Adsorption Calorimetry: Basics and Applications in Heterogeneous Catalysis

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1. Introduction & motivation
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
Introduction

- Calor (Latin): heat, warmth
- Metron (Greek): measure

Johan C. Wilcke (1732-1796)

Antoine L. Lavoisier (1743-1794)
and Marie P. Lavoisier
Introduction

- adsorption steps, surface reaction processes, and desorption steps

- the **energetics** of these surface physical-chemical events play an important role in the determination of the catalytic properties of the surface

- **Direct method to determine number, strength and energy distribution of the adsorption sites** → Adsorption Isothermal Micrcalorimetry

- allows measurement of the **differential heats** (**ads. enthalpy**) evolved when known amounts of gas probe molecules are adsorbed on the catalyst surface

- the **evolved heat** is related to the **energy of the bonds** formed between the adsorbed species and the adsorvent and hence to the **nature of the bonds** and to the **chemical reactivity of the surface**

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

- The data obtained are of substantial importance for **comparing theoretical and experimental hypotheses** about reaction pathways.

▷ Analyzing of the catalytic data with respect to the surface processes occurring on the catalyst material during adsorptive microcalorimetry.
Motivation: surface sites

- careful choice of probe molecules and the adsorption temperature
- metal oxide catalysts provides acid/base properties

Brønsted acid sites: transfer of $\text{H}^+$ from OH to Adsorbate

Lewis acid sites: coordination to an electron-deficient metal atom

- $\text{O}_2^-$
- $\text{O}^-$
- $\text{OH}^-$
- $\text{Me}^{\text{x+}}\text{O}^-\text{Me}^{-\text{y}}$
- $\text{Me}^{\text{x+}}\text{O}^-\text{Me}^{-\text{y}}$
- $\text{Me}^{\text{x+}}\text{O}^2^-\text{Me}^{-\text{y}}$

Oxygen vacancy: $\text{Me}^{\text{x+}}\text{O}^-\text{Me}^{-\text{y}}$

Metall cations under participation of oxygen: $\text{Me}^{\text{x+}}\text{O}^-\text{Me}^{-\text{y}}$

Strong basic $\text{NH}_3$ at RT
Weak basic $\text{CO}$ at 77 K

Acidic $\text{CO}_2$ at RT

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

$T_{\text{adsorption}} < T_{\text{reaction}} \rightarrow$ study of the pure ads. processes

$T_{\text{adsorption}} = T_{\text{reaction}} \rightarrow$ study of the surface chemical events during the reaction
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Equipment at the Fritz-Haber-Institute

Calorimeter
- Reference cell
- Sample cell
- Sample cell chamber
- Isolation
- Electronics
- Heating
- Heat flow
- Catalyst

Volumetric system
(probe molecule dosing system)
- Thermocouple
- Body
- Sample holder
  - L = 70 mm
  - \( \Phi = 15 \) mm

Adsorptive Microcalorimetry
- MS 70 Tian-Calvet calorimeter of SETARAM combined with a custom-designed high vacuum and gas dosing apparatus.
The Calorimetric Element

- The **sample cell** is placed into a calorimeter element.

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

- Thermopile has 2 functions:
  1. heat transfer
  2. signal generation
Heat and Heat Flow

- The heat produced by the adsorption/reaction of a dosed probe molecule 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.
Reference Cell

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 a signal “U” which is propotional to the heat transferred per time unit.

Setup according to Tian and Calvet

# Physisorption and Chemisorption

<table>
<thead>
<tr>
<th></th>
<th>Physisorption</th>
<th>Chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type of interaction</strong>&lt;br&gt;and heat of adsorption&lt;br&gt;(negative enthalpy of adsorption)</td>
<td>van der Waals forces 10 – 20 kJ/mol noble gases, CH₄, N₂&lt;br&gt;Dipole-dipole 20 – 50 kJ/mol water on oxides</td>
<td>chemical bonding, electron transfer 80 – 500 kJ/mol CO on metals&lt;br&gt;dissociative adsorption (O₂, H₂ on Pt, H₂O on oxides)</td>
</tr>
<tr>
<td><strong>Reversibility</strong></td>
<td>reversible</td>
<td>reversible or irreversible</td>
</tr>
<tr>
<td><strong>Speed</strong></td>
<td>fast</td>
<td>can be slow (e.g. activated adsorption)</td>
</tr>
<tr>
<td><strong>Coverage</strong></td>
<td>multilayers possible</td>
<td>monolayer only</td>
</tr>
</tbody>
</table>
Physisorption and Chemisorption

Fig. XIV-3. Potential energy curves for physical adsorption and chemisorption (from Ref. 7).
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Power Balance of Tian-Calvet Calorimeter & Adsorption Heat Signal

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 cell

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

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 Heats of Adsorption

- If heat is released in the cell for a limited period of time, e.g. through adsorption, then a electrical signal $U$ with an exponential decrease is obtained.
- The integral under the curve is proportional to the evolved heat

$$Q_{\text{int}} = \frac{G}{g} \int U \, dt = f \cdot A$$

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

The calorimeter can be calibrated by using an Ohm resistance which produces a certain amount of heat.

$$Q = U \cdot I \cdot t$$
$$f = \frac{(U \cdot I \cdot t)}{A_{\text{ohm resistance}}}$$ [Ws/Vs]

- Differential heats of adsorption as a function of coverage can be determined

$$q_{\text{diff}} = \left( \frac{\delta Q_{\text{int}}}{\delta n} \right)_{T,A}$$

Calculation of Adsorbed Amount
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Calibration of the volumetric system

- \( V_{\text{cal}} = 31.8 \text{ ml} \)
- \( V_{\text{Dos}} = \frac{p_{\text{Cal}} - p_{\text{Cal+Dos}}}{p_{\text{Cal+Dos}} - p_{\text{Dos}}} \) \( V_{\text{Cal}} = 134.4 \text{ ml} \)

Wall adsorption isotherm reflects number of molecules in the gas phase and on the inner walls.

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

Amount of adsorbed molecules

- Determination of the dosed amount
  \[
n_{\text{int},i} = \frac{(p_{\text{Dos,bef}} - p_{\text{Dos,aft}})V_{\text{Dos}}}{RT}
\]
- The number of molecules adsorbed in the \((i+1)^{\text{th}}\) step is then
  \[
n_{ads,i+1} = n_{\text{int},i+1} + n_{SC,w+g,i} - n_{SC,w+g,i+1}
\]
- The total number of ads. molecules in a given steps is
  \[
n_{ads,tot,i+1} = n_{ads,tot,i} + n_{ads,i+1}
\]
registered Raw Data

Raw data
equilibrium pressure

Pressure in dosing volume / hPa
Zeit / h
Pressure in sample cell / hPa

Raw data
equilibrium pressure and thermosignal (Q_{int.})

Thermosignal / V
Time / h
Equilibrium pressure / hPa

Sabine Wrabetz, Electronic Structure and Adsorption / Metals, Dept. AC, Fritz Haber Institute of the MPG, Berlin, Germany
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- Adsorption isotherm
- $q_{\text{diff}} \rightarrow$ strength of surface sites
- $q_{\text{diff}} = f (n_{\text{ads}}) \rightarrow$ distribution of surface sites
obtained results
Adsorption Isotherm

\[ n_{\text{ads}} = f(p_{\text{equ.}}) \]

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

\( n_{\text{ads}} \) (irrev.) : chemisorbed amount
Adsorption Isotherm of propane on 10%V/SBA15 catalyst active in oxidation of propane

**Analysis**

- Higher order Langmuir model,
  \[ N_{ads} = \frac{N_{mono} (Kp)^{1/n}}{1 + (Kp)^{1/n}} \]
  - The enthalpy of adsorption \( \Delta_a H (q_{diff}) \) per site is constant with coverage \( \Theta \)

- Freundlich model
  \[ N_{ads} = \frac{1}{1 + A p^n} \]
  - The enthalpy of adsorption \( \Delta_a H (q_{diff}) \) per site decreases with coverage \( \Theta \)

**Specific surface area**

\[
\text{Specific surface area}_{\text{propane}} = N_{\text{mono}} \times S \times \text{cross-section area}_{\text{propane}, T} \times \text{Avogadro constant}
\]

**Evaluation criteria**

- \( n = 1 \) non-dissociative ads.
- \( n > 1 \) dissociative ads. ;
- activated ads.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( N_{mono} ) (µmol * g(^{-1}))</th>
<th>( n )</th>
<th>( R^2 )</th>
<th>( S_{\text{propane}} ) (m(^2) * g(^{-1}))</th>
<th>( S_{\text{N2}} ) (m(^2) * g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>373 K</td>
<td>0.9 (2)</td>
<td>1.20</td>
<td>0.99983</td>
<td>226 (10)</td>
<td>329 (4)</td>
</tr>
<tr>
<td>573 K</td>
<td>1.3 (4)</td>
<td>1.22</td>
<td>0.99982</td>
<td>304 (10)</td>
<td></td>
</tr>
<tr>
<td>673 K</td>
<td>1.2 (3)</td>
<td>1.22</td>
<td>0.99905</td>
<td>290 (10)</td>
<td></td>
</tr>
</tbody>
</table>
obtained results

Differential heat versus the $n_{ads}$

Classical Calorimetric Curve

- Differential heat
- Adsorbed volume
- Enthalpy of condensation
- Strong Lewis acid sites
- Brønsted acid sites
- Heterogeneous acid site

Homogeneous acid strength

Interaction between adsorbed molecules

Plateau: homogeneously distributed and energetically uniform adsorption sites

Completion of monolayer

Amount of adsorbed propane on phase-pure MoVTeNb$_{6059}$ / mmol/g

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

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

Differential heat of adsorbed propane / kJ/mol

0.0 0.1 0.2 0.3 5 10 15 20 25 30

Differential heat of oxygen ads. / kJ/mol

0.0 0.1 0.2 0.3 5 10 15 20 25 30

Amount of ads. O$_2$ on Pd/N-CN at $T_{react.}$ / µmol/g

0.0 0.1 0.2 0.3 5 10 15 20 25 30

Most active
Less active

A. Auroux, Lecture Oct. 23, 2009
Integral heat signal of adsorption and desorption
stepwise adsorption of propane on MoVTeNb oxide at 313K

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

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

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

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

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

Background of the thermo signal during the stepwise adsorption
stepwise n-butane ads. on sulf. ZrO\(_2\) at 313 K

Background 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 experiment

**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=1kΩ $\rightarrow$ 27.45 mJ**
- $\tau_{\text{(calorimeter+cell)}} \sim 265$ s

**Shape of the integral heat signal**

$O_2$ adsorption on 2%Pd/N-CNF473K at 353K = T_{reaction}

- **0.039 µmol/g oxygen** $\Rightarrow$ A
  - $K(t)=377$ s $\Rightarrow$ Response time / 0.4 h
- **2 µmol/g oxygen** $\Rightarrow$ B
  - $K(t)=998$ s $\Rightarrow$ Response time / 0.7 h
- **14 µmol/g oxygen** $\Rightarrow$ C
  - $n_{ads.}$ $\uparrow$
  - oxygen chemisorption combined by secondary processes

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

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

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Applications

Selected calorimetric measurements on supported metal oxide and mixed metal oxides.

<table>
<thead>
<tr>
<th>Probe molecule</th>
<th>Catalyst / Activation / Catalytic activity</th>
<th>T_{adsorption} [K]</th>
<th>q_{initial} [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butane</td>
<td>0.5wt%Pt/H-Mordenite / H$_2$ reduced at 648 K / less active</td>
<td>313</td>
<td>350</td>
</tr>
<tr>
<td>n-butane</td>
<td>0.5wt%Pt/H-Mordenite / dehydr. at 723 K / active</td>
<td>313</td>
<td>42</td>
</tr>
<tr>
<td>n-butane</td>
<td>3.5wt% VO$_x$Al$_2$O$_3$ / H$_2$ reduced at 773 K / active</td>
<td>313</td>
<td>63</td>
</tr>
<tr>
<td>n-butane</td>
<td>Θ Al$_2$O$_3$ / H$_2$ reduced at 773 K / non-active</td>
<td>313</td>
<td>35</td>
</tr>
<tr>
<td>propane</td>
<td>10 wt% V$_x$O$_3$-SBA15 / dehydrated at 373 K / active</td>
<td>313</td>
<td>45 80 160</td>
</tr>
<tr>
<td>propane</td>
<td>3 wt% V$_x$O$_3$-SBA15 / dehydrated at 373 K / active</td>
<td>313</td>
<td>45</td>
</tr>
<tr>
<td>propane</td>
<td>SBA15 / dehydrated at 373 K / non-active</td>
<td>313</td>
<td>32</td>
</tr>
<tr>
<td>propane</td>
<td>hydrothermal synth. – M1 / dehydr. at 423 K / active, 58*</td>
<td>313</td>
<td>71</td>
</tr>
<tr>
<td>propane</td>
<td>precipitation – M1 / dehydrated at 423 K / active, 43*</td>
<td>313</td>
<td>56</td>
</tr>
<tr>
<td>propane</td>
<td>SHWVT ** – M1 / dehydrated at 423 K / active, 5*</td>
<td>313</td>
<td>64</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>CNFox functionalized by NH$_3$ at 873 K</td>
<td>313</td>
<td>150 50 90</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Fe-CNT / dehydrated at 373 K</td>
<td>313</td>
<td>272 191</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>FeIO-XT 24PS-CT / dehydrated at 373 K</td>
<td>313</td>
<td>191</td>
</tr>
<tr>
<td>O$_2$</td>
<td>2wt%Pd/#N-CNT873K / dehydrated at 353 K</td>
<td>353</td>
<td>500-700</td>
</tr>
<tr>
<td>O$_2$</td>
<td>2wt%Pd/#N-CNT473K / dehydrated at 353 K</td>
<td>353</td>
<td>500</td>
</tr>
<tr>
<td>O$_2$</td>
<td>2wt%Pd/CNT / H$_2$ reduction at 423 K</td>
<td>313</td>
<td>175</td>
</tr>
<tr>
<td>O$_2$</td>
<td>precipitation – M1 / H$_2$ activated at 653 K</td>
<td>473</td>
<td>218</td>
</tr>
<tr>
<td>O$_2$</td>
<td>precipitation – M1 / propane activated at 653 K</td>
<td>473</td>
<td>257</td>
</tr>
</tbody>
</table>

The method was broadly employed in several projects of our department and yielded a surprising spread of energetic data for the same molecule on different surfaces.

In addition, we observed significant differences of the energetic data for the same molecule on slightly modified surfaces.
**CO adsorption on Pt/Al$_2$O$_3$ at 40°C**

**Adsorption isotherm of CO**

Saturation concentration

\[ n_{ads.} \text{ (irreversible)} = 20.4 \, \mu\text{mol/g} \]

**Model: higher order Langmuir model**

\[ q_{diff} = 200 \, \text{kJ/mol} = \text{constant versus } n_{ads} \]

\[ R^2 = 0.88731 \]

\[ N_{\text{mono}} = 0.02631 \, (1^{st}\text{run}) - 0.00583 \, (2^{nd}\text{run}) \]

\[ K = 1662.35201 \rightarrow \text{irreversibility} \]

\[ n = 1.15679 \]

**Differential heat of adsorbed CO**

\[ Pt-CO = 1:1 = 206 \, \text{kJ/mol} \]

\[ Pt_2-CO = 94 \, \text{kJ/mol} \]

\[ J.\text{Therm. Anal. Cal., 82, (2005) 105} \]

**Saturation concentration**

\[ S_{CO} = N_{\text{mono}} \times S \times \text{cross-section-area}_{CO,T} \times \text{Avogadro constant} \]

\[ S_{CO} = 20.4 \times 10^{-6} \, \text{mol/g} \times 1 \times 16.2 \times 10^{-20} \, \text{m} \times 6.022 \times 10^{23} \, \text{mol}^{-1} = 1.99 \, \text{m}^2/\text{g} \]
**Aim:** structure-activity relationship study of Pt/HM for n-butane isomerization

**n-butane isomerisation**

15 kPa n-butane in H\textsubscript{2} at 300 °C

- **fully H\textsubscript{2}-reduced Pt/HM**
  - catalyst activated in H\textsubscript{2} at 350 °C for 2 h
- **not completely H\textsubscript{2}-reduced Pt/HM**
  - catalyst activated in H\textsubscript{2} at 300 °C for 1 h

**Differential heat of ads. n-butane at 40 °C**

IR spectra of ads. CO at RT at 0.7 mbar

- 200 μmol/g
- 450 μmol/g

**Equilibrium pressure of n-butane [mmol/g]**

**The active states of Pt/HM are characterized by:**

- a small amount of strong Lewis acid sites (Al\textsuperscript{3+}oct., extraframework alumina)
- well dispersed metallic platinum particles (1-3 nm)
- higher number of n-butane adsorption sites
- weak interaction of the surface acid sites with n-butane.

The weaker interaction with the alkane is apparently favorable for the catalytic performance; perhaps because of facile product desorption.
Fe/sulf.ZrO$_2$ is active in isomerization of n-butane to isobutane at low temp. (100°C)

**Question:** Does iso-butane (product) reacts with surface species of Fe/sulf. ZrO$_2$ at low temperature?

**Differential heat of adsorbed iso-butane & neo-pentane at 40°C**

The neo-pentane heat profile follow the classical calorimetric heat profile - heat decreases with increasing the coverage → pure ads.

The scattering of the diff. heats for iso-butane at low coverage indicates the presence of exothermic and endothermic processes during the adsorption. → ads. + reaction

**Answer:** Yes, iso-butane (product) reacts with surface species of Fe/sulf. ZrO$_2$ at low temperature.
Sabine Wrabetz, Electronic Structure and Adsorption / Metals, Dept. AC, Fritz Haber Institute of the MPG, Berlin, Germany

pure-phase MoVTeNb catalyst active in direct oxidation of propane to acrylic acid (aa)

Aim: study of the post-reaction state of the surface “used catalyst” in comparison with the prepared state of the surface “fresh catalyst”

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

- phase-pure M1, $S_{aa} = 53\%$
  - $S_{propane} = 11.4m^2/g$
- oxidized M1, $S_{aa} = 37\%$
  - $S_{propane} = 10.3m^2/g$
- MoV oxide, $S_{aa} = 1.8\%$
  - $S_{propane} = 13.4m^2/g$

$S_{aa} \uparrow \rightarrow$ homogeneity $\uparrow$ $\rightarrow$ strength of interaction between educt and surface sites $\downarrow \rightarrow$ density of propane ads. sites $\uparrow$

- energetically uniform ads. sites
- (which is apparently favorable for catalytic performance; perhaps because of facile intermediate desorption)

$\rightarrow$ the prepared state of the surface is different from the post-reaction state of the surface

$\rightarrow$ dynamic surface during reaction

Sabine Wrabetz, Yury V. Kolen’ko, Jutta Kröhnert, Lenard Csepei, Olaf Timpe, Wei Zhang, Annette Trunschke, and Robert Schlögl,
Characterization of MoVTeNb catalyst in their as prepared and active state by adsorption microcalorimetry and -FTIR spectroscopy; in preparation 2010.
**Aim:** Study of the educt and product interaction with the surface of sulf. ZrO$_2$ if the surface at the state of highest activity in the $n$-butane isomerization

The state of maximum activity of sulf. ZrO$_2$ is characterized by:

A stronger interaction with $n$-butane (~70kJ/mol, educt) than with $iso$-butane (~45kJ/mol, product). The weak interaction with $iso$-butane and the equilibrium constant ($K_{iso$-butane}=0.011$) indicate an increasing easiness of desorption of $iso$-butane from the surface sites.
Microcalorimetric titration of basic sites on N-CNFs by \( \text{CO}_2 \) adsorption at 40°C

Oxidation of VGCNF by HNO\(_3\) at 373K for 2h and amination using NH\(_3\) at 473/673/873 K.

Different oxygen and nitrogen species in CNFs

**Differential heat of adsorbed \( \text{CO}_2 \)**

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<tr>
<th></th>
<th>N-CNF873K</th>
<th>N-CNF473K</th>
<th>N-CNF673K</th>
<th>VGCNF</th>
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</tbody>
</table>

Partially irreversible adsorbed

Differential heat of adsorbed \( \text{CO}_2 \) [kJ/mol]

Amount of adsorbed \( \text{CO}_2 \) [\( \mu \text{mol/g} \)]

Depending on the \( T_{\text{amination}} \) the N-CNF surface provides energetically different basic sites which are heterogeneously distributed.

CNF surface chemistry plays a crucial role in Metal/CNF interaction.

Fe/N-CNF873K is the best catalyst in electrocatalytic conversion of \( \text{CO}_2 \).

Pd/N-CNF873K is the best catalyst in oxidation of benzyl alcohol to benzaldehyde.
Conclusion

Microcalorimetry alone or combined with other techniques, is applied for the characterization of catalysts, supports and adsorbents, and to the study of catalytic reactions (adsorption-desorption phenomena).

- very sensitive and hence a selective surface characterization method
- but very time consuming (~1 week for 1 experiment)

The nature of the reactive surface sites can be studied by measuring the thermal effects during the reaction.

- The knowledge about the energetics of the surface chemical events helps better to understand the catalytic properties of the surface and hence the catalytic reaction characteristics.

- The calorimetric data obtained are of substantial importance for comparing theoretical and experimental hypotheses about reaction pathways.


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Thank you for your attention!