption sites

**Reversibility:** CO is mainly irreversible adsorbed on Pt at 40°C

$\dot{q}_{\text{diff}} = 200 \text{ kJ/mol}$: chemisorption! $\Delta C_H = 200 \text{ kJ/mol}$

- Pt-CO terminal CO $\Delta C_H = 209 \text{ kJ/mol}$
- (Pt)$_n$, $n>1$ bridged CO $\Delta C_H = 94 \text{ kJ/mol}$

$\nu_{\text{CO}} \sim 2055 \text{ cm}^{-1}$

$\nu_{\text{CO}} \sim 1822 \text{ cm}^{-1}$

J. Therm. Anal. Cal., 82, 2005 105

higher order Langmuir model for activated adsorption

$$N_{ads} = \frac{N_{\text{mono}} (Kp)^{\frac{1}{n}}}{1 + (Kp)^{\frac{1}{n}}}$$

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CO adsorption on Pt\textsubscript{H2-673K-2h}/Al\textsubscript{2}O\textsubscript{3} Quantachrome at 40°C

**Linearization**

\[
N_{ads} = \frac{N_{\text{mono}} \left( Kp \right)^{\frac{1}{n}}}{1 + \left( Kp \right)^{\frac{1}{n}}}
\]

\[
1/(n_{\text{mono}} K_{ads}^{1/n}) + (1/n_{\text{mono}}) p_{CO} = p_{CO} / n_{ads}
\]

\[
1/n_{\text{mono}} = 38.29 \text{ g/mmol} \rightarrow n_{\text{mono}} = 26.11 \times 10^{-3} \text{ mmol/g}
\]

\[
1/(n_{\text{mono}} K_{ads}^{1/n}) = 0.0298 \text{ mbar g/mmol} \rightarrow K_{ads} = \left( 1/n_{\text{mono}} A \right)^n
\]

\[
K_{ads} = 3945.96 \text{ mbar}^{-1}
\]

\[
S_{Pt} = 10563 \text{ cm}^2/\text{g} \approx 1.1 \text{ m}^2/\text{g};
\]

\[
S_{Pt} \text{; certified by Quantachrome} = 1.146 \text{ m}^2/\text{g}
\]

**Graph**

- **Linearized Langmuir isotherm of activated CO ads. on Pt/Al\textsubscript{2}O\textsubscript{3}**

- **Parameter**
  - **Value**
  - \( A \): 0.0298
  - \( B \): 38.29

**Adsorption order?**

- **Parameter**
  - **Value**
  - \( n_{\text{mono}} \): 0.02631
  - \( K_{ads} \): 2438.062
  - \( n \): 1.1567
  - \( R^2 \): 0.88731
Comparison

Kinetic parameters determined for the CO ads. on Pt/Al₂O₃

\[ n_{\text{mono}} = 26 \times 10^{-6} \text{ mol} \cdot \text{g}^{-1} \]
\[ K_{\text{ads}} = 3946 \text{ mbar}^{-1} \]
\[ \Delta H_{\text{ads.}} = 200 \pm 4 \text{ kJ} \cdot \text{mol}^{-1} \]
\[ S_{\text{Pt}} \approx 1.1 \text{ m}^2 \cdot \text{g}^{-1} \]

Kinetic parameters determined for the H₂ ads. on Pt/Al₂O₃

\[ n_{\text{mono}} = 24 \times 10^{-3} \text{ mmol} \cdot \text{g}^{-1} \]
\[ K_{\text{ads}} = 10851 \text{ mbar}^{-1} \]
\[ \Delta H_{\text{ads.}} = 215 \pm 4 \text{ kJ} \cdot \text{mol}^{-1} \]
\[ S_{\text{Pt}} \approx 1.0 \text{ m}^2 \cdot \text{g}^{-1} \]

Validation

of the SETARAM calorimeter combined with a custom-designed high vacuum and gas dosing apparatus.

\[ J. \text{ Therm. Anal. Cal.}, 82 \ (2005) 105 \]
\[ \Delta C_H = 209 \text{ kJ/mol} \]
\[ \Delta C_H = 200 \pm 4 \text{ kJ/mol} \]
\[ S_{\text{Pt}} \text{; certified by Quantachrome} = 1.146 \text{ m}^2/\text{g} \]
\[ \Delta C_H = 200 \pm 4 \text{ kJ/mol} \]
\[ S_{\text{Pt}} = 1 \pm 0.1 \text{ m}^2/\text{g} \]
Titration of acid sites
on the surface of MoVTeNb oxide catalyst #6059
using NH₃ at 80°C
Titration of acid sites on the surface of M1 using NH₃ at 80°C

**Brønsted acid sites**

- **Strong Lewis acid sites**
  - ~ 140 μmol/g
- **Lewis acid sites**
  - ~ 80 μmol/g

Saturation concentration

Condensation enthalpy of NH₃ at 80°C = 12.8 kJ/mol

**FTIR spectra**

- Brønsted-NH₄⁺: 1419 cm⁻¹
- Lewis sites: Mₓ⁺-NH₃: 1486, 1249, 1225, 1196 cm⁻¹

**Determination of the amount of Brønsted and Lewis acid sites using the extinction coefficients from the literature:**

- Brønsted acid sites: ~ 40 μmol/g
- Lewis acid sites: ~ 90 μmol/g
Development of a NEW METODE:

Quantification of Brønsted Acid Sites on Catalyst Surfaces via Temperature Programmed Surface Reaction of n-Propylamine

VALIDATION via Calorimetry
NH₃ ads. on H-ZSM5 zeolite at 80°C
NEW METODE of Quantification of Brønsted acid sites on catalyst surfaces by temperature programmed surface reaction of n-Propylamin.
VALIDATION via Calorimetry & FTIR

Motivation:
Development of a standard characterization method for the quantification of acid sites on surfaces.
Gorte et al. developed a method that uses alkylamines as reactive probe molecules for TPSR experiments on zeolites.
It was investigated if the needed information can be readily obtained by a commercial TPD machine.

Alkylamines are protonated at Brønsted acid sites

Combination of TPSR and TPD/MS:
quantify Brønsted acid sites is the amount of desorbed olefin

Samples:
- H-ZSM5-30 (H-ZSM5 zeolite with a SiO₂/Al₂O₃ ratio of 30)
- H-ZSM5-80 (H-ZSM5 zeolite with a SiO₂/Al₂O₃ ratio of 80)

Microcalorimetry
Differential heat of ads. NH$_3$ at 80°C

**H-ZSM5-30**
SiO$_2$/Al$_2$O$_3$ ratio of 30

\[ n \text{ Brønsted acid sites} = 560 \mu\text{mol/g} \]

\[ n \text{ Brønsted acid sites} = 560 \mu\text{mol/g} \]

\[ \text{strong acidity Lewis} \]

\[ \sim 60 \mu\text{mol/g} \]

\[ \text{n Lewis acid sites from FTIR} \sim 80 \mu\text{mol/g} \]

\[ \sim 1100 \mu\text{mol/g} \]

\[ \text{weaker Brønsted acidity} \]

\[ \sim 620 \mu\text{mol/g} \]

\[ \text{irrev. ads sites} \]

**H-ZSM5-80**
SiO$_2$/Al$_2$O$_3$ ratio of 80

\[ n \text{ Brønsted acid sites} = 312 \mu\text{mol/g} \]

\[ n \text{ Brønsted acid sites} = 312 \mu\text{mol/g} \]

\[ \sim 312 \mu\text{mol/g} \]

\[ \text{n Lewis acid sites from FTIR} \sim 4 \mu\text{mol/g} \]

\[ \sim 80 \mu\text{mol/g} \]

\[ \text{Lewis acid sites} \]

\[ \text{n relevant Brønsted acid sites} = n \text{ irrev. ads sites} - n \text{ Lewis acid sites} \]

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Stoichiometric and measured acidities for H-ZSM5 zeolites
TPSR/TPD & microcalorimetry & FTIR

Quantification of Brønsted Acid Sites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stoichiometric acidity (\mu\text{mol/g})</th>
<th>FTIR (\mu\text{mol/g})</th>
<th>Microcalorimetry (\mu\text{mol/g})</th>
<th>Alkylamine TPD (\mu\text{mol/g})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM5-30</td>
<td>525</td>
<td>437</td>
<td>560</td>
<td>557</td>
</tr>
<tr>
<td>H-ZSM5-80</td>
<td>204</td>
<td>269</td>
<td>312</td>
<td>297</td>
</tr>
</tbody>
</table>

- The comparison shows that the obtained results from the TPSR are consistent with the microcalorimetry and IR measurements.

Titration of basic sites on the surface of ceria using CO$_2$ at 40°C
**Intention:** Understanding CeO$_2$ as a Deacon catalyst, characterize ceria in its fresh CeO$_2$-F and post-reaction states CeO$_2$-D.

The basic character of the ceria surface has been eliminated upon reaction, indicating that most of the basic lattice O sites are exchanged by chlorine and that the OH groups formed are rather acidic.

**DEACON reaction**

\[
4 \text{HCl} + \text{O}_2 \xrightarrow{T = 430^\circ\text{C}, \text{HCl/O}_2/\text{N}_2, 100\text{ml/min}} 2 \text{Cl}_2 + 2 \text{H}_2\text{O}
\]

**Adsorption sites on the CeO$_2$(111) surface**

Structural defects such as edges in nanoparticles $^1$ or vacancies in more open facets such as (110)$^2$

DFT calculation: formation of carbonate species with the basic O atoms 43kJ/mol

DFT calculation: partially hydroxylated surfaces or oxygen vacancies are filled by one of the O atoms of the CO$_2$ molecules 18kJ/mol

**NH$_3$ ads. 40°C**

fresh: 30 kJ/mol 75μmol/g acid sites used: 50 kJ/mol 75μmol/g acid sites

increased acidity of the chlorinated surface

---

Investigation of the oxidation process:
Oxidation of HCl to Cl₂ over bare and supported CeO₂
Oxidation of HCl to Cl\textsubscript{2} over bare and supported CeO\textsubscript{2} DEACON reaction

Heat of adsorption of O\textsubscript{2} at 200°C / HT1000
Pretreatment: H\textsubscript{2} reduction at 200°C

Best reactivity was obtained from bare CeO\textsubscript{2} and CeO\textsubscript{2}/ZrO\textsubscript{2}.

One essential parameter seems to be the reducibility of the catalyst in order to create catalytically important oxygen vacancies.

Reactivity seems to be linked with the reducibility of the surface.


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Study of catalytic relevant sites via calorimetry close to the reaction conditions:

Oxidation of alcohol over vanadium supported Al$_2$O$_3$
Oxidation of alcohol over vanadium supported $\text{Al}_2\text{O}_3$

C$_2$H$_5$OH + $\frac{1}{2}$O$_2$ $\rightarrow$ C$_2$H$_4$O + H$_2$O  \[ \Delta_R H = -178.5 \text{ kJ/mol} \]

**Catalyst:** $V_xO_y/\gamma$-Al$_2$O$_3$

**Reaction:** $T_{reaction} = 140 - 200 \degree C$

**Intention:** Determination of kinetic data: $N_{ads}$, $K_{ads}$ and $\Delta H_{ads}$ of Ethanol on $V_xO_y/\text{Al}_2\text{O}_3$

**Differential heats of Ethanol at 40^\circ C**

**Ethanol isotherms at 40^\circ C**

**Langmuir isotherms**

$R^2 = 0.99722$

$N_0 = 2.077 \text{ mmol*g}^{-1} \pm 0.030$

$K_{exp} = 1.472 \text{ hPa}^{-1} \pm 0.038$

**Kinetic parameters determined for the ethanol ads. on $V_xO_y/\text{Al}_2\text{O}_3$**

$N_{mono} = 2.077 \text{ mmol*g}^{-1}$

$K_{ads} = 1.47 \text{ hPa}^{-1}$

$\Delta H_{ads} = 90 \pm 10 \text{ kJ*mol}^{-1}$
Study of catalytic relevant sites via calorimetry close to the reaction conditions:

New insights on active sites of oxygen functionalized carbon nanotube (oCNT) for oxidative dehydrogenation (ODH)
Oxidative dehydrogenation over oxygen functionalized carbon nanotube - oCNT

Carbon based materials are active catalysts for the oxidative dehydrogenation (ODH) reaction \[1\]

The well defined active surface oxygen sites will be created by oxygen functionalization of the CNTs with HNO$_3$.

Quinone groups are believed to be the active sites. These nucleophilic oxygen species can selectively abstract hydrogen atoms \[2-5\]

**Intention:**

To establish a mechanistic model for carbon catalyzed ODH.

Ads. properties are important input for kinetic modeling.

The research project was performed in a multidisciplinary approach (quasi *in situ* adsorption microcalorimetry, *in situ* XPS, kinetics, DFT).
We choose the ODH of propane and ethylbenzene (EB) as the model reactions.

**Model reaction**

- **Propane**
  - C–H bond strength: 410.5 kJ mol\(^{-1}\)
  - Reaction: \( \text{C}_3\text{H}_8 / \text{O}_2 / \text{He} = 10/5/85 \) over oCNT
  - 400 °C, 50 ml min\(^{-1}\)

- **Propylene**
  - Production

- **Ethylbenzene**
  - C–H bond strength: 357.3 kJ mol\(^{-1}\)
  - Reaction: \( \text{C}_8\text{H}_{10} / \text{O}_2 / \text{He} = 2/1/97 \) over oCNT
  - 300 °C, 50 ml min\(^{-1}\)

- **Styrene**

**Quasi in situ Adsorption**

- Probe molecule: propane, propylene and ethylbenzene
- \( T_{\text{adsorption}} = 313K < 673K = T_{\text{reaction}} \)
- Selected catalyst: 370mg used MW oCNT #6420

**Microcalorimetry**

Differential heats of propane, propene and EB adsorption at 40°C [1]

~8 μmol/g active sites equilibrated in EB and propane ODH reaction

3-5% of the surface is covered by high-energy adsorption sites which can be correlated to 4-5% of surface oxygen determined by XPS [2]

EB reacts stronger (80 kJ/mol) than propane (45 kJ/mol).

Graphite (free of oxygen) shows a constant low level of diff. heats for propane (32kJ/mol) and propylene (40kJ/mol); reversible

O1s ranges of XP spectra

MW oCNT catalyst under different atmospheres @ 350°C.

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>$I_{C=O} / I_{C-O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EB</td>
<td>0.168</td>
</tr>
<tr>
<td>EB/O₂</td>
<td>0.283</td>
</tr>
<tr>
<td>C₃H₈/O₂</td>
<td>0.313</td>
</tr>
<tr>
<td>O₂</td>
<td>0.315</td>
</tr>
</tbody>
</table>

Atmosphere I

- C=O
- C-O

**Intensity**

- EB
- O₂

**$E_b$ / eV**

- EB/O₂ 1:1
- C₃H₈/O₂ 1:1

**REACTIVITY**

nucleophilic oxygen
ketones & quinones

quasi neutral oxygen
lactone/ester, ethers, phenols

electrophilic oxygen
carboxylic anhydrides, carboxylic acid
Site classification & quantification from microcalorimetric analyses, XPS, and TPD not shown of active surfaces of oCNT catalysts in ODH of propane and EB [1,2].

<table>
<thead>
<tr>
<th>ODH substrate</th>
<th>C\textsubscript{3}H\textsubscript{8} [1]</th>
<th>EB [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-q\textsubscript{ini} (kJ mol\textsuperscript{-1})</td>
<td>45</td>
<td>80</td>
</tr>
<tr>
<td>n\textsubscript{ads} (µmol g\textsuperscript{-1})</td>
<td>0 - 8</td>
<td>0 - 8</td>
</tr>
<tr>
<td>-q\textsubscript{ads} (kJ mol\textsuperscript{-1})</td>
<td>45±0.5</td>
<td>80±0.5</td>
</tr>
<tr>
<td>n\textsubscript{ads} (µmol g\textsuperscript{-1})</td>
<td>10 - 120</td>
<td>10 - 110</td>
</tr>
<tr>
<td>-q\textsubscript{ads} (kJ mol\textsuperscript{-1})</td>
<td>45 - 33</td>
<td>80 - 55</td>
</tr>
</tbody>
</table>

- [a] could not be determined


Sabine Wrabetz, Electronic Structure and Adsorption, Dept. of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany.
Adsorption Isotherm  40°C

Explanation:
- high energy ads. sites reacts irreversibly to C-OH groups

→ formation of H₂O during initial reaction → blocked active sites → turns the surface more hydrophilic → hindering the ads. of non-polar EB molecule

→ reversible 2nd ads. run of EB without reaction (consumed C=O groups) and hence no formation of H₂O

→ more weak ads. sites available for EB

2nd run of EB ads. reveals a drastic increase of the total adsorption capacity
Note: - Adsorption Isotherms only for oxygenated sites which are relevant for catalysis
- Adsorption isotherms of propylene and EB have not been evaluated because of irreversible processes and surface reactions.

**Energetically uniform sites**

→ Langmuir model

![Graph showing adsorption isotherm for C₃H₈ on CNTs](image)

\[ \theta = \frac{K \ p}{1 + K \ p} \]

K: Langmuir adsorption constant

\[ \theta = \frac{RT}{q_{ads}(\theta=0) - q_{ads}(\theta=1)} \ln \left( \frac{1 + \frac{p}{p^*} \exp \frac{q_{ads}(\theta=0)}{RT}}{1 + \frac{p}{p^*} \exp \frac{q_{ads}(\theta=1)}{RT}} \right) \]

\( p^* \): is a constant combining surface and molecular properties

**Energetically non-uniform sites** (decay of \( q_{ads} \) with increasing coverage) → Temkin model
Analyzing of Adsorption Isotherm  40°C

**Langmuir**

- C\textsubscript{3}H\textsubscript{8} on oCNT
- C\textsubscript{3}H\textsubscript{8} on B\textsubscript{2}O\textsubscript{3}-oCNT
- Langmuir fit

\[ q_{\text{initial}} = 45\text{kJ/mol} \]

**Temkin**

- C\textsubscript{3}H\textsubscript{8} on CNTs
- C\textsubscript{3}H\textsubscript{8} on B\textsubscript{2}O\textsubscript{3}-CNTs
- Temkin fit

<table>
<thead>
<tr>
<th></th>
<th>( K ) (Langmuir adsorption constant)</th>
<th>( p^* ) (Temkin factor, combining surface and molecular properties)</th>
</tr>
</thead>
<tbody>
<tr>
<td>oCNT</td>
<td>2250 bar\textsuperscript{-1} (45kJ/mol)</td>
<td>0.0065 bar</td>
</tr>
<tr>
<td>B\textsubscript{2}O\textsubscript{3}-oCNT</td>
<td>370 bar\textsuperscript{-1} (40kJ/mol)</td>
<td>0.048 bar</td>
</tr>
</tbody>
</table>
Electronic structure theory calculations by DFT [1]

Energy Diagram for ODH of propane and EB (1st H-abstraction) over zigzag-termination of the carbon cluster

Propane

- the barrier for activation of propane is higher than for EB
- the zigzag-termination is much more active than the armchair geometry

Ethylbenzene

1st H-abstraction from EB over zigzag-termination

Quinones

Hydrogen

Carbon

Conclusion

- Classification and quantification of the carbon surface under reaction conditions.
- EB: lower activation barriers and stronger irreversible adsorption well correlate with the lower stability of the benzylic C-H bond over the aliphatic C-H bond in propane.

Two-site redox kinetics:

- The redox cycle of surface C=O and C-OH groups is the key process, which includes only a small fraction of surface O species (2.4 m² g⁻¹, 8 μmol/g, 3-5% Calo/XPS) and favorably occurs at the zigzag-termination of sp2 carbon planes.
Study of catalytic relevant sites via calorimetry close to the reaction conditions:

Selective oxidation of propane to acrylic acid over MoVTeNb oxide catalyst
Intention: study of the post-reaction state of the surface “used catalyst” in comparison with the prepared state of the surface “fresh catalyst” in order to describe a structure-selectivity relationship.

**Adsorption**

- **propane** as probe molecule
- **Microcalorimetry**:
  - $T_{\text{adsorption}} = 313 \text{K} < 673 \text{ K} = T_{\text{reaction}}$
  - selected catalysts: different selective catalysts
    - pure-phase MoVTeNb
    - modified MoVTeNb by an oxidizing agent
    - MoV oxide

**Catalyst:**

- Highly crystalline MoVTeNb oxide catalyst
- Particle size: Ø 199 nm length, Ø 115 nm width

**Equation:**

\[
\text{propane} + 2 \text{O}_2 \rightarrow \text{acrylic acid} + 2 \text{H}_2\text{O}
\]

\[T = 673 \text{K}, \ p=1\text{bar}
\]

\[C_3/O_2/H_2O/N_2 = 3/6/40/51 \text{ (vol.-%)}
\]

**Catalyst:**

- propane to acrylic acid
- Selective oxidation of propane to acrylic acid over M1


Active catalyst surface stable under ambient conditions?

**CATALYTIC TEST**
(provisional / used catalyst)

Propane oxidation data obtained from fresh and used MoVTeNb catalyst

---

**SURFACE STUDY**
(provisional / used catalyst)

*in situ* XPS: surface element composition during and after PO over MoVTeNb catalyst

---

Surface composition of the used M1 is similar to the composition measured in the *in situ* experiment in the presence of steam.


---

*ex situ* surface analysis of the used catalyst can be done

---

Careful termination of the reaction under steam and N₂ with a cooling rate of 5 K/min.
Propane adsorption isotherms of different selective catalysts

- **phase-pure MoVTeNb, \( S_{aa} = 53\% \)**
  - \( S_{\text{propane}} = 11.4 \text{ m}^2/\text{g} \)

- **oxidized MoVTeNb, \( S_{aa} = 37\% \)**
  - \( S_{\text{propane}} = 10.3 \text{ m}^2/\text{g} \)

- **MoV oxide, \( S_{aa} = 1.8\% \)**
  - \( S_{\text{propane}} = 13.4 \text{ m}^2/\text{g} \)

---

Selectivity to acrylic acid at 55% conversion / %

- phase-pure MoVTeNb oxide
- oxidized MoVTeNb oxide
- MoV oxide
- \( \text{MoO}_3 \)
- \( \text{TeO}_2 \)
- \( \text{V}_2\text{O}_5 \)
- \( \text{Nb}_2\text{O}_5 \)

---

Amount of adsorbed propane / \( \mu\text{mol}\cdot\text{m}^{-2} \)

- 0
- 0.5
- 1
- 1.5
- 2
- 2.5
- 3
Differential heats of adsorbed propane of different selective catalysts

**phase-pure MoVTeNb, $S_{aa} = 53\%$**

$S_{propane} = 11.4 \text{ m}^2/\text{g}$

**oxidized MoVTeNb, $S_{aa} = 37\%$**

$S_{propane} = 10.3 \text{ m}^2/\text{g}$

- Strength of interaction of propane with the surface changes during reaction.
- $S_{aa}$ is correlated with energetically homogenous distributed propane adsorption sites
- $S_{aa}$ is associated with reduced interaction of propane and active surface sites
- $CO \& CO_2$ ads. exp. : weak acid/basic sites
Structure-selectivity relationship

- the prepared state of the surface is different from the post-reaction state of the surface
  - dynamic surface during reaction

- remarkable selective ($S_{aa} = 53\%$) MoVTeNb oxide surface is characterized by high density of energetically uniform propane adsorption sites with weak acid-base character

- The weaker interaction of propane with the post-reaction state of the surface is apparently favorable for the catalytic performance; perhaps because of facile product desorption.

Study of catalytic relevant sites via calorimetry under reaction conditions:

**Active Site Quantification on Propylene Metathesis over MoOx/SBA-15**
Active Site Quantification on Propylene Metathesis over MoOx/SBA-15

Intention: Studying of the catalytically active surface sites - quantification

**Adsorption Microcalorimetry:**
- propylene as probe molecule
- $T_{\text{adsorption}} = 50^\circ\text{C} = T_{\text{reaction}}$
- selected catalysts: different activity

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metathesis rate $\mu$mol/m$^2$/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>13% MoOx/SBA15</td>
<td>3.0</td>
</tr>
<tr>
<td>10% MoOx/SBA15</td>
<td>13.0</td>
</tr>
<tr>
<td>5% MoOx/SBA15</td>
<td>1.5</td>
</tr>
<tr>
<td>SBA15</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Metall-carbene sites (M=CHR) generated from the reactant propene are believed as the active centers for the metathesis.

Active Site Quantification on Propylene Metathesis over MoOx/SBA-15

Propene Metathesis Activity

\[ T = 50 \, ^\circ\text{C} \]

- 13 % MoOx/SBA15
- 10 % MoOx/SBA15
- 5 % MoOx/SBA15

SBA15

15 \( \mu \text{mol}_\text{Mo=CHR} \, \text{g}^{-1} \)

3.0 \( \mu \text{mol}_\text{Mo=CHR} \, \text{g}^{-1} \)

3.7 \( \mu \text{mol}_\text{Mo=CHR} \, \text{g}^{-1} \)

Time on stream / h

- Activity strongly depends on the Mo loading

Microcalorimetry

Differential heat of propene adsorbed on MoOx/SBA15

\[ T_{\text{reaction}} = 50^\circ \text{C} \]

- 15 \( \mu \text{mol} \, \text{g}^{-1} \)
- 3-4 \( \mu \text{mol} \, \text{g}^{-1} \)

Correlation between amount & strength of \( \text{C}_3\text{H}_6 \) adsorption sites and catalytic activity.

Post-reaction carbene titration

Active site counting was performed after metathesis using post-reaction ethene-\( d_4 \) (\( \text{CD}_2=\text{CD}_2 \)) metathesis to titrate the formed metal-carbene (Mo=CH-CH\(_2\)) sites.

\[ \text{Mo=CH-CH}_3 + \text{CD}_2=\text{CD}_2 \rightarrow \text{Mo=CD}_2 + \text{CD}_2=\text{CH}_2-\text{CH}_3 \]
Active Site Quantification on Propylene Metathesis over MoOx/SBA-15

A long decay time and fine structure in the exothermic signal indicate reactive adsorption.

Generation of the active Metall-carbene sites (M=CHR).

K_t = 1742 s
K_t = 2786 s
7 h
10 h

Metathesis activity
The active catalyst is characterized by:
- higher amount of ads. sites for propylene
- strong and irreversible adsorption of propylene on MoOx sites
- energetically homogenously distributed active sites

Catalytic activity is directly correlated with the strength of the propylene interaction with the active surface site.

ca. 1% of Mo atoms formed active sites

Study of catalytic relevant sites via calorimetry under reaction conditions:

Silver as a catalyst for the ethylene epoxidation
- Ag-O system in catalysis -
The Ag-O system in catalysis

- **Ag** is used as a catalyst in two important large scale processes in the chemical industry, the **ethylene epoxidation** and **methanol oxidation**. The **economic relevance** of these processes motivated the extensive investigation of the Ag-O system in past years. The mechanisms behind the **remarkable selectivity** are still unclear.

- The current understanding of oxidation reactions on Ag catalysts rely on the knowledge about the **oxygen species formed on silver** [1].

- Final goal is to safely **translate the electronic signatures** obtained by X-ray spectroscopies into **structural information**, which can be used to construct reaction mechanisms [4,5].

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The Ag-O system in catalysis

epoxidation of ethylene over silver catalyst

\[ T = 180 - 230 \, ^\circ C \]

Intention: to construct reaction mechanisms. The energetic data provided by calorimetry is essential to any reaction mechanism. It will provide additional information to interpret the spectroscopic measurements and it will also be used as reality check for the predictions of the computational calculations.

**quasi in situ**

**Adsorption:**

\[ \star \quad T_{\text{reaction}} = 230 \, ^\circ C \]

**Microcalorimetry**

\[ \star \quad \text{selected catalyst: Ag powder <45micron} \]
The Ag-O system in catalysis

Initial State

Cleaning of the silver surface observed by calorimetry
Differential heat of O$_2$ ads. at 150°C

DFT
- O$_2$ adsorbs more strongly on Ag modified by O$_\text{sub}$ and defect sites: $E_{\text{ads.}} = 180 – 240$ kJ/mol
- Surface reconstructions: $E_{\text{ads.}} = 120 – 160$ kJ/mol

$q_{\text{diff}}$↑ is due to the exothermic reaction of oxygen atoms with the carbon contaminants (CH$_x$/CO$_3$).

References:
- 200 to 400 kJ/mol: combustion of impurities $^4$
- 50 to 420 kJ/mol: combustion of contaminants $^5$
- 171 kJ/mol at 170°C: combustion of impurities $^6$

Note: mild pre-treatment (150°C, 0.1 mbar, 2h) is enough to clean the samples also observed by NAP-XPS


The Ag-O system in catalysis

Steady State

Differential heat of O\textsubscript{2} ads. on the clean Ag surface at 230°C = T\text{reaction}

References:

[12] H is the standard enthalpy of formation for model adsorbates at 298.15 K

- O\text{ads.}: \( H = -63.0 \text{ kJ/mol} \)
- O\textsubscript{2 ads.}: \( H = -44.5 \text{ kJ/mol} \)
- O\text{ads.} / O\text{surface}: \( H = -103.0 \text{ kJ/mol} \)


- 109 – 99 kJ/mol

Note: The enthalpy is insignificantly affected by the temperature (DFT)

References:

The Ag-O system in catalysis

Steady State

Differential heat of O\textsubscript{2} ads. on the clean Ag surface at 230°C = \textit{T}_{\text{reaction}}

\[ \text{Specific surface area of Ag for O}_2 \text{ at } \text{\textit{T}}_{\text{reaction}} = 230{\degree} \text{C} \]

\[ S_{\text{Ag}} = \frac{n_{\text{ads}} \cdot \text{ Avogadro constant}}{\text{Surface sites density } \Gamma_{\text{fcc lattice, Ag}}} \]

\[ 2 \cdot 10^{-6} \text{ mol} \cdot 6.022 \cdot 10^{23} \text{ particles} \cdot \text{ cm}^2 \]

\[ \frac{\text{g} \cdot 1.4 \cdot 10^{15} \text{ atoms} \cdot \text{ mol}}{\text{g}} \]

\[ S_{\text{Ag-O}} = 0.86 \text{ m}^2/\text{g} \]

\[ \text{BET}_{\text{N}_2, 77K} = 0.72 \text{ m}^2/\text{g} \]

\[ \Delta S = 0.14 \text{ m}^2/\text{g} \]

The excess can be due to dissolving of oxygen into the Ag subsurface.
### Experiment

**Dissociative adsorption**

- $10^{-3}$, $10^{-2}$, $10^{-1}$
- 1, 4, 10 mbar

### Theory

#### DFT calculations

<table>
<thead>
<tr>
<th>System</th>
<th>Eads per 1/2 O$_2$ [kJ/mol]</th>
<th>Eads per O$_2$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reconstructions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_{ads}$ stronger on Ag(110)</td>
<td><strong>60-80</strong></td>
<td>120-160</td>
</tr>
<tr>
<td>Unreconstructed O$_{ads}$ on hollow sites of Ag(111)</td>
<td>40-60</td>
<td>80-120</td>
</tr>
<tr>
<td>On subsurface O</td>
<td><strong>110-120</strong></td>
<td>220-240</td>
</tr>
<tr>
<td>Surface defects</td>
<td><strong>90-120</strong></td>
<td>180-240</td>
</tr>
<tr>
<td>Subsurface</td>
<td>&lt;10</td>
<td>10</td>
</tr>
<tr>
<td>Grain boundaries</td>
<td>10-20</td>
<td><strong>20-40</strong></td>
</tr>
<tr>
<td>O$_2$ clean surface</td>
<td>5-10</td>
<td>10-20</td>
</tr>
<tr>
<td>O$_2$ on sub O</td>
<td>10-20</td>
<td><strong>20-40</strong></td>
</tr>
<tr>
<td>O$_2$ on defects</td>
<td>20-30</td>
<td><strong>40-60</strong></td>
</tr>
</tbody>
</table>

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The Ag-O system in catalysis

O1s XPS spectra for Ag powders
measured in situ under 0.5 mbar O₂ at 180 °C

The distribution of O species on the Ag surface dynamically changes with time as the catalyst surface equilibrates with the gas phase at mbar pressure and temperatures typical of alkene (180-230 °C).

→ Dynamics at 180 °C
Ag-O dynamics depend on time / temperature and pressure

<table>
<thead>
<tr>
<th>$T$ °C</th>
<th>$p_{O2}$ mbar</th>
<th>$n_{ads}$ $\mu$mol$O_2$/g$Ag$</th>
<th>$q_{diff}$ kJ/mol</th>
<th>Ag-O dynamics</th>
</tr>
</thead>
</table>
| Cleaning 150 | $< 10^{-1}$ | 0.5 | $>120 - 260$ | ➢ dissociative adsorption  
➢ cleaning the surface from CH$_x$/CO$_3$  
➢ initial formation of the surface reconstructions |
| Reaction 230 | $10^{-1} - 1$ | 1.5 | $>50 - 120$ | ➢ extensive structural changes *  
➢ oxygen begins to dissolve to subsurface **  
oxide-like structures = 60 - 80 kJ/mol$[^8]$  
➢ chemisorbed oxygen modified by a subsurface oxygen *** |
| Reaction 230 | $>1 - 10$ | 1 | $< 50$ | ➢ molecular oxygen adsorbed on surface vacancies ****  
➢ formation of electrophilic oxygen *****  
➢ O$_2$ on subsurface oxygen |

* Ag atoms moving from defects and edges to form the reconstructions. Island formation at low coverages.
** Formation of oxide like reconstruction and/or surface oxide layer.
*** Depends on time/temperature because its formation is limited by oxygen diffusion to subsurface.
**** Proposed by theory and calorimetry. In this case the time/temperature dependence is related to the defect formation.
***** The active site for epoxidation! Two interpretations are believed: O$_2$ stabilized on defects on O covered surface (DFT) or surface oxygen modified by sub-surface species (XPS)
Study of catalytic relevant sites via calorimetry under reaction conditions:

1-hexyne adsorption at $T_{\text{react.}}$ on supported ceria, being unexpectedly active in the hydrogenation of 1-hexyne
Intention: Does calorimetry offer the possibility to distinguish between catalysts of similar characteristic properties (IR, XRD, TEM, XPS, BET), but different catalytic activity?

Adsorption Microcalorimetry:

- 1-hexyne as probe molecule
- \( T_{\text{adsorption}} = 80^\circ \text{C} \) \( \leftarrow \) as the Arrhenius plot of 1-hexyne hydrogenation is smooth in the whole 75 - 135 \(^\circ\)C range
- selected catalysts: different active catalysts
  - 20 wt\% CeO\(_2\)/TiO\(_2\) - WI very active (wet impregnation; # 17380)
  - 20 wt\% CeO\(_2\)/TiO\(_2\) - DI less active (dry impregnation; # 17378)
1-hexyne adsorption at $T_{\text{react.}} = 80^\circ\text{C}$ on supported ceria

**Differential heats**

![Graph showing differential heats for 1-hexyne adsorption](image)

- **active 20 wt% CeO$_2$/TiO$_2$ –WI**
- **less active 20 wt% CeO$_2$/TiO$_2$ -DI**

**DFT calculations** [1]

The initial step of the C$_2$H$_2$ hydrogenation to C$_2$H$_4$ is the dissociative homolytic adsorption of C$_2$H$_2$. This process is strongly exothermic. (-1.77eV)

**Dehydrogenation and adsorption steps**

- **$\Delta H_{\text{ads}}$, initial stage**: 
  - < **200 - 900 kJ/mol**
  - $10\mu\text{mol/g}$ → very strong irreversible ads.
  - → multiple dehydrogenation steps [1]
  - formation of stable surface intermediates [2]

  **$\Delta H_{\text{ads}}$, plateau**
  - ~ **200 kJ/mol**
  - $60\mu\text{mol/g}$ → dissociative homolytic adsorption of C$_6$H$_{10}$
  - → single dehydrogenation step [1]

---


1-hexyne adsorption at $T_{\text{react.}} = 80^\circ C$ on supported ceria

Adsorption Isotherm

$\Delta H_{\text{ads}} > 50$kJ/mol - chemisorption

very active 20 wt% CeO$_2$/TiO$_2$ –WI $\rightarrow$ 190 $\mu$mol/g reacted 1-hexyne molecules

less active 20 wt% CeO$_2$/TiO$_2$ -DI $\rightarrow$ 130 $\mu$mol/g reacted 1-hexyne molecules
1-hexyne adsorption at $T_{\text{react.}} = 80^\circ \text{C}$ on supported ceria

Corresponding integral heats

*The temporal evolution of the thermo signal during 1-hexyne ads.*

1$^{\text{st}}$ ads. step = 0.00023 mmol/g
1$^{\text{st}}$ ads. step = 0.00039 mmol/g

4$^{\text{th}}$ ads. step = 0.0031 mmol/g
3$^{\text{rd}}$ ads. step = 0.0029 mmol/g

5$^{\text{th}}$ ads. step = 0.0053 mmol/g
4$^{\text{th}}$ ads. step = 0.0050 mmol/g

7$^{\text{th}}$ ads. step = 0.0153 mmol/g
7$^{\text{th}}$ ads. step = 0.0166 mmol/g

The adsorption signature is composed of two main contributions:
- physisorption / fast-signal
- reaction / delayed signal

The most active sample has such sites that will hold 1-hexyne very weakly until the molecule chemisorb stronger. **dynamic**

In the less active sample the physisorbed molecule undergoes much faster side reactions or strong chemisorption.
The regeneration of the catalyst surface using H₂ (at 150°C) has been somewhat more successful for the more active catalyst.
Summary

Yes, calorimetry is a useful tool to distinguish between catalysts of similar characteristic properties.

Key-note:
under reaction conditions a significant portion of the surface sites is covered by dehydrogenated species and is not available for hydrogenation. Nevertheless, the remaining small number of surface sites is active and selective in alkyne hydrogenation.

The ads. of 1-hexyne at $T_{\text{react.}}$ is composed of 2 main processes:
1) unspecific adsorption (physisorption <50kJ/mol)
2) time-consuming secondary process is due to single or multiple dehydrogenation steps and potentially oligomerization. [10] (>50 – 900 kJ/mol)

The most active catalyst is characterize by:
- higher amount of adsorption places for 1-hexyne  190 $\mu$mol/g
- slightly easier regeneration of the surface after 1-hexyne contact at $T_{\text{react.}}$
- pronounced trapped and phys. state of the adsorbates to find the most suitable place for reaction $\rightarrow$ dynamic surface is apparently favorable for the catalytic performance

Reactants induced responses of catalyst surface:

Propane and ethane ads./des. cycles (40°C) on MoV oxide model catalyst for oxidative dehydrogenation of alkanes.
MoV oxide\(^1\) has been studied as a **model system** for a better understanding of the complex V-containing bulk MoVTeNb oxide catalyst.

→ **different dynamic behavior** of the MoV oxide surface under reaction conditions due to the different chemical potential of the feeds while the chemical potential of the solid remains the same.

- specific ads. phenomena of PROPANE and ETHANE at 40°C
- reactants induced response of the MoV oxide surface via ads./des. cycles.
Differential heat of 
**propane** adsorption at 40°C

- **used surface**
- **Dynamic response of the surface**
- **1st run**
- **2nd run**
- **3rd run**

Contrast

Differential heat of 
**ethane** adsorption at 40°C

- **fresh surface**
- **1st run**
- **2nd run**
- **3rd run**

- **condensation enthalpy of propane at 40°C**: 13.69 kJ/mol
- **condensation enthalpy of ethane at 40°C**: <5 kJ/mol

- **$S_{\text{specific for propane}} \approx 3.6 \, \text{m}^2/\text{g}$**
- **$BET = 25.52 \, \text{m}^2/\text{g}$**

- **$S_{\text{specific for ethane}} \approx 2.9 \, \text{m}^2/\text{g}$**
- **$BET = 25.52 \, \text{m}^2/\text{g}$**

$S_{\text{MoV oxide}} = n_{\text{ads}} \cdot \text{Avogadro const.} \cdot S_{1:1} \cdot \text{cross-section area}$

- Assumed 39Å² for propane
- Assumed 22Å² for ethane
Differential heat of propane adsorption at 40°C

\[ \text{In-situ photoelectron spectroscopy} \]

with TOS (presents of \( \text{H}_2\text{O} \)) the surface is progressively enriched in V\(^{5+} \), which leads to a decrease in selectivity. \(^1\)

- Segregation of V\(^{5+} \) occurs already at r.t.
- Alkanes are already activated at r.t.
- Dynamic nature of the surface
- Very strong interaction of propane with used surface explains the decrease in selectivity caused by V-segregation

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Reactants induced dynamic responses of catalyst surface:

CO chemisorption cycles (30°C) on Ni/MgAl oxide catalyst for dry reforming of methane (DRM)
Task: study the influence of structural and compositional properties of nickel catalysts on the catalytic performance during DRM

Dry reforming (DRM): \[ \text{CO}_2 + \text{CH}_4 \xrightarrow{\text{Ni} \ 900 \, ^\circ\text{C}} 2 \text{CO} + 2 \text{H}_2 \quad \Delta H^0 = 247 \, \text{kJ/mol} \]

Catalyst preparation pathway:
- synthesized by constant pH co-precipitation with Ni contents between 0 and 55 wt.-%.
- decomposition to mixed oxides by calcination at 600°C

Obtained Ni/MgAl oxide catalyst
- reduction at 1000°C
- \( d_{\text{p,Ni}} = 7 \sim 9 \) nm in all samples
- \( d_{\text{p,Ni}} = 7 \sim 20 \) nm only in the 50wt% sample
catalysis / overgrowth / reactivity

- HR-TEM images of 2.5, 5 and 50 mol% Ni/MgAl oxide
- EDX, NEXAFS & FTIR/CO/77K: overgrowth might be interpreted as a NiAl$_2$O$_4$ spinel

**Activity**: conversion $X_{\text{CH}_4,10h}$ / %

- Structure sensitivity
- Free Ni sites are essential

CO adsorption at 30°C using microcalorimetry

50 mol% Ni/MgAl oxide
\( X_{\text{CH}_4,10\text{h}} = 73 \% \)

\[ \text{differential heat of adsorbed CO} \]
\[ \text{kl mol}^{-1} \text{ at 30°C} \]
\[ \text{amount of adsorbed CO at 30°C mmol g}^{-1} \]

\[ \sim 1.5 \mu\text{mol/g} \]
Oxidation

5 mol% Ni/MgAl oxide
\( X_{\text{CH}_4,10\text{h}} = 50 \% \)

\[ \text{NiAl}_2\text{O}_4 + \text{MgO} \uparrow \]

\[ \sim 3 \mu\text{mol/g} \]
Ni catalyzed oxidation of CO under consumption of surface oxygen species.

The differential heat profiles are dominated by the presence of nickel

Reactants induced dynamic responses of the catalyst surface was simulated via ads./des. cycles of CO at 30°C using microcalorimetry.

50 mol% Ni/MgAl oxide

$X_{\text{CH}_4\cdot 10\text{h}} = 73\%$

5 mol% Ni/MgAl oxide

$X_{\text{CH}_4\cdot 10\text{h}} = 50\%$

Catalytically relevant Ni$^0$ is back again!

Overgrowth NiAl$_2$O$_4$ seems to prevent the dynamic phenomena on Ni nanoparticles.

---

Estimation of the enthalpy of formation of the transition state (activation barrier):

ethane & ethylene and propane & propylene ads. on the Vanadium oxide-based and Metal-free catalysts for ODH
Vanadium Oxide-based and Metal-free Catalysts in the ODH of Ethane and Propane

Catalysts

- Identification of differences and similarities in the reaction network.

structurally similar functional groups:

V-OH / C-OH  
V=O / C=O  
V-O-V / C-O-C

Bulk MoVTeNb oxide, 6V/SBA-15 and P/oCNT have been compared in the ODH of C$_2$H$_6$ and C$_3$H$_8$ under identical conditions.  

**Similarities and Differences** in the reaction network

Strong temperature dependence $\rightarrow$ **different transition states**

---

Microcalorimetry

C$_2$H$_6$, C$_2$H$_4$, C$_3$H$_8$, C$_3$H$_6$ at 40°C

**enthalpy of formation of the transition state**

Note: $\Delta H_{ads.} \neq T_{ads.}$; ads. in quasi-equilibrium; intermediates occur in pseudo-steady-state

---

Creation of an active catalyst surface

- Feed of 10% hydrocarbon (C_3H_8 or C_2H_6) and 5% oxygen in helium with a total flow rate of 20 mL min\(^{-1}\).
- \( T_{\text{reaction}} = 400^\circ\text{C} \) for 6V/SBA-15, 360\(^\circ\text{C} \) for P/oCNT and 350\(^\circ\text{C} \) for M1
- The reaction was performed at a steady state for 20 h, subsequently, the cell was cooled down to RT in pure helium.

**ODH - Oxidative Dehydrogenation**

Adsorption Experiments
C₃H₈ & C₃H₆ Adsorption at 40°C

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Adsorption Experiments

$\text{C}_2\text{H}_6$ & $\text{C}_2\text{H}_4$ Adsorption at 40°C

**Adsorption Experiments**

$\text{C}_2\text{H}_6$ & $\text{C}_2\text{H}_4$

**Sabine Wrabetz**, Electronic Structure and Adsorption, Dept. of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany
**Data Discussion**

<table>
<thead>
<tr>
<th></th>
<th>M1</th>
<th>6V/SBA-15</th>
<th>P/oCNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{\text{BET}}$ m$^2$g$^{-1}$</td>
<td>10.6</td>
<td>355</td>
<td>229</td>
</tr>
<tr>
<td>$V_{\text{surf, O}}$ nm$^3$</td>
<td><strong>30</strong></td>
<td>1113</td>
<td>1063</td>
</tr>
<tr>
<td>$\Gamma_V$ atoms nm$^2$</td>
<td>1.7</td>
<td><strong>1.9</strong></td>
<td>2.8</td>
</tr>
<tr>
<td>$\Gamma_{\text{C3H8}}$ molecules nm$^2$</td>
<td><strong>0.44</strong> (63 kJ/mol)</td>
<td><strong>0.0014</strong> (52 kJ/mol)</td>
<td>0.013 (36 kJ/mol)</td>
</tr>
<tr>
<td>$V_{\text{surf,C3H8 ads.}}$</td>
<td>~4</td>
<td>~150</td>
<td></td>
</tr>
<tr>
<td>$\Gamma_{\text{C3H8,consumption, 0 mmol g}^{-1}}$</td>
<td><strong>5.3 ±0.2</strong></td>
<td>0.45 ±0.006</td>
<td>0.21 ±0.004</td>
</tr>
<tr>
<td>$\Gamma_{\text{C2H8,consumption, 0 mmol g}^{-1}}$</td>
<td><strong>5.4 ±0.2</strong></td>
<td>0.055 ±0.001</td>
<td>0.03 ±0.001</td>
</tr>
<tr>
<td>$q_{\text{diff}}$ (C$_3$H$_8$)</td>
<td><strong>79 / 63</strong> rev. ads.</td>
<td><strong>52 / 44</strong> irrev. ads.</td>
<td>36 rev. ads.</td>
</tr>
<tr>
<td>$q_{\text{diff}}$ (C$_2$H$_6$)</td>
<td>44 rev. ads.</td>
<td>14 rev. ads.</td>
<td>14 rev. ads.</td>
</tr>
<tr>
<td>$q_{\text{diff}}$ (C$_2$H$_4$)</td>
<td>34 rev. ads.</td>
<td>14 rev. ads.</td>
<td>14 rev. ads.</td>
</tr>
<tr>
<td>$E_a$, propane</td>
<td>80 ±3</td>
<td>110 ±2</td>
<td>103 ±7</td>
</tr>
<tr>
<td>$E_a$, ethane</td>
<td>90 ±2</td>
<td>121 ±2</td>
<td>110 ±7</td>
</tr>
<tr>
<td>intrinsic barrier for propane activation</td>
<td><strong>143</strong> (63 kJ/mol)</td>
<td><strong>162</strong> (53 kJ/mol)</td>
<td>139</td>
</tr>
<tr>
<td>intrinsic barrier for ethane activation</td>
<td><strong>124</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**6V/SBA-15:**
- $\Gamma_{\text{C3H8}} = 0.0014$ molecules nm$^{-2}$
- Intrinsic barrier for C$_3$H$_8$ activation = 162 kJ/mol
- DFT calculations by Rozanska $^2$ = 160 kJ/mol due to monomeric species $\rightarrow \sim 0.1\%$ of all V atoms.

$\sim 1\%$

- Intrinsic barrier for C$_3$H$_8$ activation = 154 kJ/mol
- DFT calculations by Rozanska $^2$ = 148 kJ/mol due to silica-supported vanadium oxide dimers $\rightarrow \sim 0.6\%$ of all V atoms.

---

Conclusion

Microcalorimetry and DFT: - quantification of propane adsorption sites in vanadium oxide monolayer catalysts - resolves different degrees of $V_xO_y$ oligomerization

<table>
<thead>
<tr>
<th>$V_xO_y$</th>
<th>Microcalorimetry (kJ/mol)</th>
<th>Density functional (DFT) Energy barriers (kJ/mol)</th>
<th>Microcalorimetry % of the total amount of $V_{\text{surf}}$:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer (a)</td>
<td>162</td>
<td>160</td>
<td>0.1</td>
</tr>
<tr>
<td>Dimer (b)</td>
<td>154</td>
<td>148</td>
<td>0.6</td>
</tr>
<tr>
<td>trimer</td>
<td>143</td>
<td>143</td>
<td></td>
</tr>
<tr>
<td>tetramer</td>
<td>143</td>
<td>139</td>
<td></td>
</tr>
</tbody>
</table>

ODH of propane over M1 phase: tetrarers of vanadium oxide species have been postulated to be the required ensemble size.

Structure - Activity Relationship
Higher activity correlates with:
- higher density of $C_3H_8$ adsorption sites
- lower intrinsic barrier for $C_3H_6$ formation

Conclusion

- Microcalorimetry and DFT: quantification of propane adsorption sites in vanadium oxide monolayer catalysts
  - resolves different degrees of $V_xO_y$ oligomerization

<table>
<thead>
<tr>
<th>$V_xO_y$</th>
<th>Microcalorimetry</th>
<th>Density functional theory DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intrinsic barrier for $C_3H_8$ activation $kJ/mol$</td>
<td>Energy barriers $kJ/mol$</td>
</tr>
<tr>
<td>Monomer (a)</td>
<td>162</td>
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<td>148</td>
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<td></td>
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</tr>
<tr>
<td>tetramer</td>
<td>143</td>
<td>139</td>
</tr>
</tbody>
</table>

Here, we use density functional theory (DFT) to provide information that cannot be easily obtained from experiments.

Limitations of method:

Propane ads. on vanadium-phosphorus-oxide / VPO

at $T_{\text{reaction}} = 100 - 400^\circ\text{C}$
Natural gas as raw material
Methane
Ethane
Propane
Butane

\[ \text{Olefines, Oxygenates} \]
Ethane, Ethylene
Ethylene, Acetic acid
Propylene, Acrylic acid
Butylenes, Butadiene,
Maleic anhydride

**Intention:**
Determination of kinetic data: \( N_0, K \) and \( \Delta H_{\text{ads}} \) of alkanes on VPO at \( T_{\text{reaction}} \)

**Adsorption**
\[ \text{propane, ethane and n-butane as probe molecule} \]

**Microcalorimetry:**
\[ T_{\text{adsorption}} = 400, 300, 200, 100 \text{ and } 40^\circ\text{C} \]

selected catalyst: VPO \#10449
The temporal evolution of the thermo signal during propane ads. at 400°C

Catalyst was oxidized at 400°C for 2h

Integral heat / pressure

Classical pressure profile

Calorimetric experiments at 400, 300, 200 and 40°C

reaction

n_ads.

VPO

vanadium-phosphorus-oxide - VPO

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Differential heat of propane / ethane / n-butane

Catalyst was oxidized at 400°C for 2h

n_{saturation} \sim 1 \, \mu\text{mol}/g

n_{saturation} \sim 2 \, \mu\text{mol}/g

n_{saturation} \sim 3.5 \, \mu\text{mol}/g

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Validation

\textit{in situ} DSC and Microcalorimetry

C$_2$H$_4$ adsorption at 40°C on Ag catalyst ethylene epoxidation
Case study: Validation, C₂H₄ adsorption on Ag catalyst

In-situ DSC
30°C, total flow 30mlm, Ptotal 1,15bar
12 hours SynAir 300°C

\[ \Delta H_{\text{ads}} = -94 \text{kJ/mol(C}_2\text{H}_4) \]

N(C₂H₄)=26μmol/g(cat)
reversible

Microcalo
40°C, Prange 0-3mbar
3 hours SynAir 300°C

\[ \Delta H_{\text{ads}} = -87\text{-}33 \text{kJ/mol(C}_2\text{H}_4) \]

N(C₂H₄)=33μmol/g(cat)
reversible

Andrey Tarasov, FHI MPG
Case study: Validation, $\text{C}_2\text{H}_4$ adsorption on Ag catalyst

In-situ DSC
30°C, total flow 30ml/m, $P_{\text{total}}$ 1.15bar, $P_{\text{C}_2\text{H}_4}$ 0.6mbar
12 hours SynAir 300°C

$\Delta H_{\text{ads}} = -94 \text{kJ/mol(C}_2\text{H}_4)$
$N(\text{C}_2\text{H}_4) = 26 \mu\text{mol/g(cat)}$

Microcalo
40°C, Range 0-3mbar
3 hours SynAir 300°C

$\Delta H_{\text{ads}} = -87-33 \text{kJ/mol(C}_2\text{H}_4)$
$N(\text{C}_2\text{H}_4) = 33 \mu\text{mol/g(cat)}$

Low energy centers may not be concerned in the flow conditions
Case study: Validation, $\text{C}_2\text{H}_4$ adsorption on Ag catalyst

**In-situ DSC**

30°C, total flow 30mlm, $P_{\text{total}}$ 1.15bar, $P_{\text{C}_2\text{H}_4}$ 0.6mbar

12 hours SynAir 300°C

**Heat flow**

$\text{C}_2\text{H}_4$

**Desorption and readsorption are occurring simultaneously with diffusion**

**Microcalo**

40°C, Prange 0-3mbar

3 hours SynAir 300°C

\[ Q / \text{kJ/mol(C}_2\text{H}_4) \]

\[ N (\text{C}_2\text{H}_4) / \text{mmol/g} \]

Low energy centers may not be concerned in the flow conditions

In UHV systems diffusion takes part in a very limited extent, while readsorption can be avoided using sufficiently high pumping speed
The adsorbate-adsorbent energy of interaction
(derived from the heat measurements)
is a basic data for any modelling and understanding.

- Calorimetric data are basic: they are a prerequisite for any understanding of adsorption
- To be fully meaningful and independent from the calorimetric procedure, these data should be expressed in terms of energy or enthalpy of adsorption or immersion, not in “heats”
- For this purpose, the total calorimetric set-up and procedure must be carefully studied
- Calorimetry is sensitive and quantitative, but not specific, therefore well complemented by spectroscopic techniques

**Determination of kinetic data:** $N_{ads}$, $K_{ads}$, $\Delta H_{ads}$, $SSA_{m2/g}$

Microcalorimetry alone or combined with to other techniques is a very powerful/sensitive tool to probe catalytically active surfaces quantitatively.

Quantitative data (*reversibility, heat of adsorption, number of adsorption sites, equilibrium constant*) provide a basis for theoretical modeling and can contribute to a better understanding of the complex microkinetics.

Microcalorimetry can applied under or close to reaction conditions!
→ investigation of the catalytic relevant surface sites
Literature

- **Calorimetry and Thermal Methods in Catalysis - Aline Auroux**
  Springer –Verlag Berlin Heidelberg 2013


Thank you for your attention

http://www.fhi-berlin.mpg.de
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