Microcalorimetry beyond Adsorption: Basics and Applications in Heterogeneous Catalysis

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Lecture Series: Modern Methods in Heterogeneous Catalysis;
10:45 - 12:15

Contents

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**

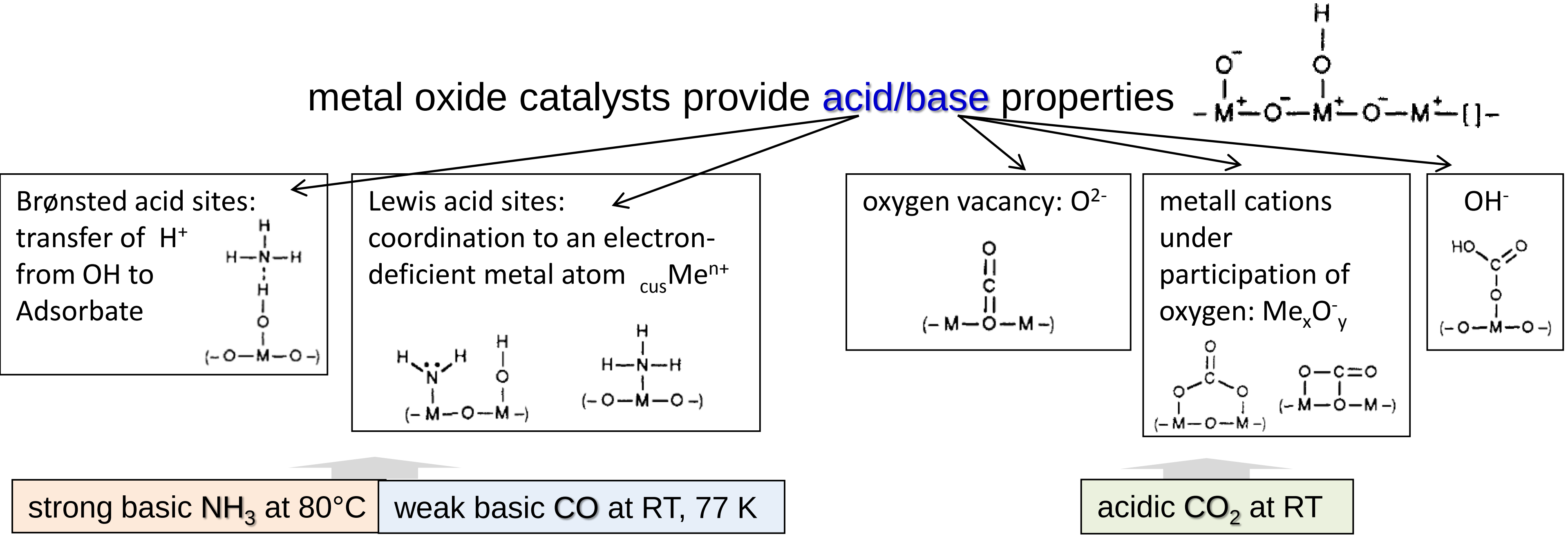
Ads. Isothermal Microcalorimetry / *Microcalorimetry beyond Ads.*

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 $_{cus}Me^{n+}$

oxygen vacancy: O^{2-}

metall cations under participation of oxygen: $Me_xO^-_y$

OH^-

strong basic NH_3 at 80°C

weak basic CO at RT, 77 K

acidic CO_2 at RT

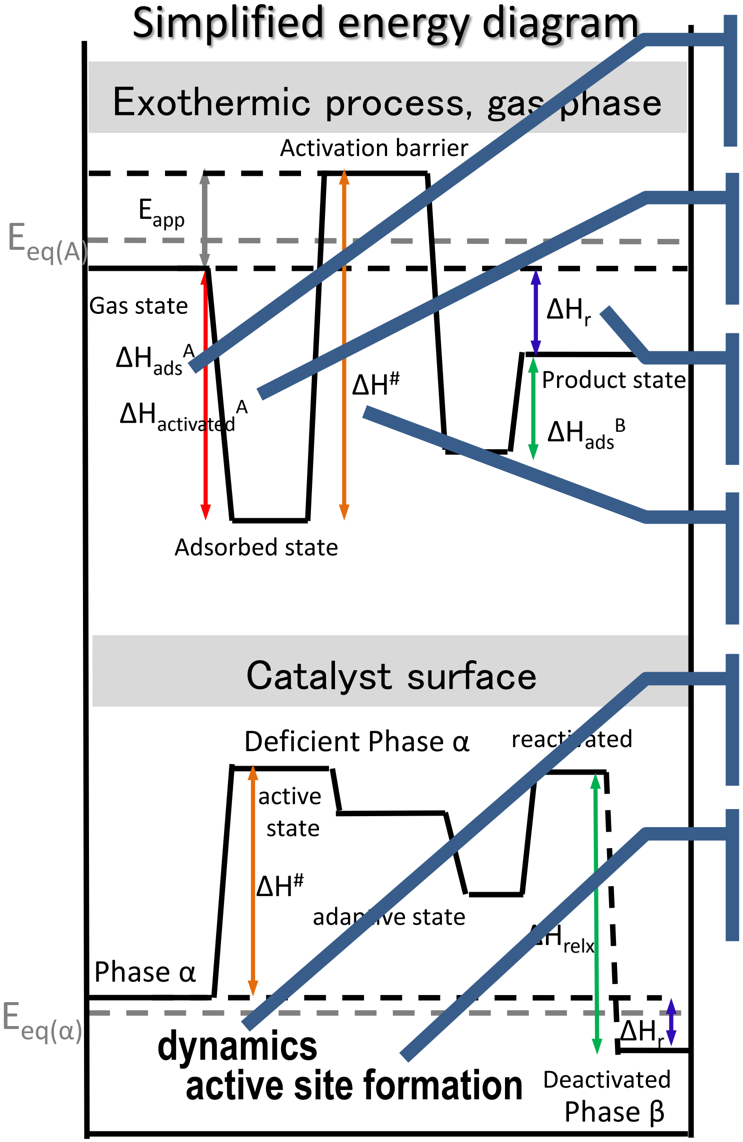
Focus

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

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

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

Introduction



Simplified energy diagram

Adapted using : van Santen, R. A., *Modern Heterogeneous Catalysis*, Wiley, 2017
Schlögl, R., *Introduction to Heterogeneous Catalysis*, Lecture, FHI Berlin, 2017

CO_2 ads.$_{chemisorption}$ on CeO_2 for DEACON reaction [5]

MoV oxide catalyst in oxidative dehydrogenation of alkanes

Ir-based catalysts for the oxygen evolution reaction at r.t. [1]

Vanadium Oxide-based and Metal-free Catalysts in the ODH of Ethane and Propane [2]

Ni based catalysts for the dry reforming of methane [3]

Propylene Metathesis over MoOx/SBA-15 [4]

1 *V. Pfeifer, T. Jones, S. Wrabetz, C. Massué, J. Velesco-Velez, R. Arrigo, M. Scherzer, S. Piccinin, M. Haevecker, A. Knop-Gericke and R. Schlögl, Chem. Sci., 2016,7, 6791-6795.*

2 *P. Kube, B. Frank, S. Wrabetz, J. Kröhnert, M. Hävecker, J. Valasco-Vélez, J. Noack, R. Schlögl, A. Trunschke, ChemCatChem 9 (2017) 1-14.*

3 *K. Mette, St. Kühl, A. Tarasov, M. G. Willinger, J. Kröhnert, S. Wrabetz, A. Trunschke, M. Scherzer, F. Girgsdies, H. Düdder, K. Kähler, K. Friedel Ortega, M. Muhler, R. Schlögl, M. Behrens, T. Lunkenbein, ACS Catal., 2016, 6 (10), pp 7238–7248.*

4 *Amakawa, K., Wrabetz, S., Kröhnert, J., Tzolova-Müller, G., Schlögl, R., Trunschke, A.; J. Am. Chem. Soc., 134 (28) (2012) 11462-11473.*

5 *Farra, R., Wrabetz, S., Schuster, M. E., Stotz, E., Hamilton, N., Amrute, A. P., Pérez-Ramírez, J., López, N., Teschner, D., Phys. Chem. Chem. Phys.,15 (2013) 3454 - 3465 .*

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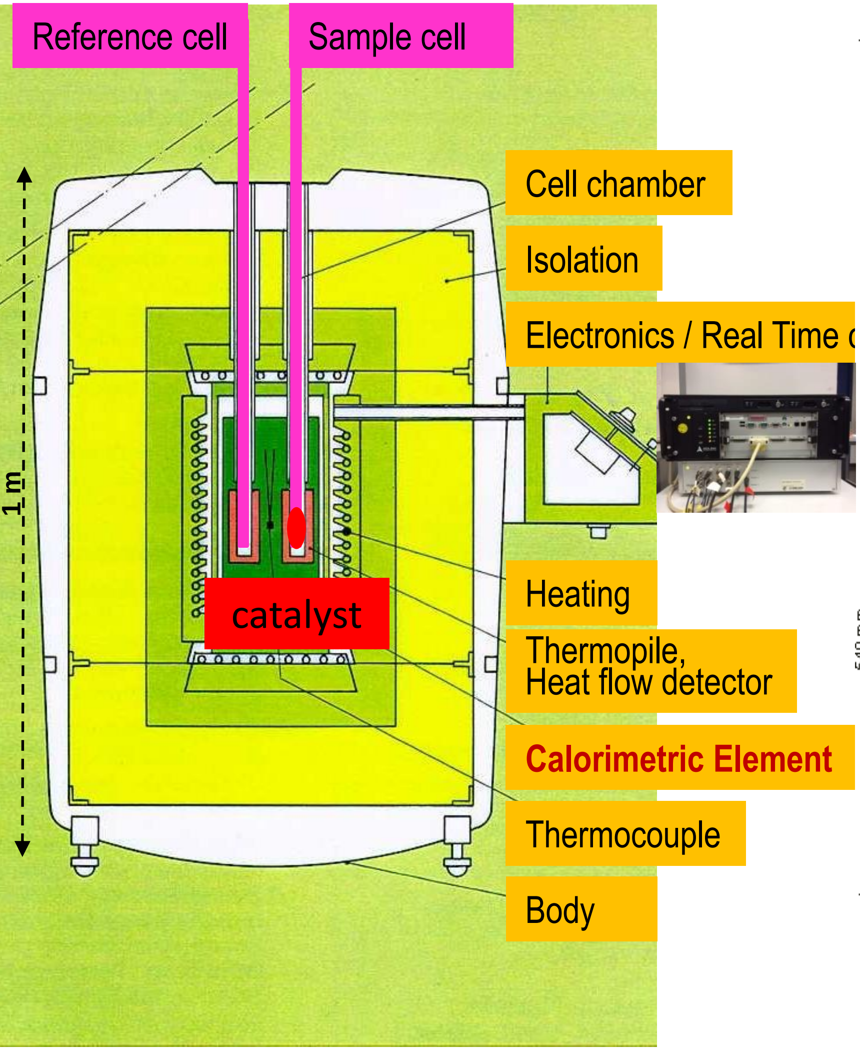
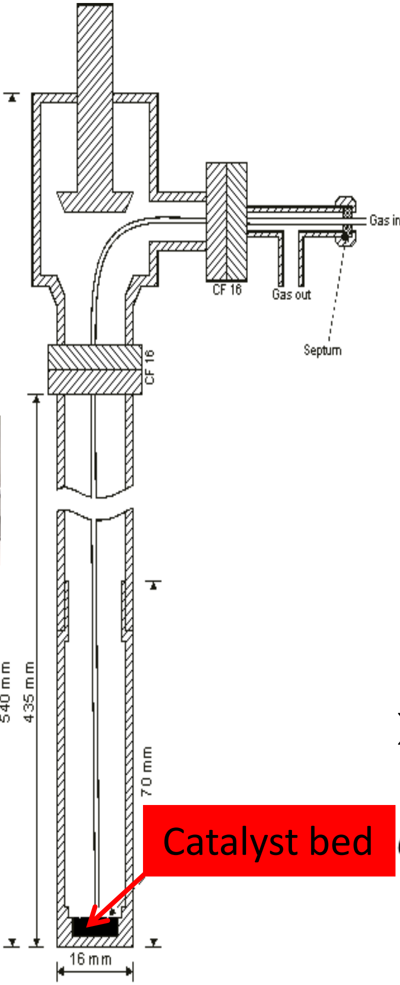
1. Introduction
2. Adsorptive microcalorimetric setup
3. Power balance of Tian-Calvet calorimeter & Evolved adsorption heat & Differential heats of adsorption
4. Volumetric-Barometric System calibration & measurement of adsorbed amount
5. Obtained physical quantities & evaluation criteria of the calorimetric results
6. Applications of microcalorimetry in heterogeneous catalysis
   - *H_2 and CO adsorption on 2%Pt / Al_2O_3 at 40°C*
   - *NH_3 adsorption on pure-phase MoVTeNb oxide at 80°C*
   - *CO_2 ads. on CeO_2 at 40°C*
   - *O_2 adsorption on supported CeO_2 at 200°C*
   - *Ethanol adsorption on $VO_x/\gamma\text{-}Al_2O_3$ at 40°C*
   - *Propane ads. On MoVTeNb oxide at 40°C*
   - *Propylene adsorption on MoO_x/SBA-15 at $T_{reaction}$=50°C*
   - *1-Hexyne ads. on CeO_2/TiO_2 at Treaction=80°C*

Adsorptive microcalorimetric setup

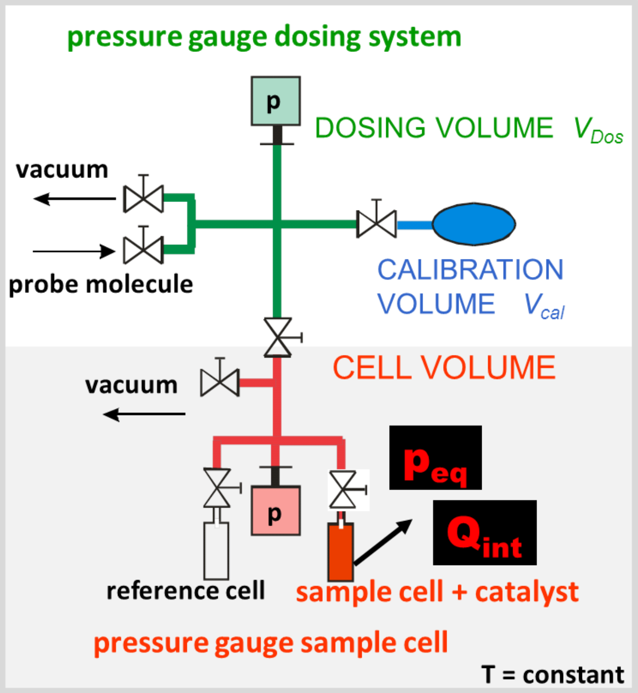
Tian-Calvet calorimeter of SETARAM



Sample cell *(static, dynamic)*



Volumetric-Barometric System



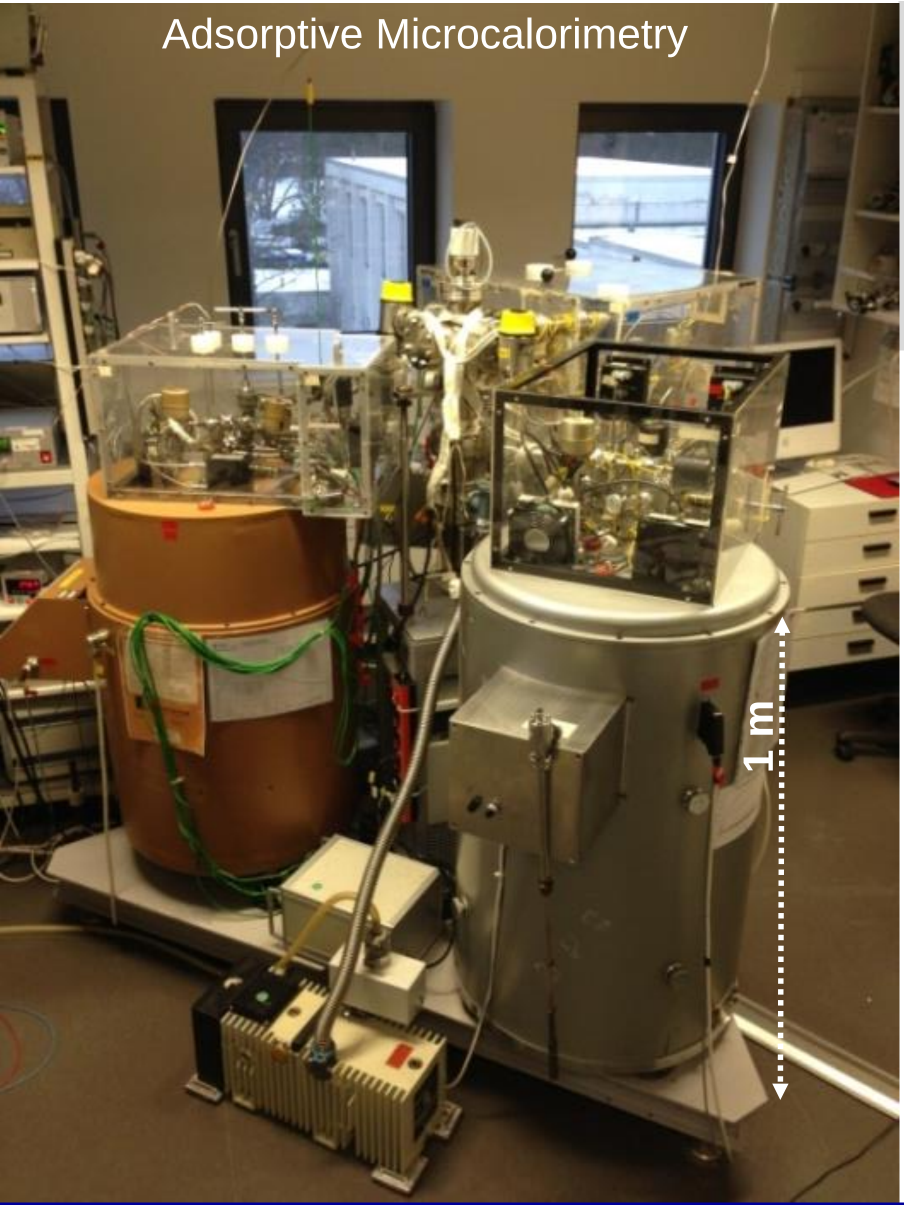
$\sum n_{ads}$ vs p_{eq} , $mmol*g^{-1}$, $mmol*m^{-2}$

$q_{diff} = \frac{Q_{int}}{n_{ads}} = \Delta H_{ads}$, kJ/mol

q_{diff} vs n_{ads} , kJ/mol

$K = K_o \exp\frac{\Delta H_{ads}}{RT}$, 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.*

Prof. Albert Tian

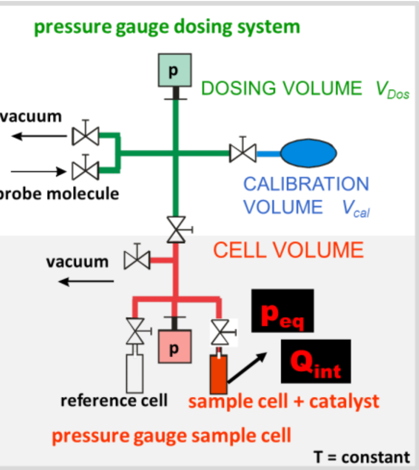
Tian described his compensation microcalorimeter for the first time in 1922, when he and his colleague COTTE used it to study the metabolism of insects. He brought further improvements to this thermocouple instrument in 1924 and 1926.

Prof. Edouard Calvet
(1895–1966)

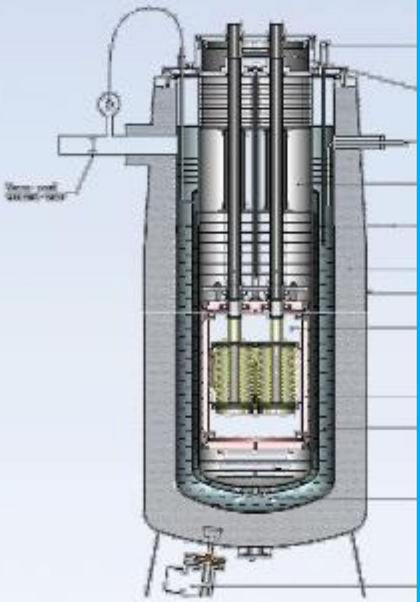
CALVET introduced the differential setup (1948) and a rational construction of the **two twinned calorimetric elements**, transforming Tian's apparatus into a true laboratory instrument that today is commercialized by Setaram.

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



BT 2.15 Calorimeter



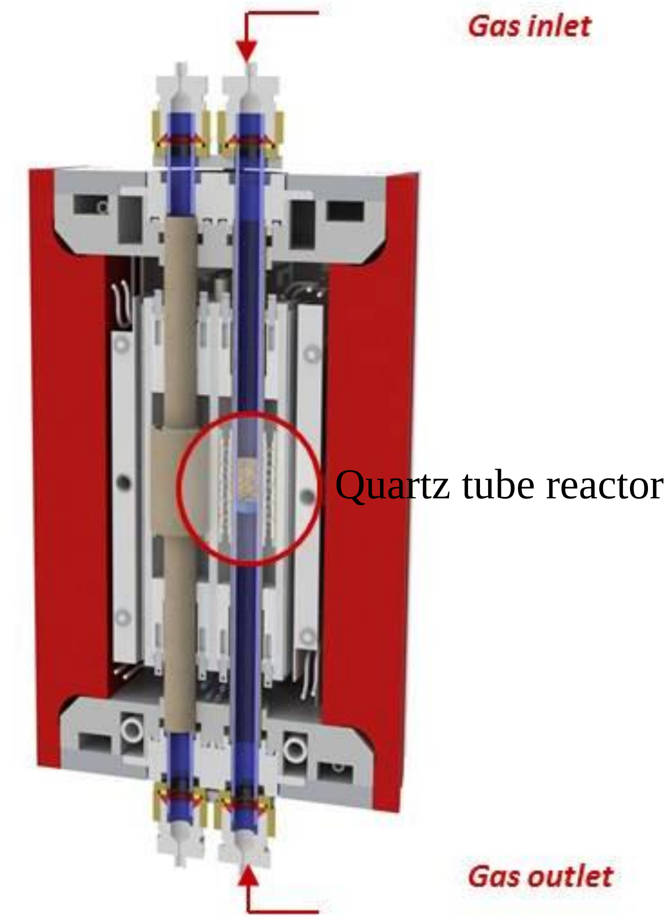
Cross-sectional view of the SETARAM BT 2.15

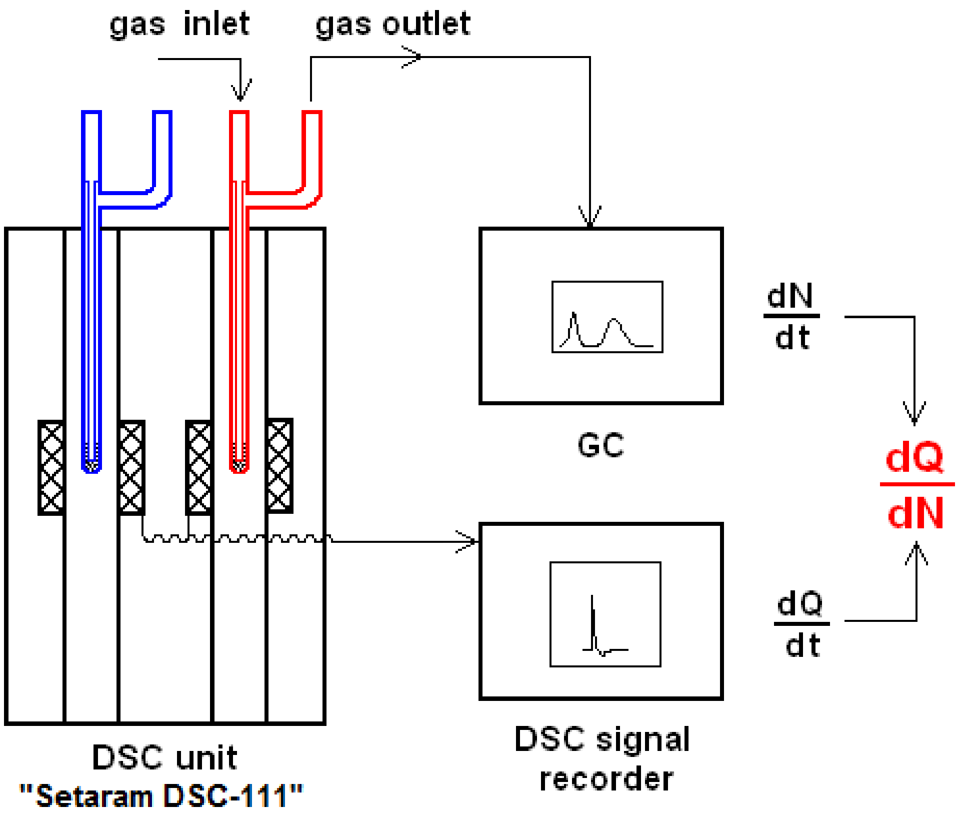
in-situ DSC setup *(Differential scanning calorimetry)*

Setaram instrument SENSYS EVO.

Dr. Andrey Tarasov

- Direct measurement of reaction enthalpy
- Precise product analysis





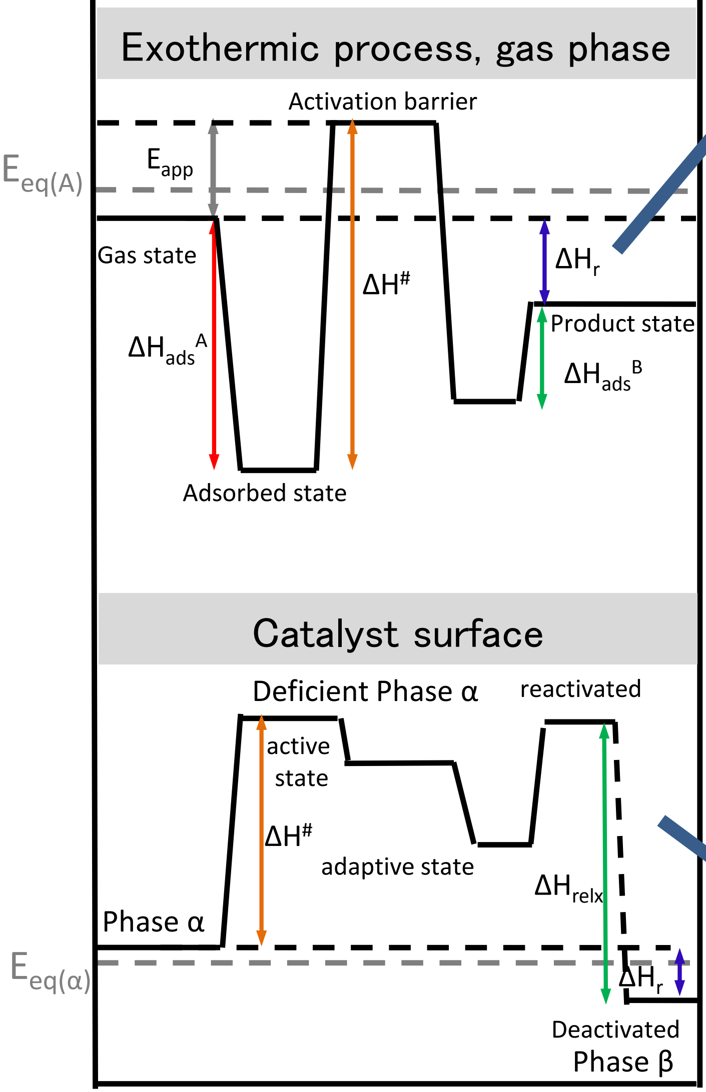
- Calvet calorimetric element
- 3D sensor totally surrounds the catalyst

in-situ DSC setup *(Differential scanning calorimetry)*

Setaram instrument SENSYS EVO.

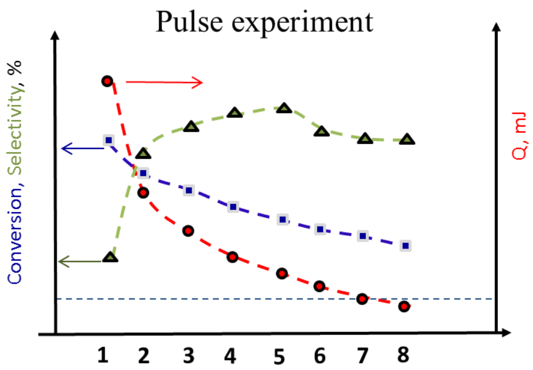
Dr. Andrey Tarasov

Simplified energy diagram

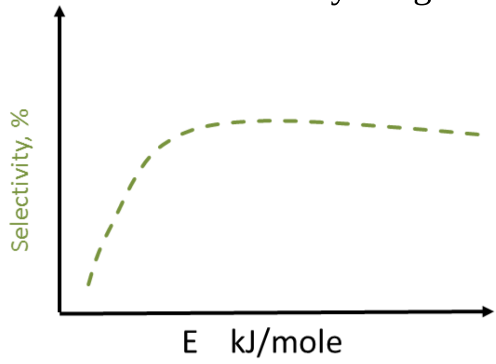


Transformation of gas phase molecules

- Information about reaction kinetics
- Simulation of different conditions *in situ*



structure – selectivity diagram
structure – reactivity diagram

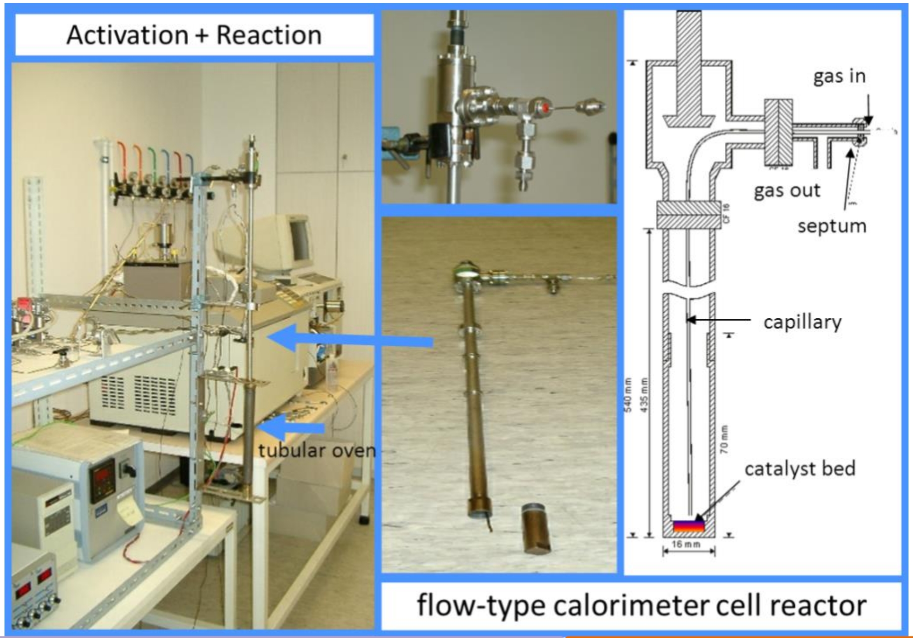


Transformation in solid state

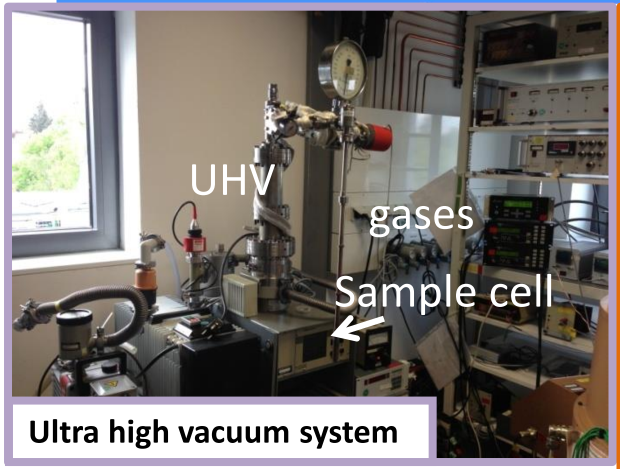
- Redox dynamics
- Thermochemistry of defects formation

Experimental procedure

Activation + Reaction



flow-type calorimeter cell reactor



Ultra high vacuum system

Microcalorimeter + volumetric system

Activation:

UHV (10^{-8}hPa), gases (H_2, O_2 ......),
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

S. Wrabetz, F.C. Jentoft etal, J. Catal. 269 (2010) 351-358

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.

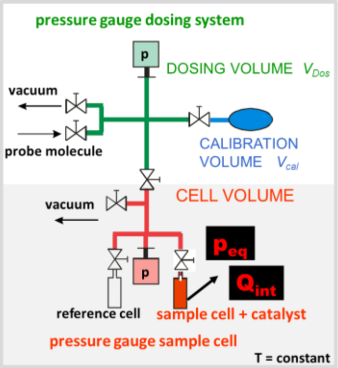
Adsorption Calorimetry - Standard procedure

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

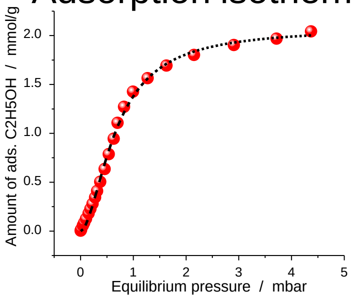
- For each adsorption step, the **adsorbed amount** must be determined (isotherm)

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

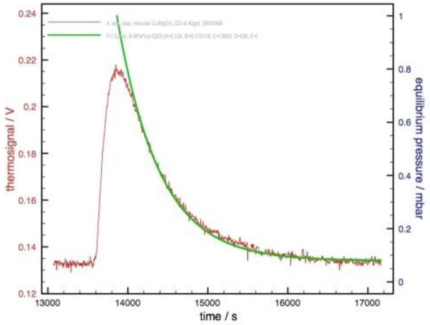
- The **differential heat (ΔH_{ads})** can then be determined by dividing the evolved heat through the number of molecules adsorbed in a particular step



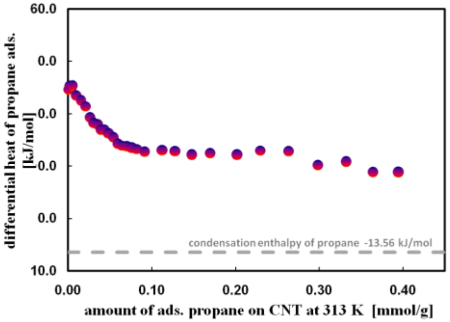
Adsorption isotherm



Integral heat of ads.



ΔH_{ads} / energy distribution



Introduction

	Physisorption	**Chemisorption**
Type of interaction and heat of adsorption (negative enthalpy of adsorption)	van der Waals force $0 < \Delta_P H < 50$ kJ/mol Noble gases, CH_4, N_2 Dipole-dipole interaction 20 – 25 kJ/mol H_2O, NH_3	chemical bonding, electron transfer $60 < \Delta_C H < 400$ kJ/mol CO on metals (Pt, Pd) Dissociative adsorption (O_2, H_2 on Pt, H_2O on oxides)
Reversibility	reversible	reversible , irreversible or partially irreversible
Speed	fast	can be slow (e.g. activated adsorption, dissociative adsorption)
Coverage	non-specific and weak multilayers possible	specific (chemisorbed molecule blocks surface sites) monolayer only

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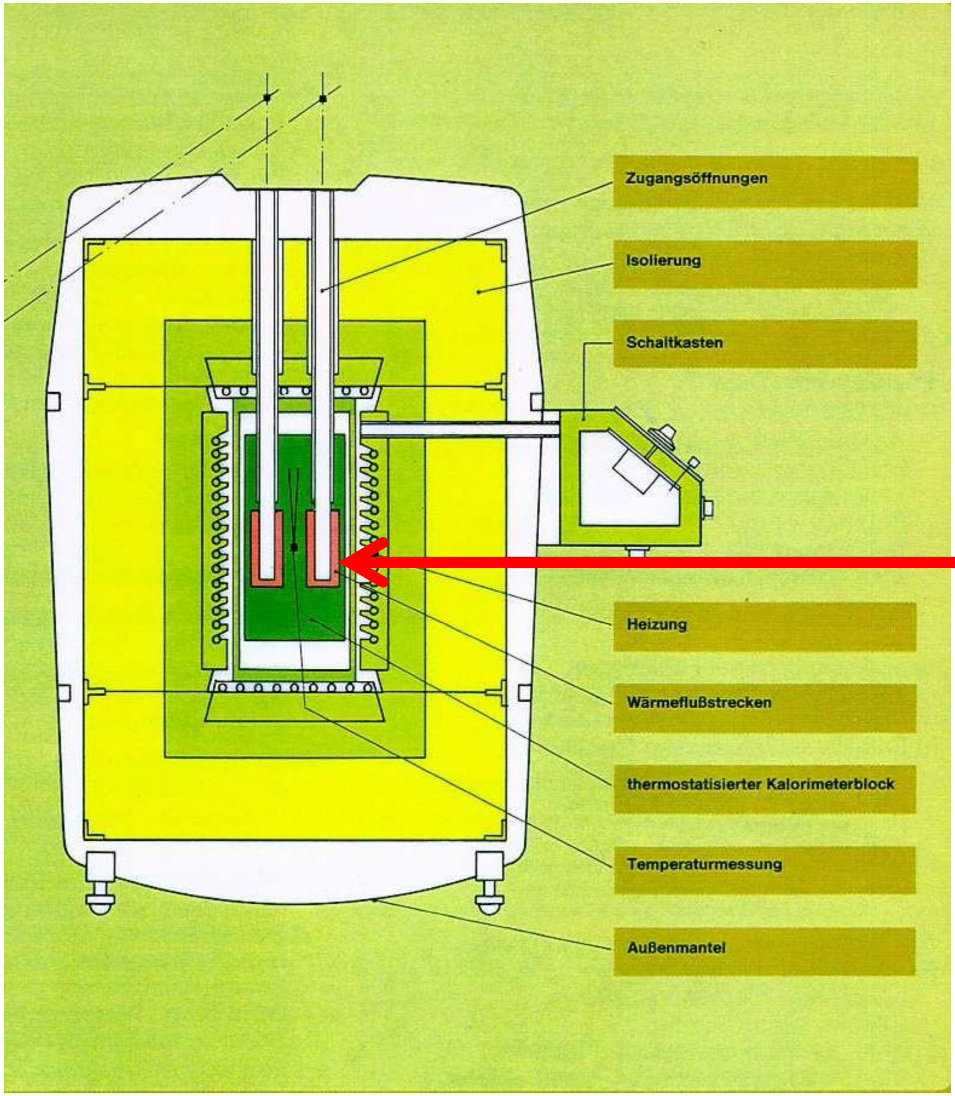
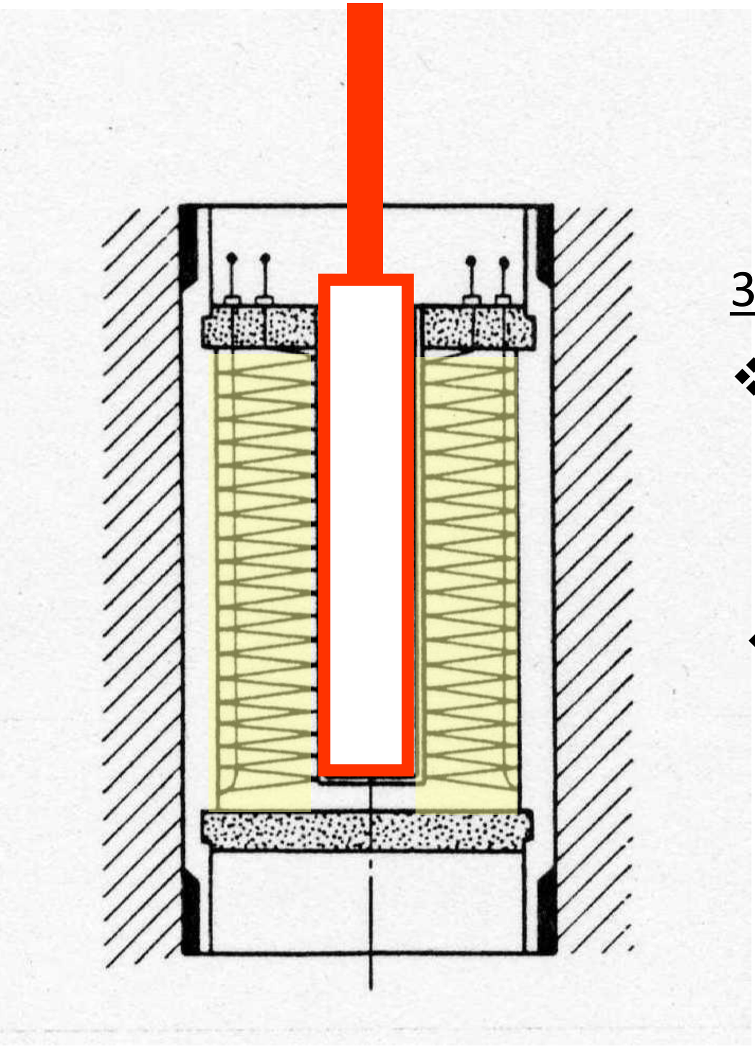
The Calorimetric Element



Calorimetric Element

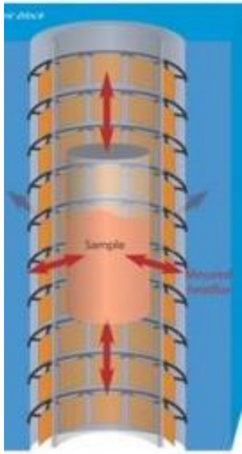
The Calorimetric Element



- The sample cell is placed into a calorimeter element

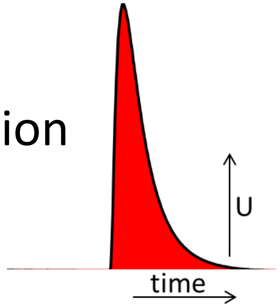
3D Calvet heat flow sensor

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

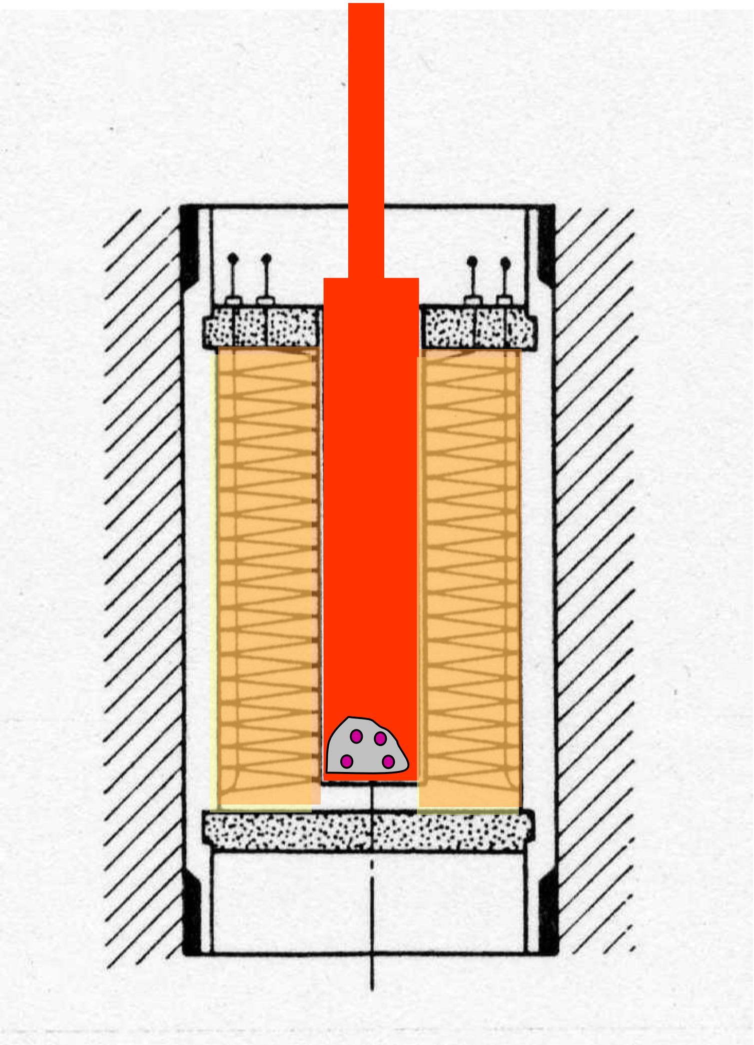


- Thermopile has 2 functions:

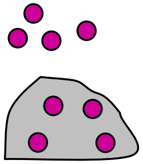
1. heat transfer
2. signal generation



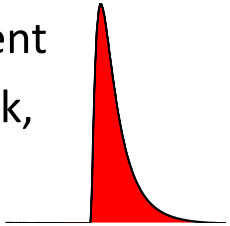
Heat and Heat Flow



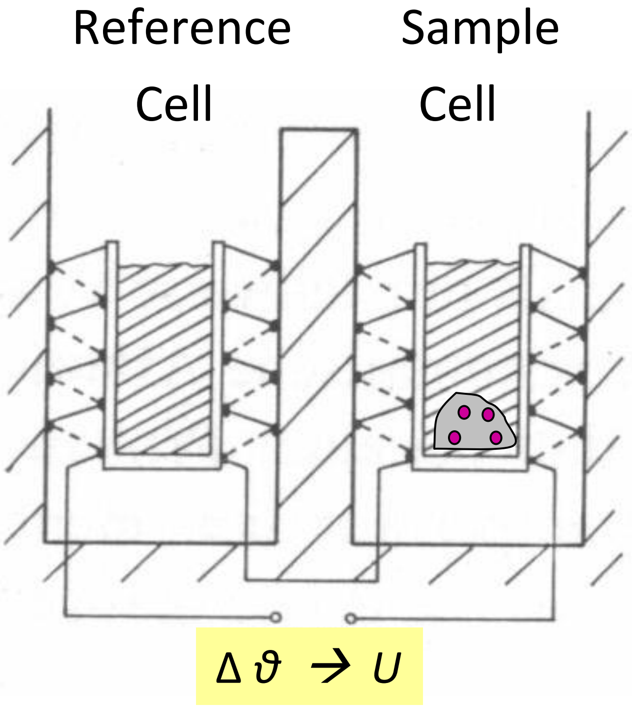
- The **heat** produced by the adsorption/activation/reaction of a dosed **probe molecule** on/with the **catalyst** surface is consumed by 2 processes



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



Reference cell



Setup according to Tian and Calvet

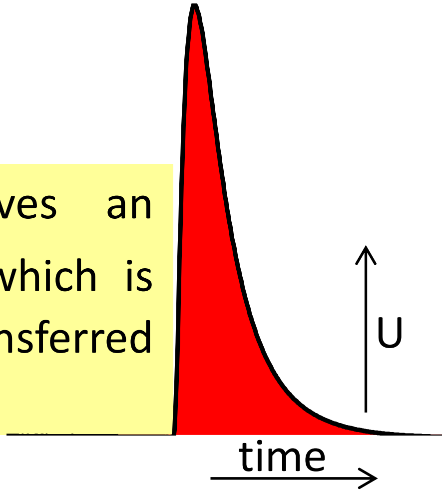
N. C. Cardona-Martinez and J.A. Dumesic, Advances in Catalysis 38 150-243.

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 $\Delta\vartheta$

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



Power balance, measuring signal and the Tian equation

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

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

The heat flow Φ [power] is proportional to the temperature gradient Δθ 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

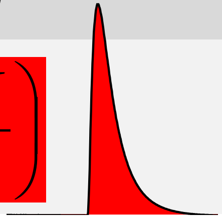
$$P_{total} = \frac{C}{g}\frac{dU}{dt} + \frac{G}{g}U$$

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

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

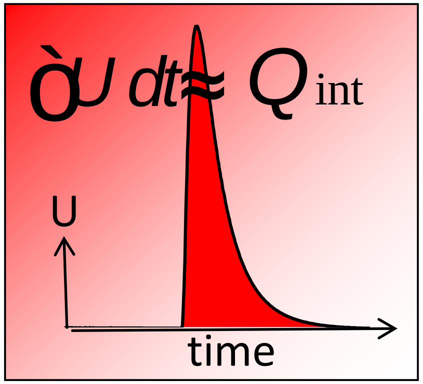
The Tian equation shows that the power is not proportional to the temperature difference, the power is delayed with respect to the signal **U** produced by the cell

$$\boxed{P_{total} = \frac{G}{g}\left(U + \tau\frac{dU}{dt}\right)}$$



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

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

A: area under curve [Vs]

f: calibration factor [J/(Vs)]

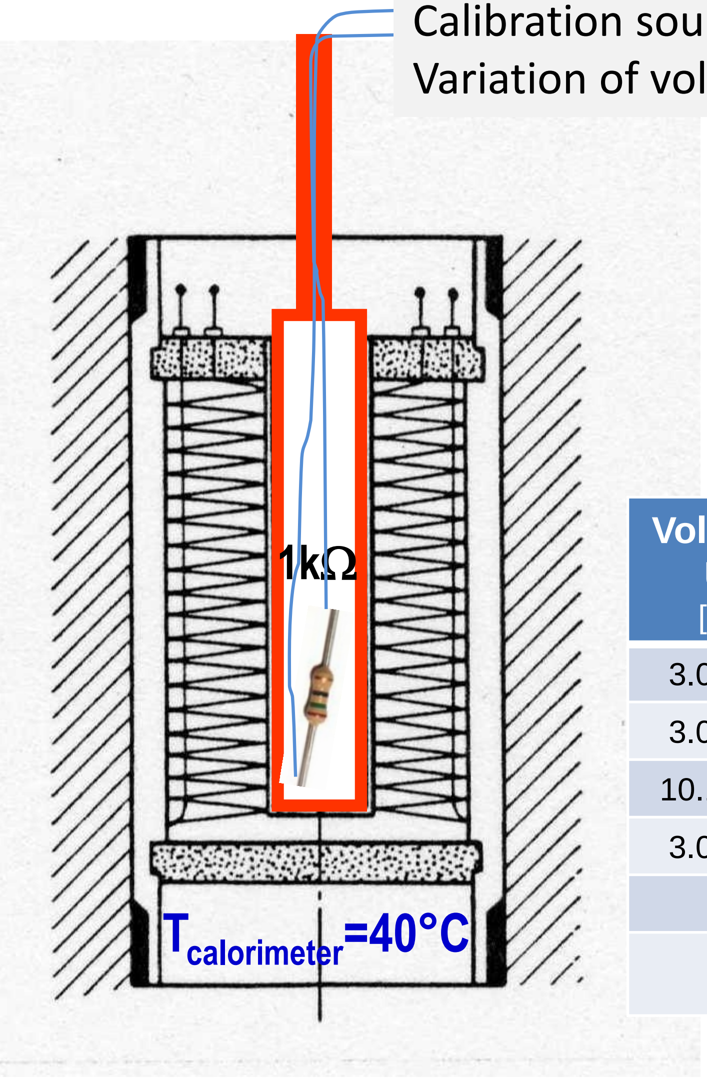
The heat signal of the calorimeter can be calibrated by:

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

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

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

Heat signal calibration at 40°C

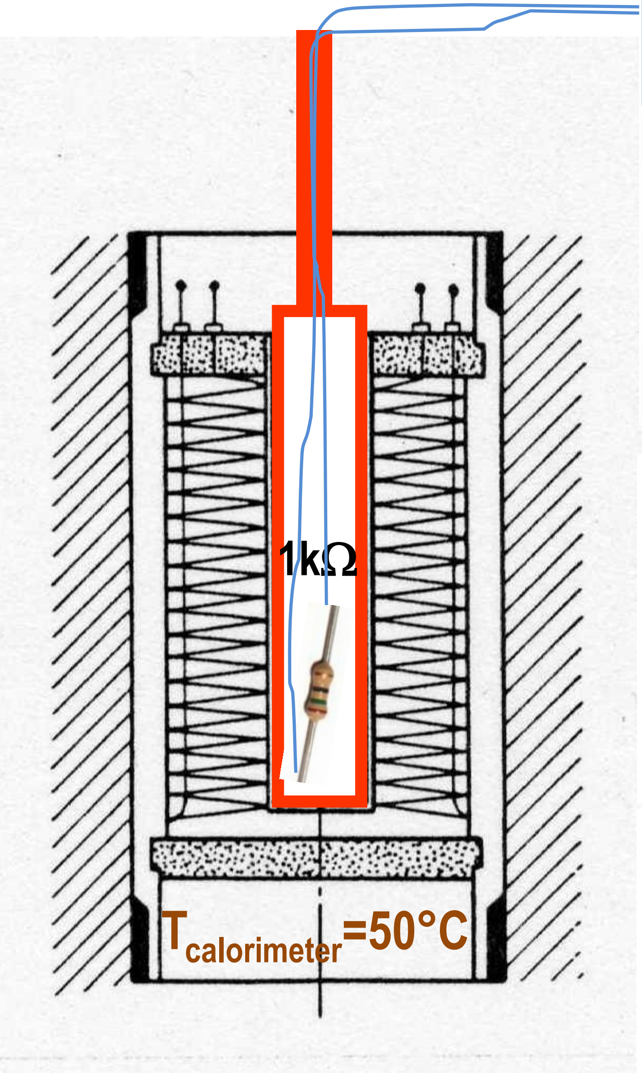


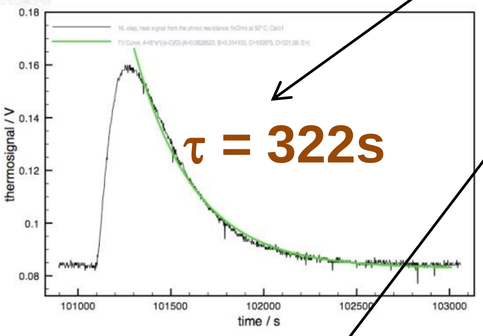
Calibration source:
Variation of voltage, current and time

Voltage **U** [V]	**Current** **I** [mA]	**time** **t** [s]	**Q** introduced **=U·I·t** [mWs, mJ]	**Q** integral [Vs]	$f = \frac{Q_{\text{introduced}}}{Q_{\text{integral}}}$ [mJ/Vs]
3.0528	3	3	27.48	45.544	1657.64
3.0527	3	6	54.95	91.143	1658.69
10.1733	10	10	1017.33	1692.075	1663.25
3.0563	3	1	9.16	14.978	1635.30
					⋮
					$f_{40°C} = 1659$

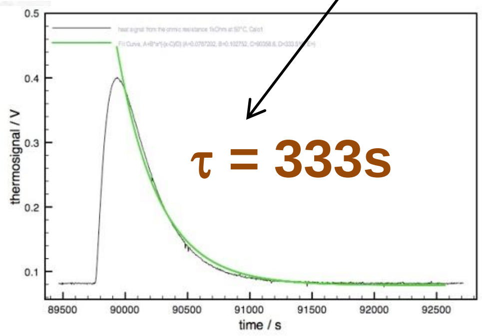
Heat signal calibration, time constant τ at 50°C

Voltage U [V]	**Current** I [mA]	**time** t [s]	**Q** introduced =U·I·t [mWs, mJ]	**Q** integral [Vs]	$f = \frac{Q_{introduced}}{Q_{integral}}$ [mJ/Vs]
10.18	10	3	305.4	511.077	1673,47
2.03	2	5	20.30	34.631	1705.96
3.07	3	10	92.10	152.98	1661.02
10.17	10	3	305.10	514.63	1686.76
					$f_{50°C} = 1674$

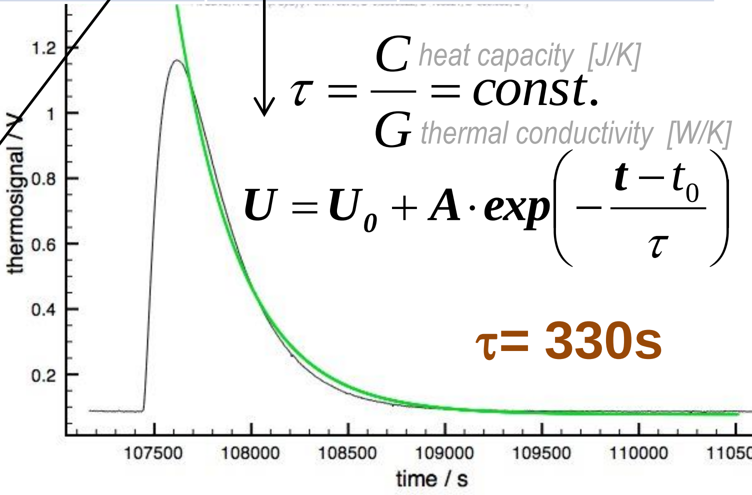




τ = 322s



τ = 333s



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

C heat capacity [J/K]

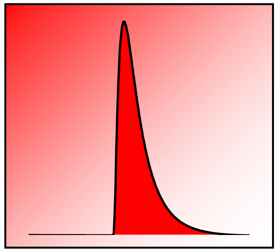
G thermal conductivity [W/K]

$$U = U_0 + A \cdot \exp\left(-\frac{t-t_0}{\tau}\right)$$

τ= 330s

$\tau_{calorimeter,50°C}$ = 300 - 350s

Evolved Heat &
Differential Heat of Adsorption



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

A: area under curve [Vs]

f: calibration factor [J/(Vs)]

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

$$q_{diff} = (\delta Q_{\text{int}} / \delta n)_{T,V,p(equ.)}$$

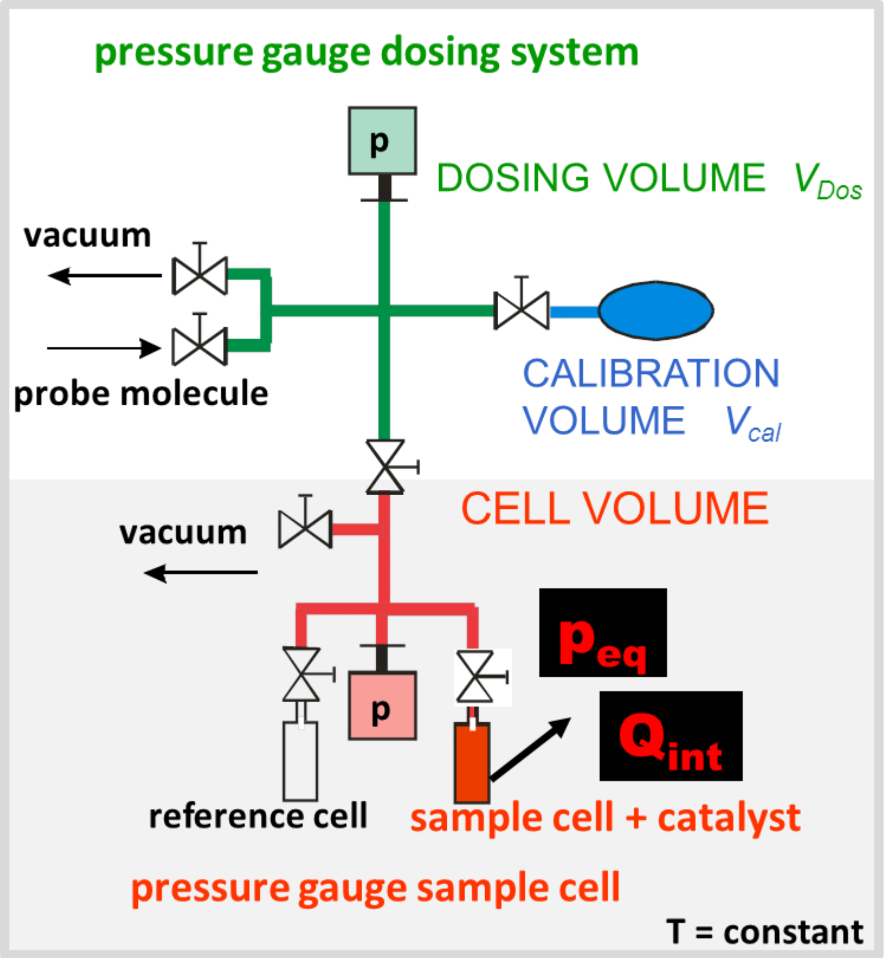
Calculation of the adsorbed amount

Contents

Measurement of the adsorbed amount

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

Volumetric-barometric system



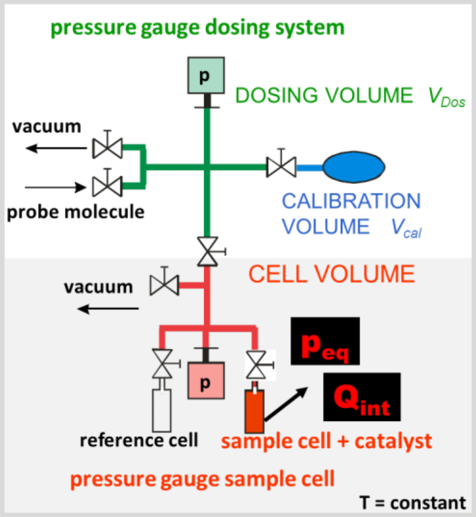
➢ **V_{dos} V_{cal} $n_{introduced}$**

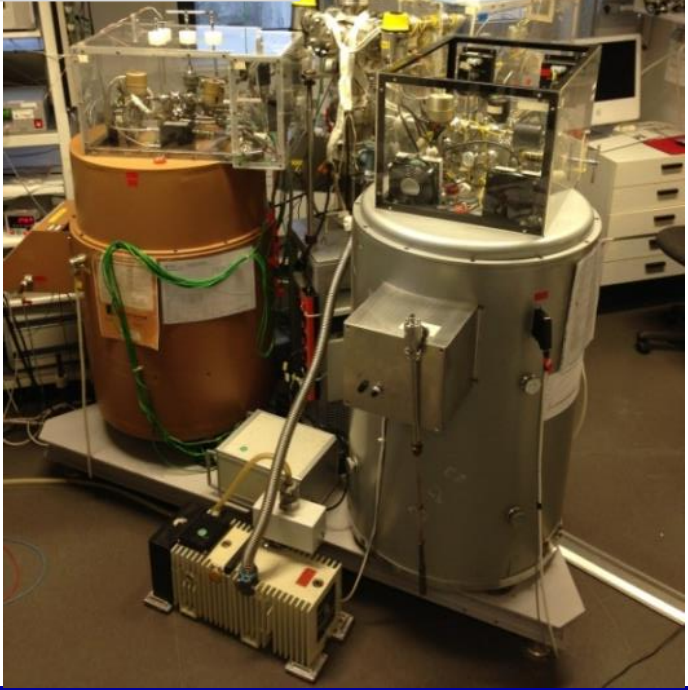
calibration isotherm $n_{inner\ wall\ +\ gas} = f\,(p_{equ})$

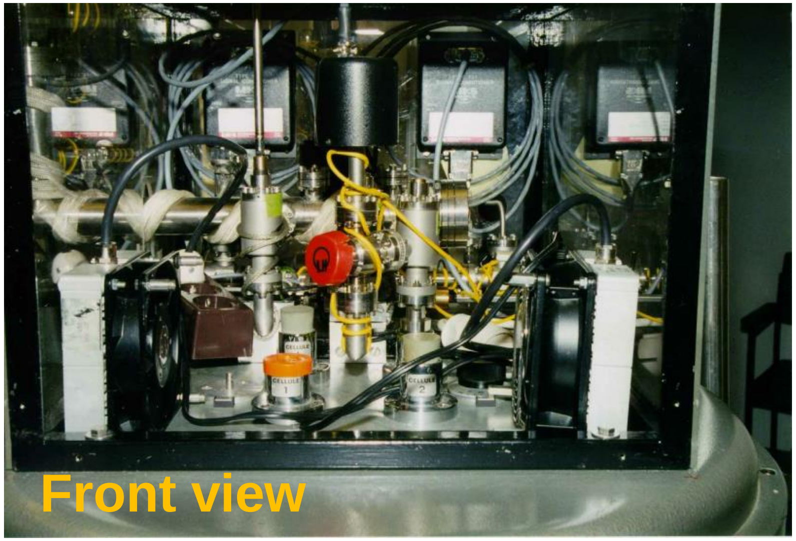
adsorbed amount

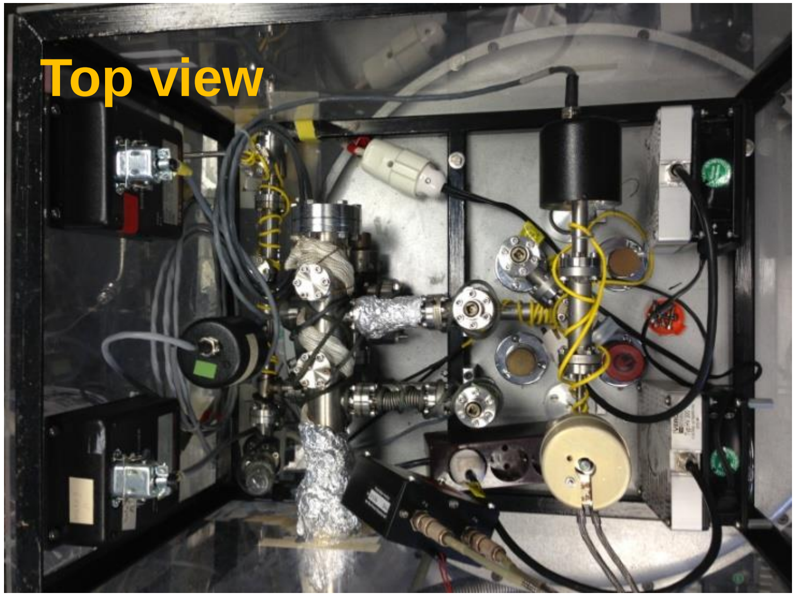
on the surface of the catalyst

Volumetric-Barometric System



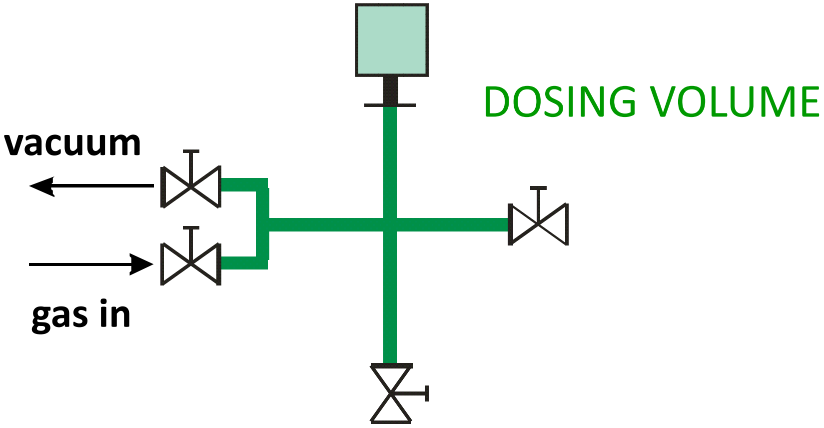






The Dosing Volume V_{Dos}

pressure gauge dosing system

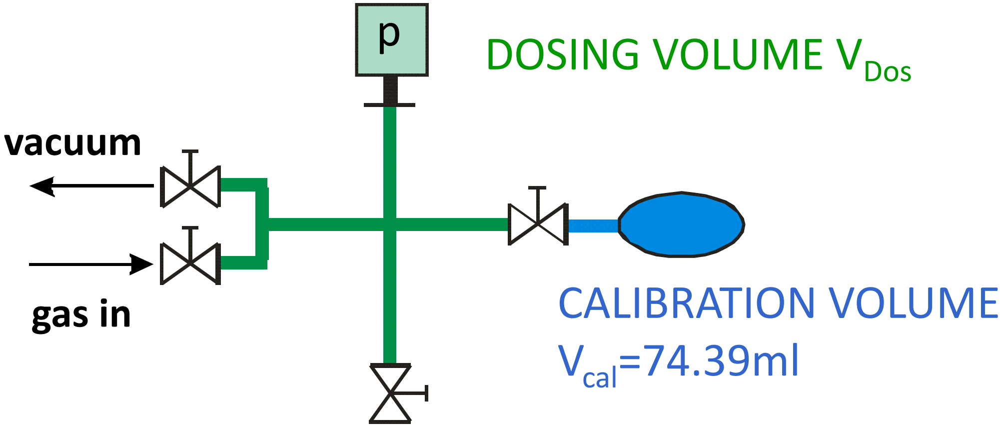


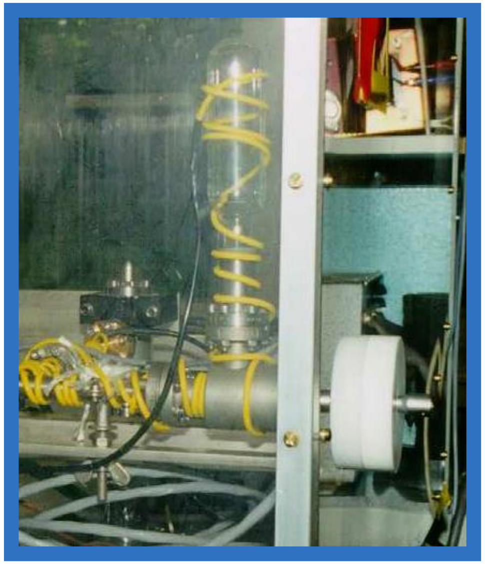
- p, T can be easily measured
- **V needs to be determined**

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

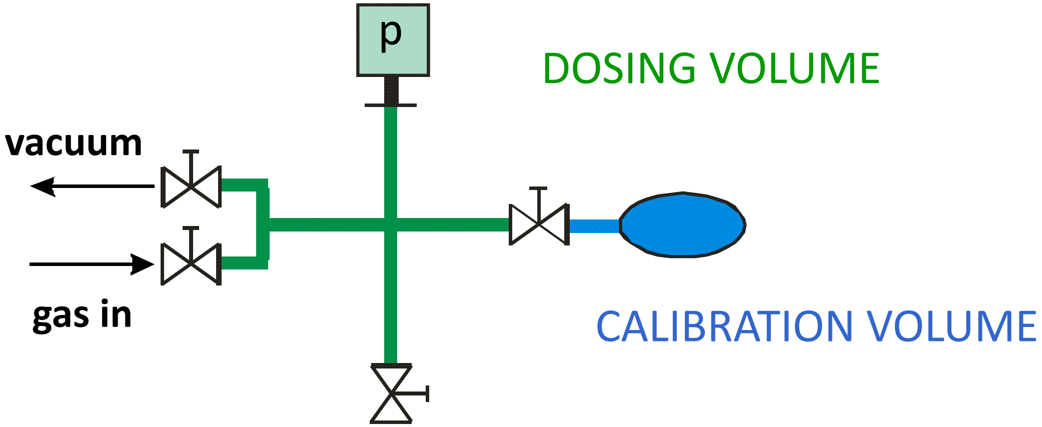




- fill V_{Cal} and V_{Dos}, same pressure
- close valve between V_{Cal} and V_{Dos}
- set pressure in V_{dos} to p_{Dos}
- open valve, equilibrate

Calibrating the Dosing Volume

pressure gauge dosing system



p

DOSING VOLUME

vacuum

gas in

CALIBRATION VOLUME

- Initial situation:
- After opening valve:
- n, T are constant

$$nRT = p_{Cal}V_{Cal} + p_{Dos}V_{Dos}$$

$$nRT = p_{fin}\left(V_{Cal} + V_{Dos}\right)$$

$$V_{Dos} = \frac{p_{Cal} - p_{fin}}{p_{fin} - p_{Dos}} V_{Cal}$$

Example Data

Propane at 40°C (*Project: V_xO_y/SBA15 for ODH of propane*)

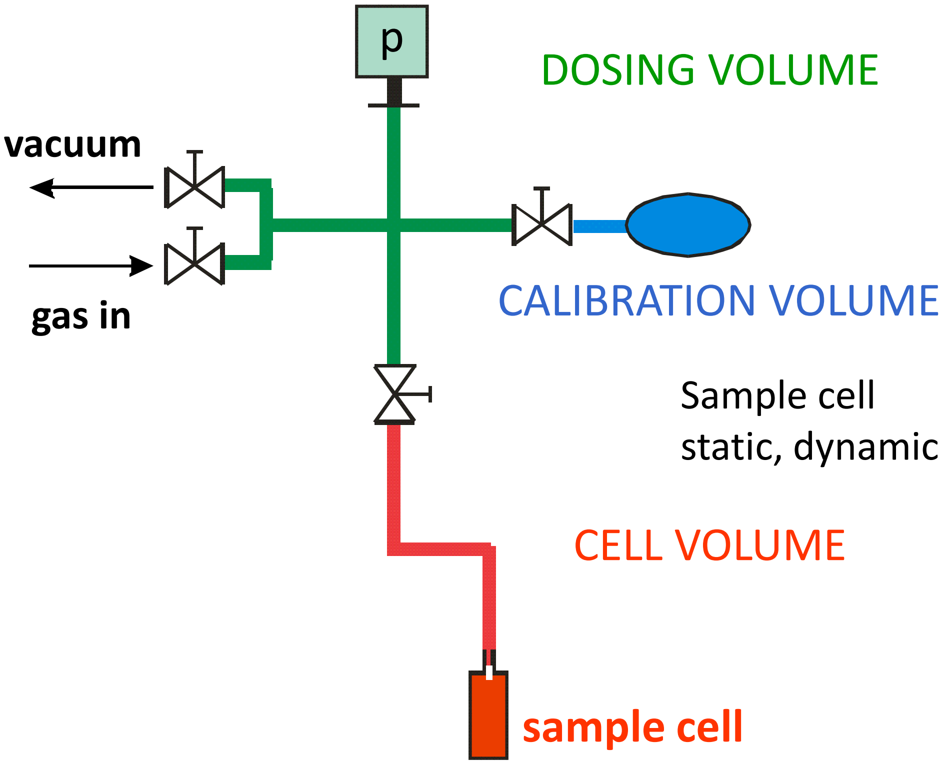
Nr	p_{Cal} [mbar]	p_{Dos} [mbar]	p_{fin} [mbar]	V(Dos) [ml]
	before	before	after equilibration	
1	5,314	9,467	8,683	137
2	8,683	7,648	7,843	137
3	7,638	6,341	6,585	137
4	6,585	4,768	5,111	137
5	5,111	4,712	4,787	137
6	4,786	3,197	3,496	137
7	3,469	2,701	2,846	136

$$V_{Dos} = \frac{p_{Cal} - p_{fin}}{p_{fin} - p_{Dos}} V_{Cal}$$

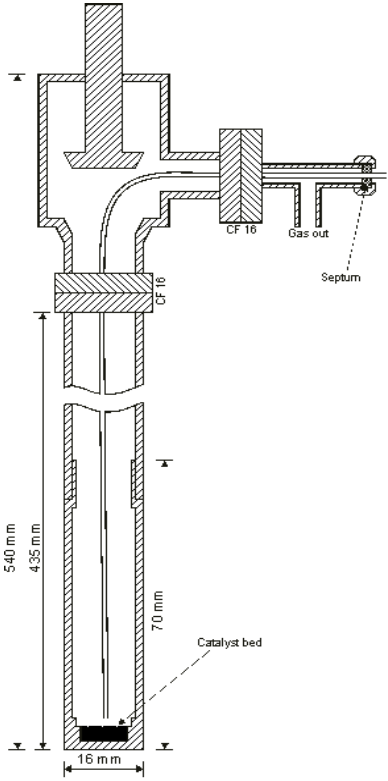
- It is important that the entire system is at the same constant temperature!

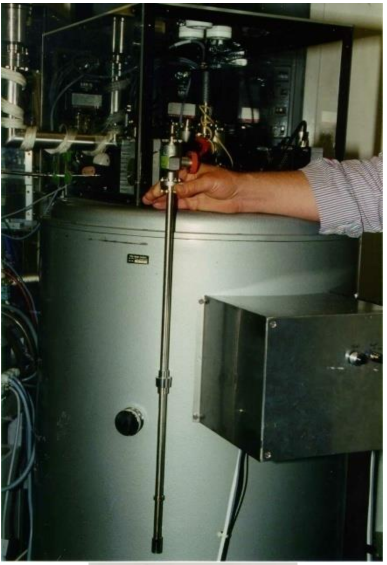
Determining the Dosed Amount $n_{int, i}$

pressure gauge dosing system



Sample cell
static, dynamic





sample holder
L = 70 mm
∅ = 15 mm

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

Total Number of Molecules in Sample Cell

- Total number of molecules accumulated in cell

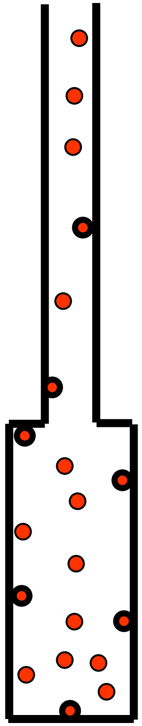
$$n_{SC,tot,i} = \sum_i n_{\mathrm{int},i} = n_{SC,tot,i-1} + n_{\mathrm{int},i}$$

- i.e. the sum of

  the number of molecules already in the cell

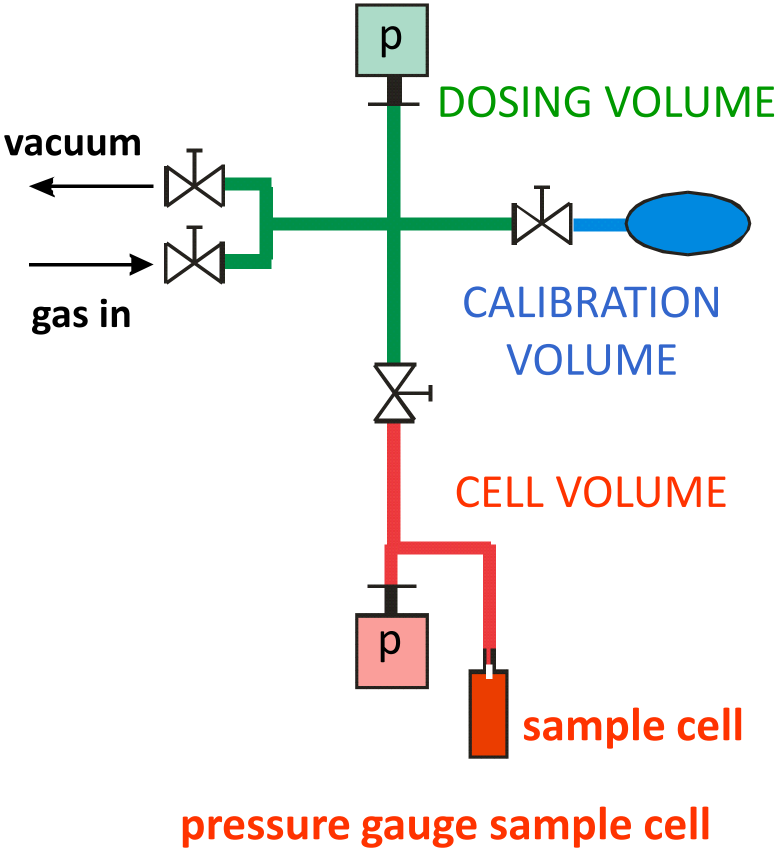
  the number of molecules introduced in the ith step

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

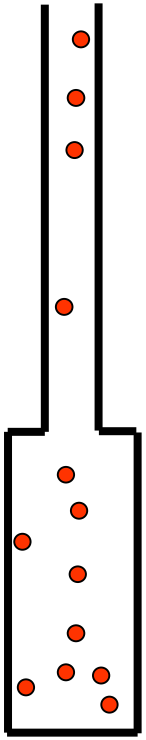


Inner wall Adsorption Blank Measurement

- Measure the pressure in the cell as a function of the total number of molecules introduced into the cell

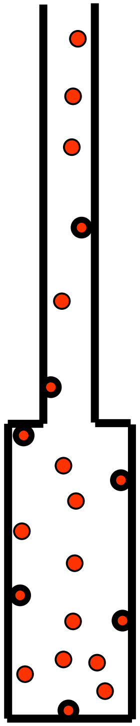
- Without wall adsorption and without sample, the relation between pressure and number of molecules in the sample cell would be given by the ideal gas law

$$p_{SC,i} = \frac{n_{SC,tot,i} RT}{V_{SC}}$$



Inner wall Adsorption Blank Measurement

- 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

Nr	$p_{Dos,bef}$/mbar	$p_{Dos,aft}$/mbar	$p_{SC,i}$ /mbar	$n_{int,i}$/µmol	$n_{SCtot,i}$ /µmol
1	9,682	9,674	0,007	0,04	0,04
2	9,653	9,641	0,026	0,06	0,10
3	9,607	9,591	0,054	0,08	0,18
4	9,562	9,544	0,081	0,09	0,27
5	9,499	9,481	0,117	0,09	0,36
6	9,442	9,428	0,147	0,07	0,43
7	9,392	9,371	0,181	0,11	0,54
9	9,230	9,195	0,283	0,18	0,72
10	9,128	9,091	0,344	0,19	0,91
11	9,024	8,988	0,403	0,19	1,10
13	8,814	8,758	0,537	0,29	1,39
14	8,644	8,582	0,640	0,32	1,71
15	8,466	8,386	0,755	0,42	2,13
16	8,209	8,122	0,909	0,45	2,58
17	7,783	7,612	1,208	0,90	3,48
19	6,672	6,487	1,870	0,97	3,45
20	5,893	5,526	2,436	1,93	5,38
21	4,477	4,041	3,314	2,30	7,68
22	9,146	8,409	4,056	3,88	11,56

Isobutane at 40°C

without catalyst

(Project:

isomerisation of

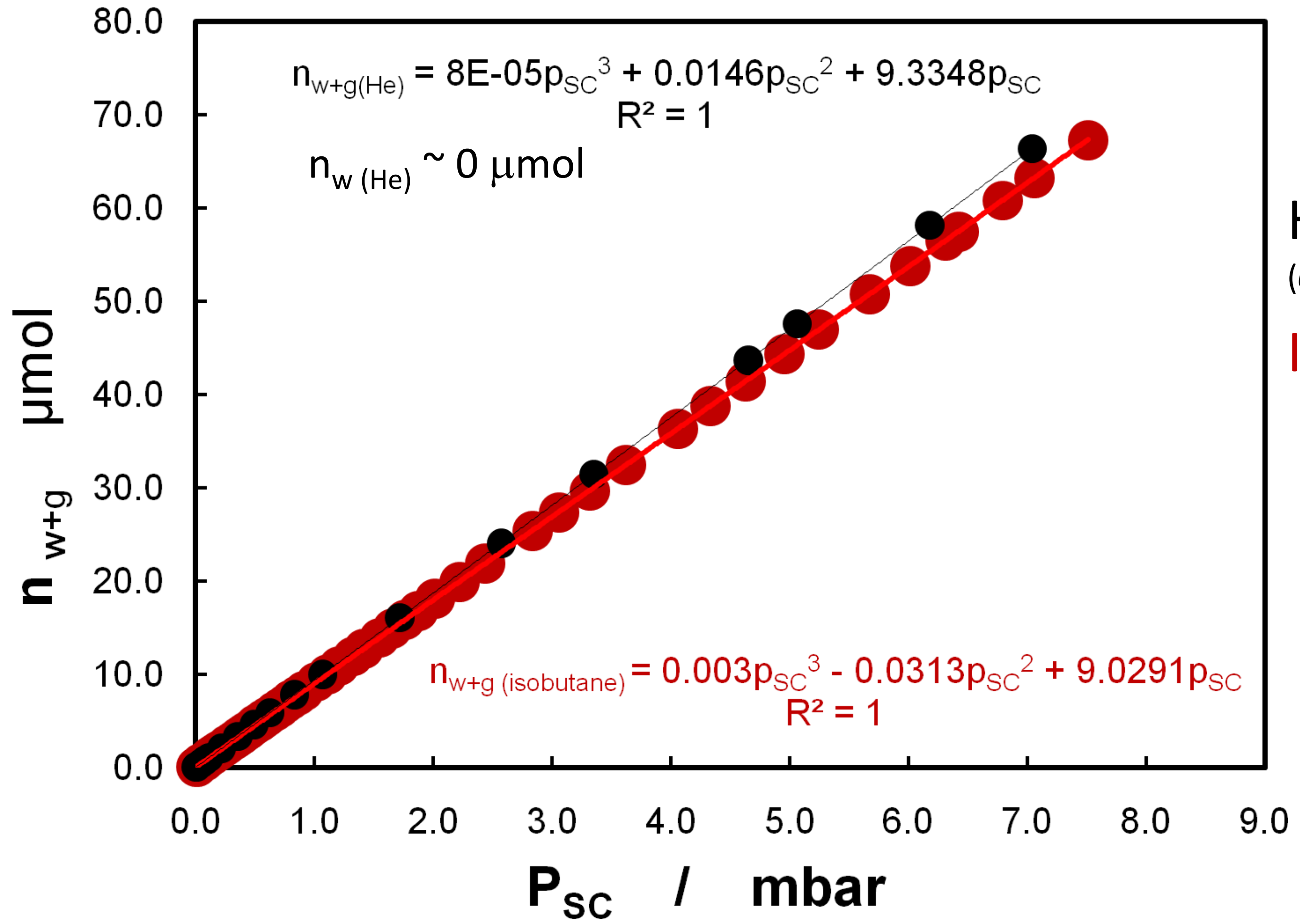
n-butane to isobutane

over sulf. ZrO_2)

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

$$n_{SC,tot,i} = \sum_i n_{\text{int},i} = n_{SC,tot,i-1} + n_{\text{int},i}$$

Correction for Wall Adsorption



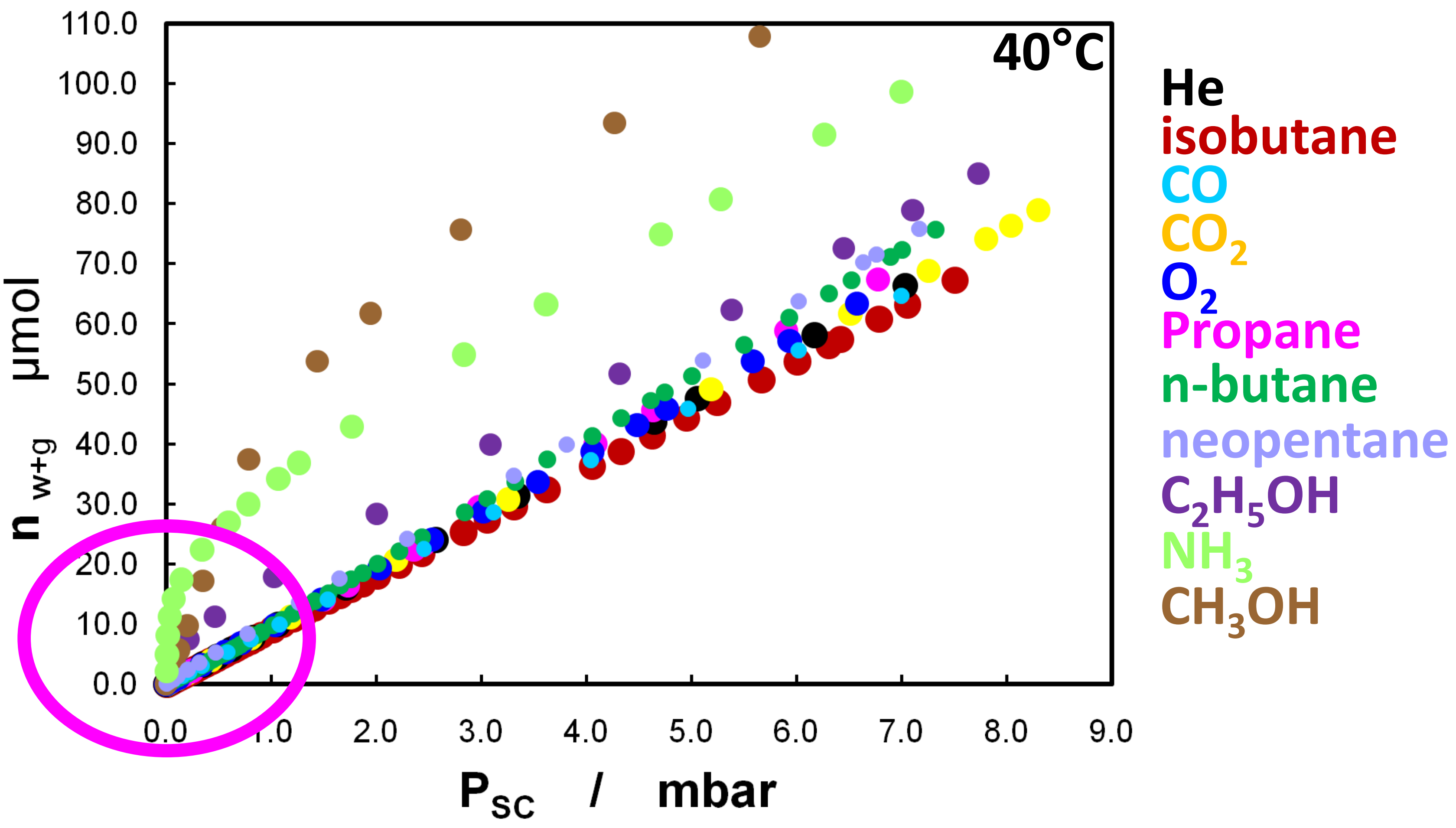
He @ 40°C

(does not stick to the walls)

Isobutane @ 40°C

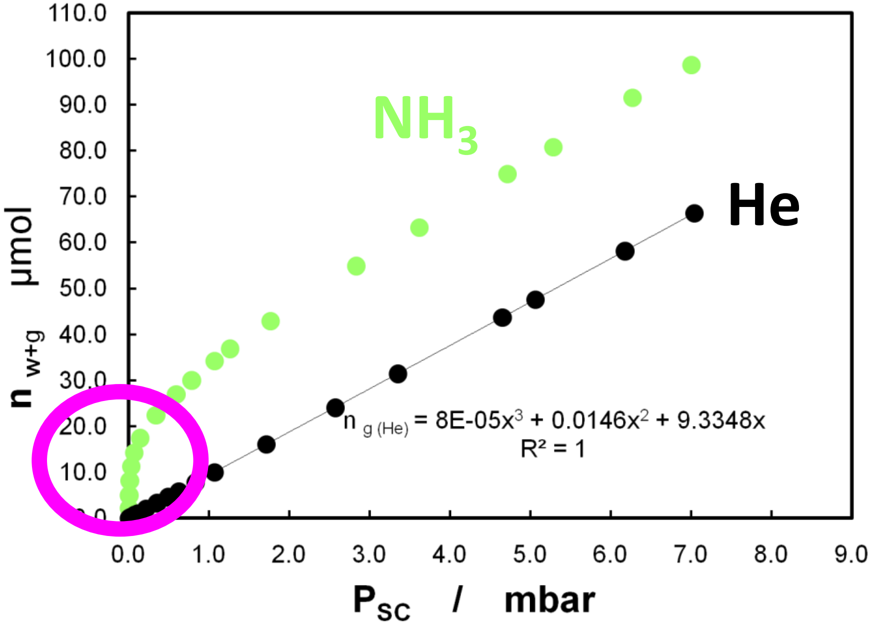
- The adsorption of isobutane on the walls is insignificant

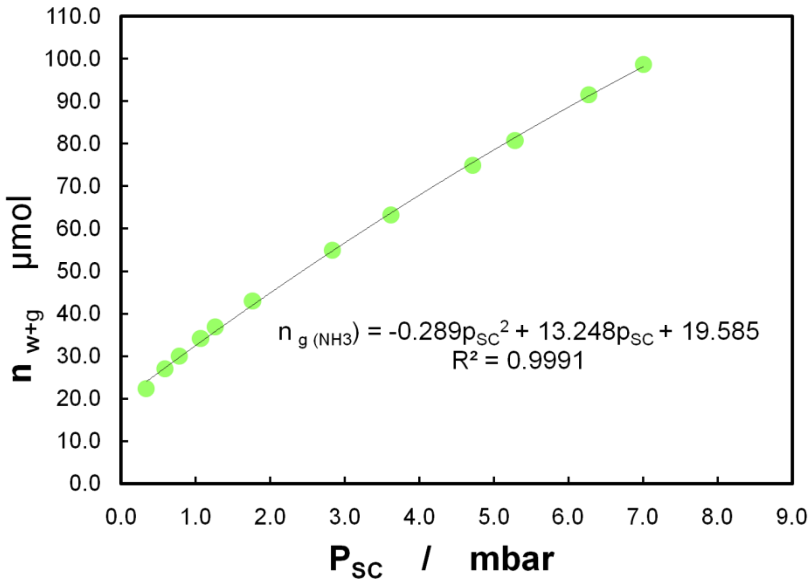
Correction for Wall Adsorption

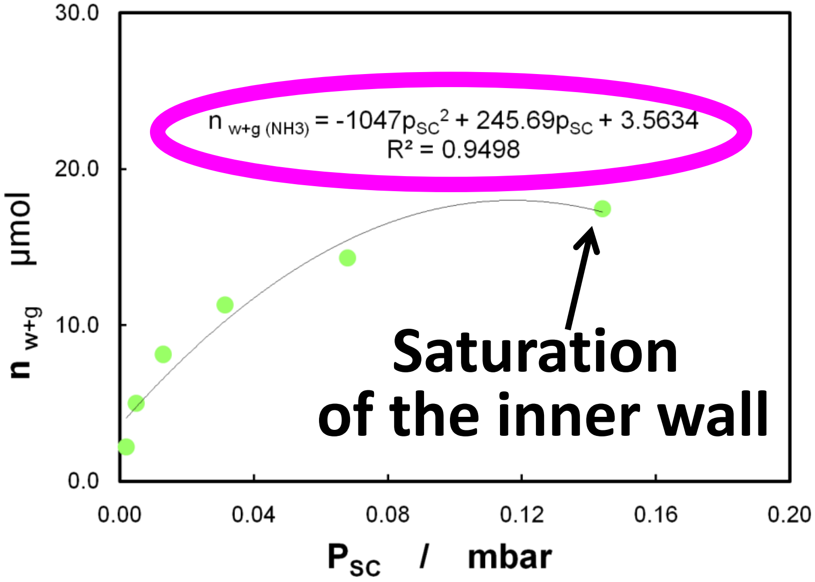


- The adsorption of e.g. C_2H_5OH NH_3 CH_3OH on the walls is significant

Correction for Wall Adsorption







Saturation of the inner wall

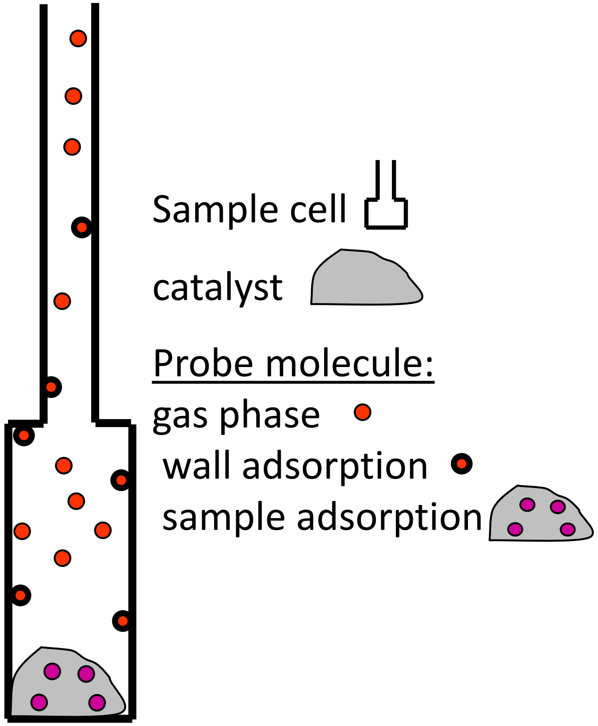
Calculation of Adsorbed Amount

- Total number of molecules in sample cell after the ith step

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

- Total number of molecules in sample cell after the (i+1)th step

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



- The difference in number of molecules between ith and (i+1)th step is the number of molecules introduced in the (i+1)th step

Calculation of Adsorbed Amount

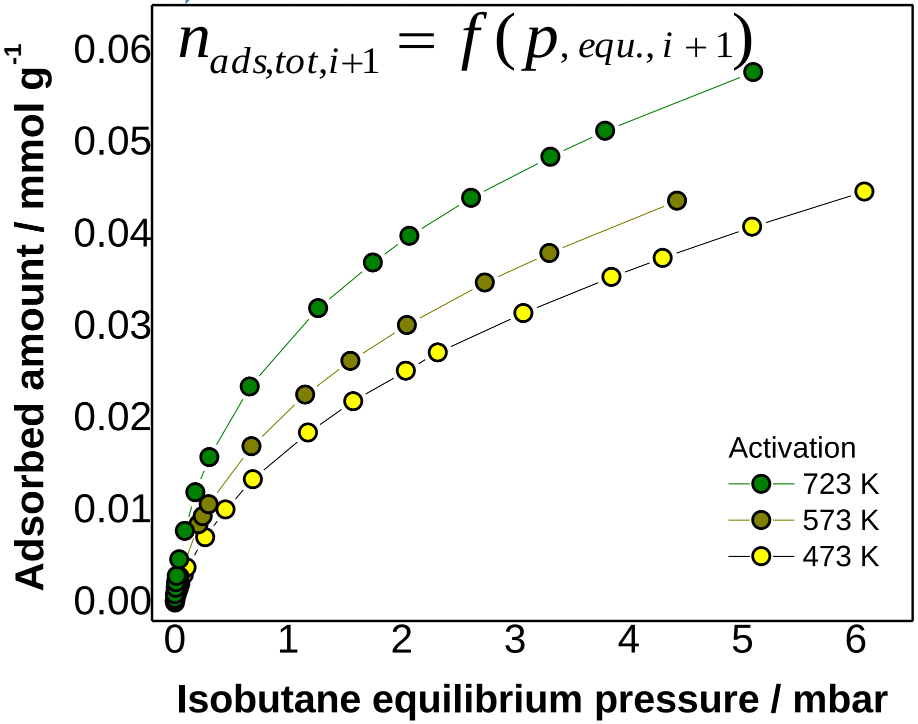
- The number of molecules adsorbed in the (i+1)th step is then

$$n_{ads,i+1} = n_{\mathrm{int},i+1} + n_{SC,w+g,i} - n_{SC,w+g,i+1}$$

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

$$n_{ads,tot,i+1} = n_{ads,tot,i} + n_{ads,i+1}$$

Adsorption isotherm



$$n_{ads,tot,i+1} = f\,(p_{,\,equ.,\,i\,+\,1})$$

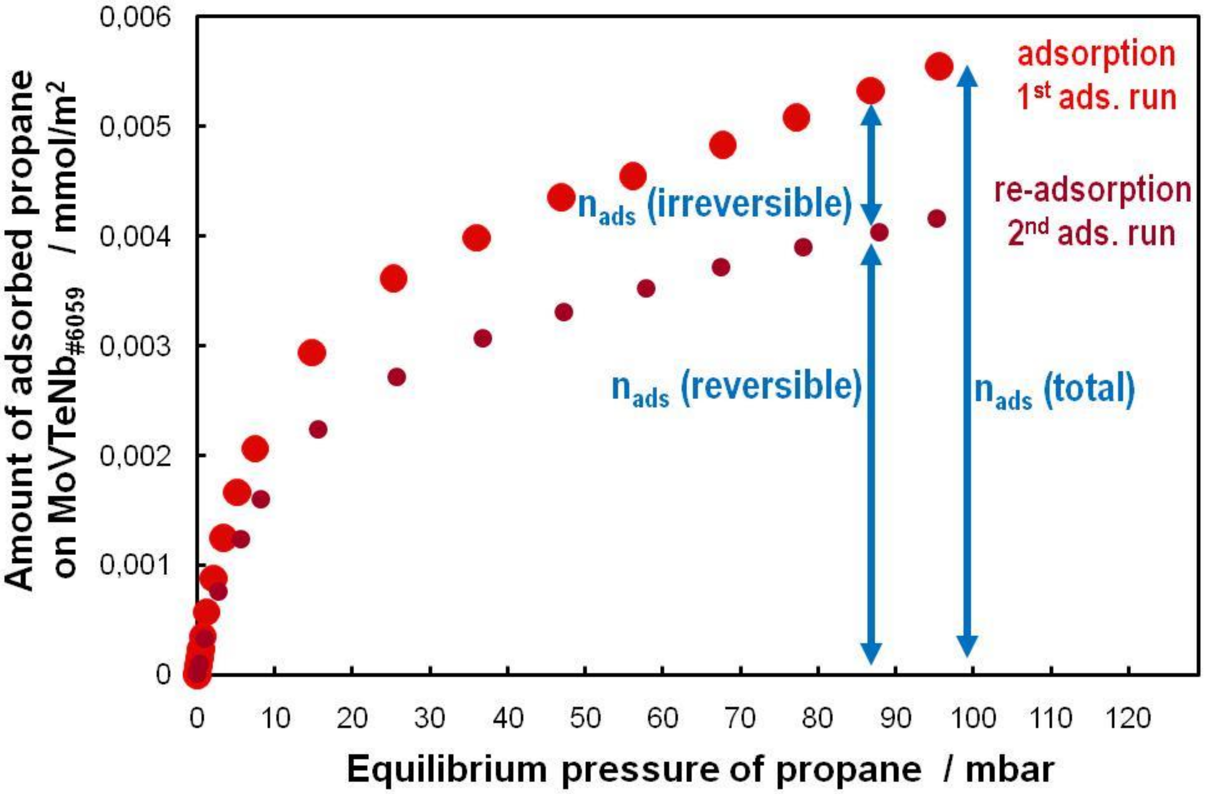
Isobutane adsorption on different activated sulf. ZrO_2 at 40°C.

(Project: isomerisation of n-butane to isobutane over sulf. ZrO_2 *[S. Wrabetz, F.C. Jentoft etal, J. Catal. 269 (2010) 351-358.]*)

Contents

Obtained physical quantities & evaluation criteria of the calorimetric result

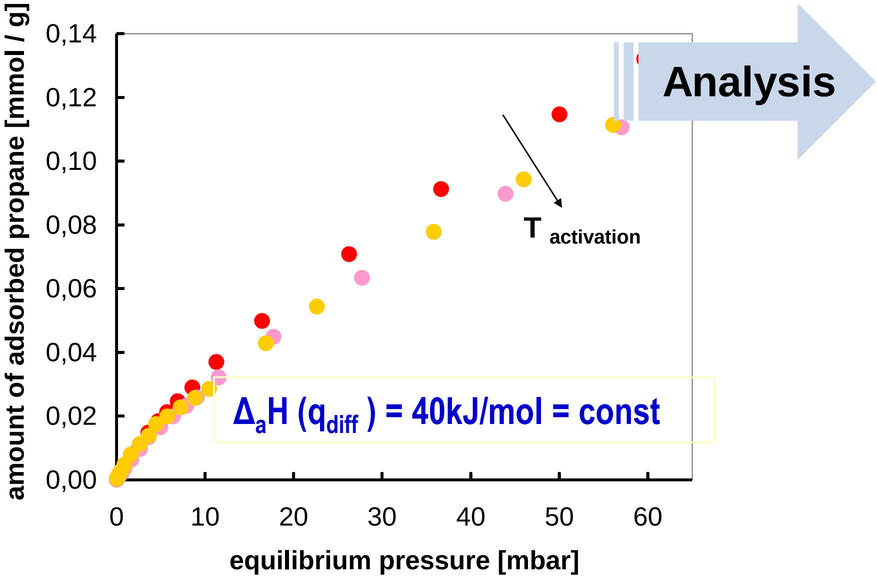
Adsorption Isotherm - $n_{ads} = f\,(p_{equ.})$



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

n_{ads} (irrev.) : chemisorbed amount

Analysis of the Adsorption Isotherm



Adsorption Isotherm

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

$\Delta_a H$ (q_{diff}) = 40kJ/mol = const

Langmuir model: The enthalpy of adsorption $\Delta_a H$ per site is constant with coverage Θ

- Langmuir model for dissociative adsorption

$$\theta_H = \frac{n_{ads}}{n_m} = \frac{\sqrt{p_{H_2}K_{ads}}}{1+\sqrt{p_{H_2}K_{ads}}}$$

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 *[S. Wrabetz et.al., Catal. 2010, 269, 351 –358.]*

- Langmuir model $\theta = \frac{Kp}{1+Kp}$

Freundlich isotherm:
The enthalpy of adsorption $\Delta_a H$ per site decreases exponential with coverage Θ

$$N_{ads} = \frac{A\,p^{\frac{1}{n}}}{1+A\,p^{\frac{1}{n}}}$$

Tempkin isotherm: The enthalpy of adsorption $\Delta_a H$ per site decreases linear with coverage Θ

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

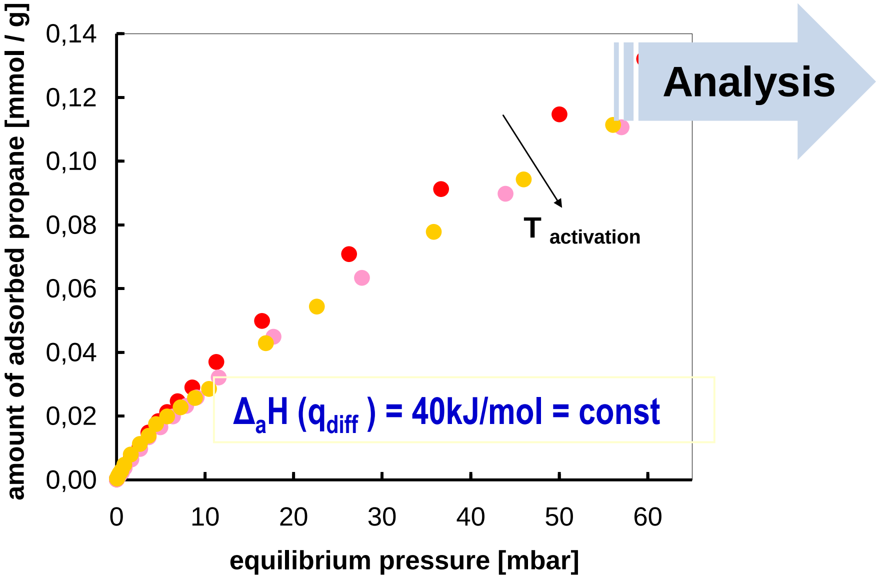
e.g., propane adsorption (313 K) on the oxygen surface groups of CNT and B_2O_3–CNT catalysts used in ODH of propane *[B. Frank, S. Wrabetz et.al., ChemPhysChem 2011, 12, 2709 – 2713]*

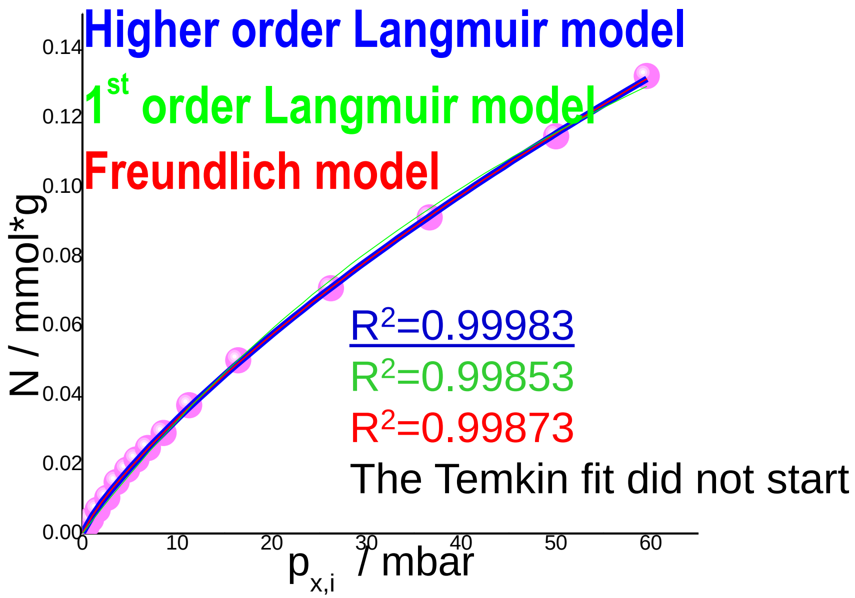
CO Adsorption on supported Gold nanoparticle catalysts
[Ch. J. Pursell et.al., J. Phys. Chem.C, 2012, 116(20),11117]

Analysis of the Adsorption Isotherm

Adsorption Isotherm

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





Specific surface area = N_{mono} * Avogadro constant * $S_{1:1, \text{assumed}}$ * cross-section area $_{39 \text{Å}2 \text{ for propane}}$

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

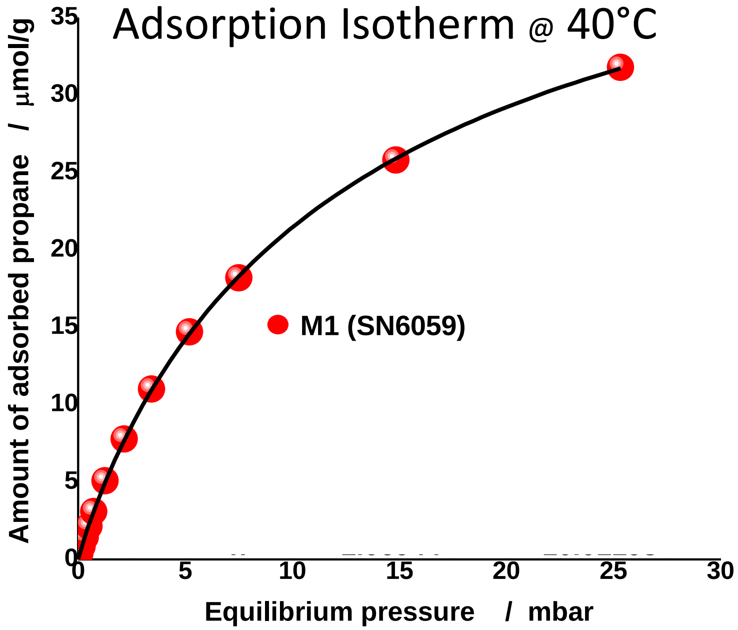
$$N_{ads} = \frac{N_{mono}(Kp)^{\frac{1}{n}}}{1+(Kp)^{\frac{1}{n}}}$$

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

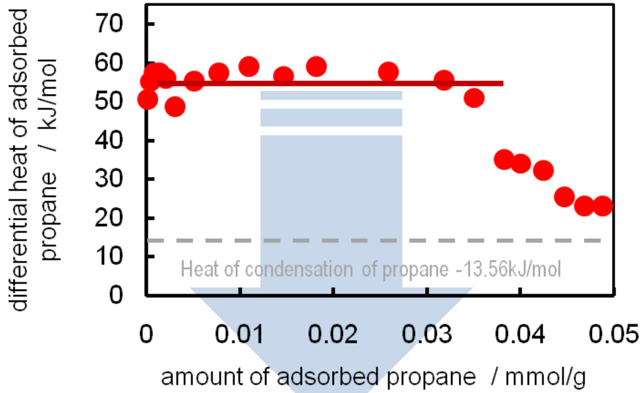
10%V/SBA15 dehydration temperature	N_{mono} µmol *g^{-1}	**n**	R^2	**$S_{propane}$** m^2*g^{-1}	**BET** S_{N2} m^2*g^{-1}
373 K	0.9 (2)	**1.20 (2)**	0.99983	**226 (10)**	**329 (4)**
573 K	1.3 (4)	**1.22 (2)**	0.99982	304 (10)	
673 K	1.2 (3)	**1.22 (2)**	0.99905	290 (10)	

Analysis of the Adsorption Isotherm

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



$\Delta_a H$ (q_{diff}) @ 40°C ~ 58 kJ/mol = const



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

Langmuir model for activated ads. :

The enthalpy of adsorption $\Delta_a H$ per site is constant with coverage Θ

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

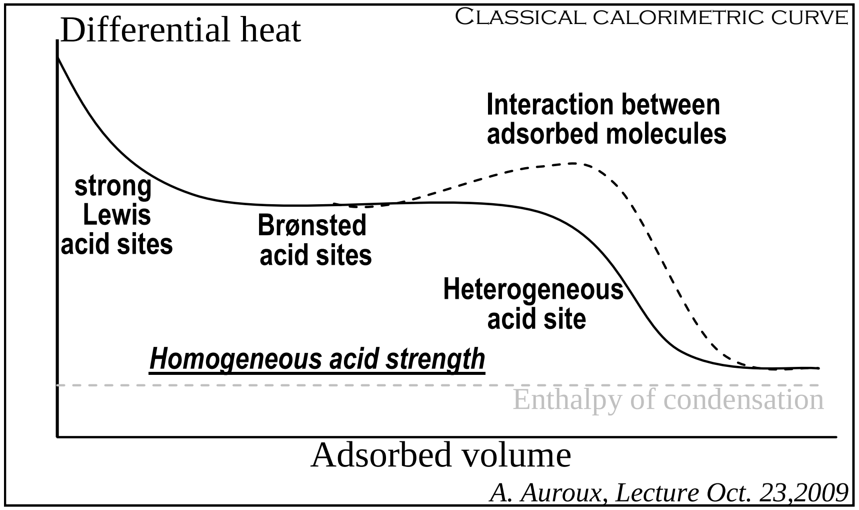
[A. L. McClellan et.al., J. of Colloid and Interface Science, 23 (1967) 577]

Catalyst (ID)	$N_{monolayer}$ µmol *g^{-1}	R^2	$S_{propane}$ m^2*g^{-1} $A_{propane}$~39 $Å^2$	BET m^2*g^{-1} A_{N2} =16.2 $Å^2$
M1 (5630)	34.9 (2)	0.99951	8.2 (1)	6.6
M1 (6059)	**48.5 (8)**	**0.99991**	**11.3 (1)**	**8.8**
M1 (5737)	42.3 (8)	0.99986	9.9 (1)	13.4

N_{ads}	- coverage with certain equilibrium pressure
N_{mono}	- monolayer coverage
p	- equilibrium pressure
n	- adsorption order
K/A	- adsorption equilibrium constant
R^2	- correlation coefficient; goodness of fit
S	- stoichiometry

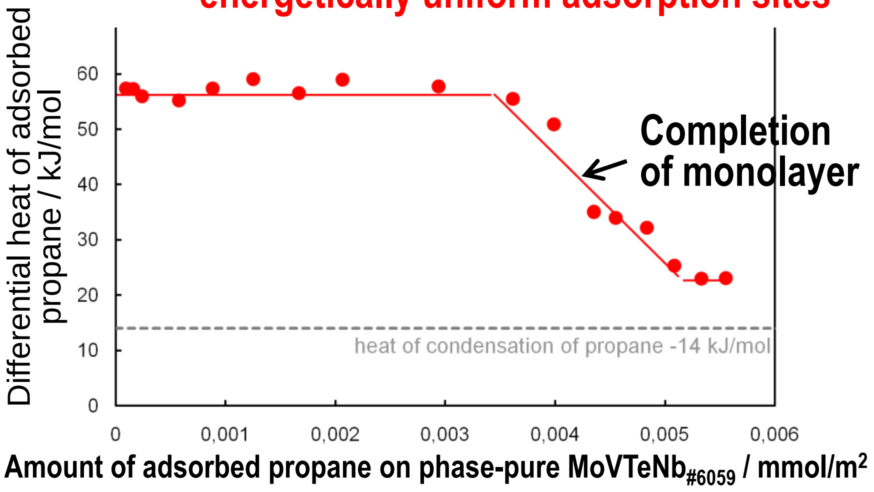
Obtained physical quantities & evaluation criteria of the calorimetric result

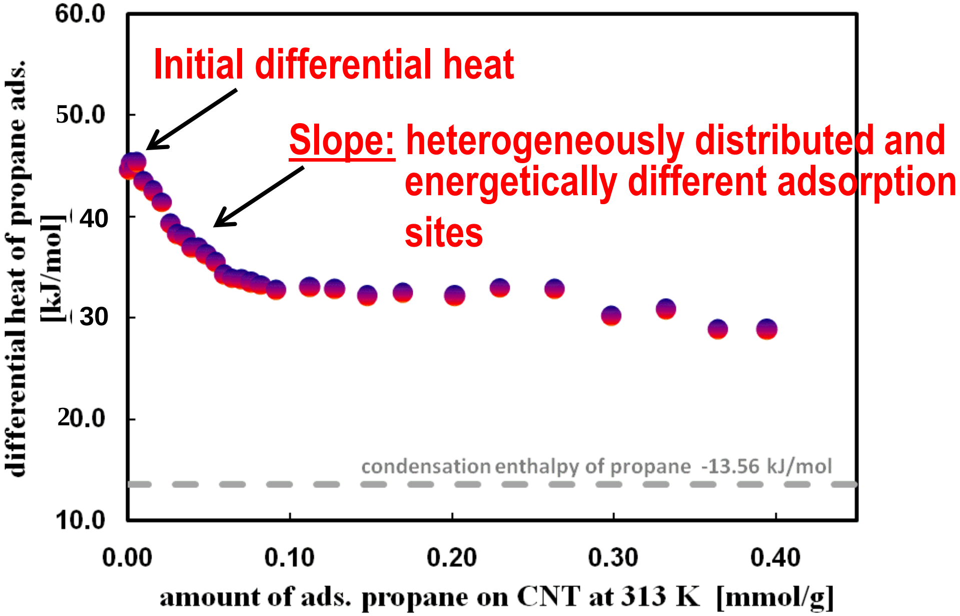
Classical Calorimetric Curve



A. Auroux, Lecture Oct. 23,2009

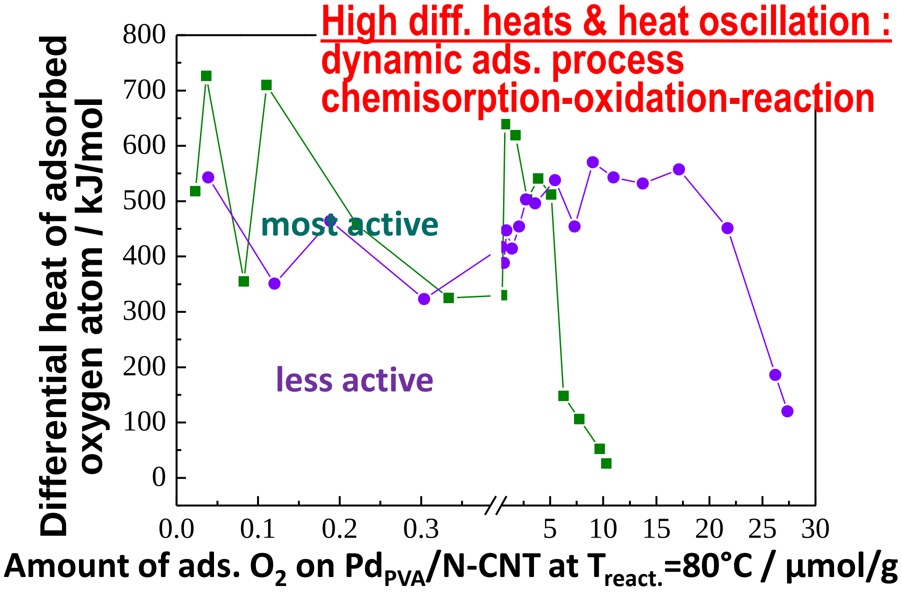
Plateau: homogeneously distributed and energetically uniform adsorption sites





Initial differential heat

Slope: heterogeneously distributed and energetically different adsorption sites

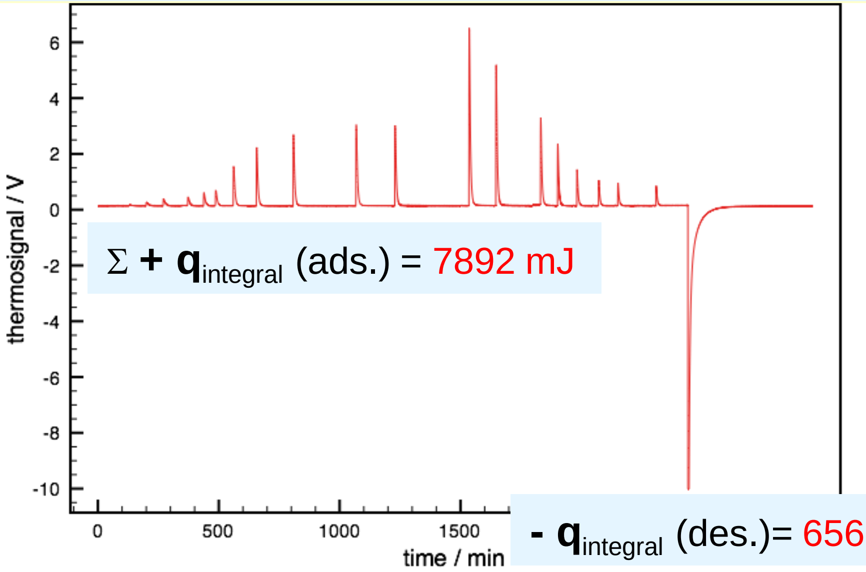


High diff. heats & heat oscillation : dynamic ads. process chemisorption-oxidation-reaction

Evaluation criteria of the calorimetric result

Integral heat signal of adsorption and desorption

stepwise adsorption of propane on MoVTeNb oxide at 40°C



Σ **+ $q_{integral}$** (ads.) = 7892 mJ

- $q_{integral}$ (des.)= 6560 mJ

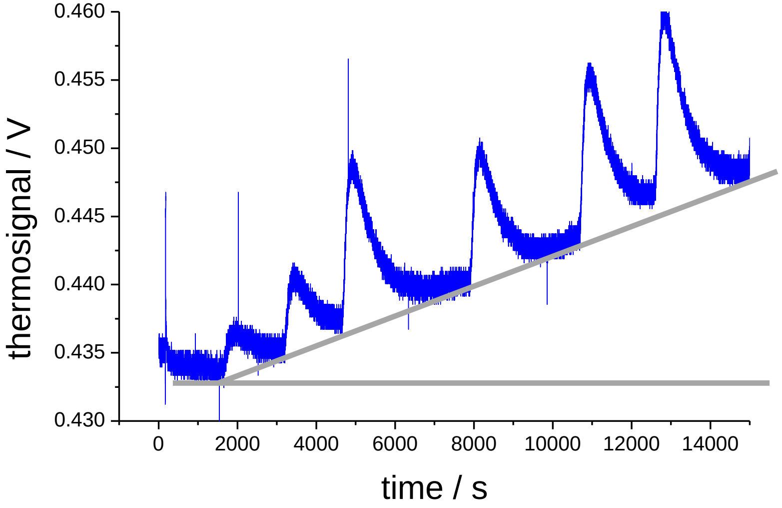
Σq_{int} (ads.) > q_{int} (des.) → partially irreversible ads.; activated ads. process

Σq_{int} (ads.) < q_{int} (des.) → instability of the catalyst in the presence of probe molecule

Σq_{int} (ads.) = q_{int} (des.) → reversible ads. process

Background of the thermo signal during the stepwise adsorption

stepwise n-butane ads. on sulf. ZrO_2 at 40°C < 60°C=$T_{reaction}$



Heat signal deviates from the base-line

→ Adsorption process is accompanied by secondary processes

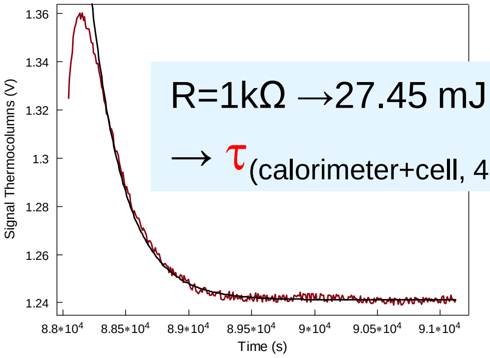
e.g. during n-butane ads. a partial isomerization of n-butane to isobutane in the calorimeter cell was observed

Evaluation criteria of the calorimetric result

Determination of the time constant τ of the integral heat signal

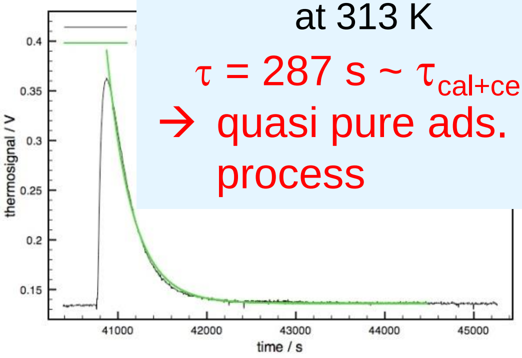
$$\frac{\text{heat capacity}}{\text{thermal conductivity}} \quad \frac{C}{G}$$

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



R=1kΩ →27.45 mJ

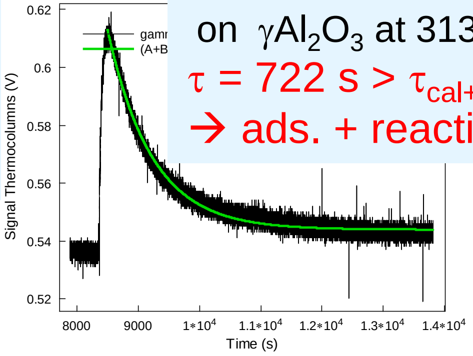
→ $\tau_{\text{(calorimeter+cell, 40°C)}}$ ~265 s



5.9 µmol/g propylene adsorbed on MoVTeNb at 313 K

τ = 287 s ~ $\tau_{\text{cal+cell}}$

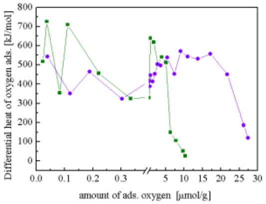
→ quasi pure ads. process



4.8 µmol/g methanol adsorbed on γAl_2O_3 at 313 K

τ = 722 s > $\tau_{\text{cal+cell}}$

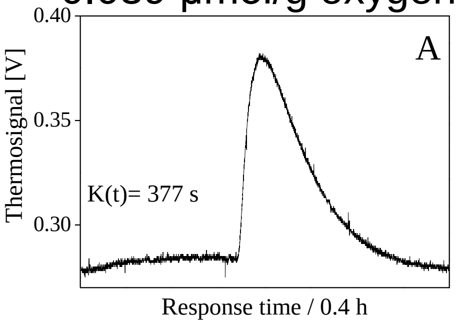
→ ads. + reaction



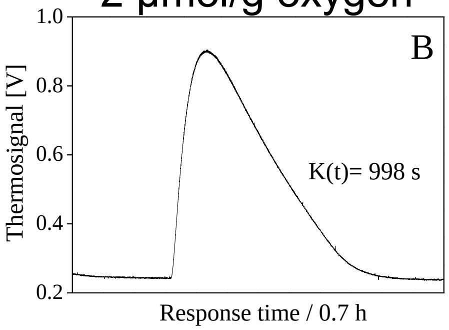
Shape of the integral heat signal

O_2 adsorption on 2%Pd/N-CNT473K at 353K=T_{reaction}

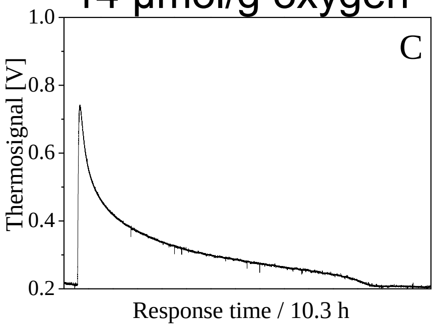
0.039 µmol/g oxygen



2 µmol/g oxygen



14 µmol/g oxygen



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

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

6. Applications of microcalorimetry in heterogeneous catalysis

Specific surface area of Pt: ***H_2 and CO ads. on 2%Pt/Al_2O_3 at 40°C***

Titration of acid or basic surface sites:
- ***NH_3 ads. on pure-phase MoVTeNb oxide at 80°C***
- ***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 VO_x/γ-Al_2O_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 MoO_x/SBA-15 at $T_{reaction}$=50°C***
- **O_2 ads. on Ag for ethylene epoxidation at $T_{reaction}$=230 °C**
- ***1-Hexyne chemisorption on CeO_2/TiO_2 at $T_{reaction}$=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***

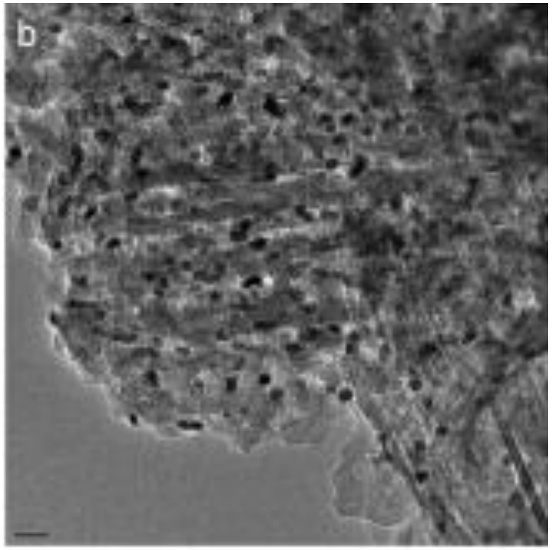
Estimation of the enthalpy of formation of the transition state (activation barrier):
- ***ethane & ethylene and propane & propylene ads. on the Vanadium oxide-based and Metal-free catalysts for ODH***

VALIDATION

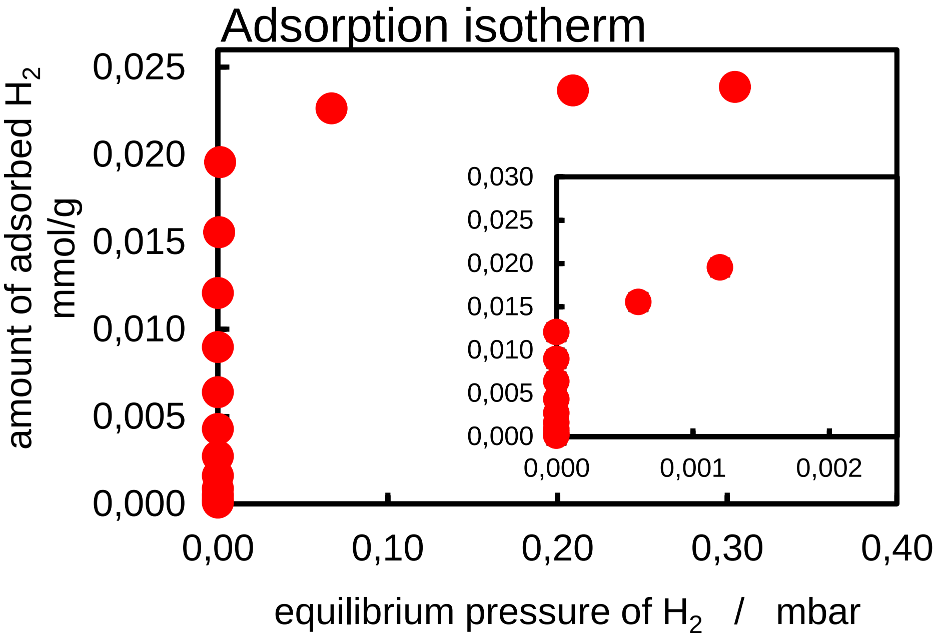
H_2 chemisorption on 2 wt.% $Pt_{H2\text{-}673K\text{-}2h}/Al_2O_3$ at 40°C

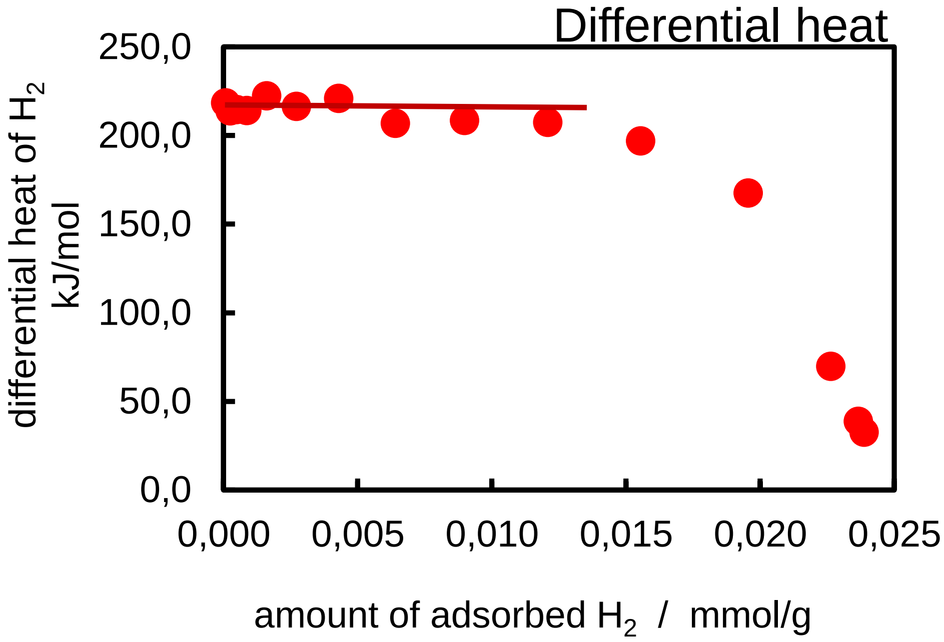
Reference Material from Quantachrome INSTRUMENTS

Active Metal Surface Area = 1.146 $m^2\ g^{-1}$



H_2 adsorption on $Pt_{H2\text{-}673K\text{-}2h}/Al_2O_3$ *Quantachrome* at 40°C





<u>Heat plateau:</u> homogeneously distributed and **energetically uniform** adsorption sites

<u>q_{diff} = 215 kJ/mol</u> : chemisorption ! $\Delta_C H$ **= 215 kJ/mol**

Hydrogen is dissociative adsorbed on platinum

$H_2 + Pt + Pt \rightarrow Pt\text{-}H + Pt\text{-}H \quad \Delta_C H = 266$ kJ/mol

2.5% Pt/silica

J.A. Dumesic et.al., Catal. Letters 45 (1997) 155-163.

Langmuir isotherm
for dissociative adsorption

$$\theta_H = \frac{n_{ads}}{n_m} = \frac{\sqrt{p_{H_2} K_{ads}}}{1 + \sqrt{p_{H_2} K_{ads}}}$$

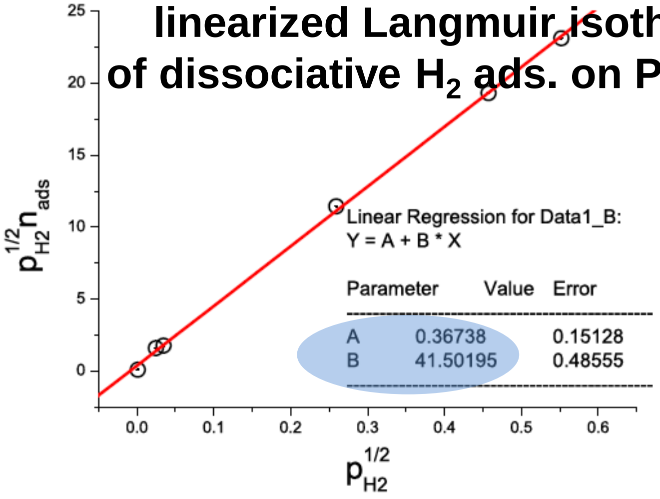
H_2 adsorption on Pt/Al_2O_3 *Quantachrome* at 40°C

Linearization

$$\theta_H = \frac{n_{ads}}{n_m} = \frac{\sqrt{p_{H_2} K_{ads}}}{1+\sqrt{p_{H_2} K_{ads}}}$$

$$n_{ads}\left(1+\sqrt{p_{H_2}}\sqrt{K_{ads}}\right) = n_m \sqrt{p_{H_2}}\sqrt{K_{ads}}$$

$$\frac{1}{n_m\sqrt{K_{ads}}} + \frac{1}{n_m}\sqrt{p_{H_2}} = \frac{\sqrt{p_{H_2}}}{n_{ads}}$$



linearized Langmuir isotherm of dissociative H_2 ads. on Pt/Al_2O_3

Linear Regression for Data1_B:
Y = A + B * X

Parameter	Value	Error
A	0.36738	0.15128
B	41.50195	0.48555

registered $\frac{p_{H_2}}{mbar}$	10^{-6}	$6 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$	$6.69 \cdot 10^{-2}$	$2.09 \cdot 10^{-1}$	$3.05 \cdot 10^{-1}$
calculated from the calibrated volumetric system $\frac{n_{ads}}{(mmol \cdot g^{-1})}$	$1.208 \cdot 10^{-2}$	$1.555 \cdot 10^{-2}$	$1.956 \cdot 10^{-2}$	$2.264 \cdot 10^{-2}$	$2.366 \cdot 10^{-2}$	$2.387 \cdot 10^{-2}$
calculated $\frac{\sqrt{p_{H_2}}}{\sqrt{mbar}}$	10^{-3}	$24.5 \cdot 10^{-3}$	$34.6 \cdot 10^{-3}$	$259 \cdot 10^{-3}$	$457 \cdot 10^{-3}$	$552 \cdot 10^{-3}$
calculated $\frac{\frac{\sqrt{p_{H_2}}}{n_{ads}}}{\frac{\sqrt{mbar \cdot g}}{mmol}}$	0.083	1.58	1.77	11.44	19.32	23.13

B

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

Specific surface area of Pt $m^2{}_{Pt}/g_{cat}$

A

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

$$\Rightarrow K_{ads} = 10851\ mbar^{-1}$$

H_2 adsorption on Pt/Al_2O_3 *Quantachrome* at 40°C

Specific surface area of Pt *m^2_{Pt} / g_{cat}*

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

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

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

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

Final Results

Kinetic parameters determined for the H_2 ads. on Pt/Al_2O_3

$n_{mono} = 24 * 10^{-6}\ \text{mol} \cdot \text{g}^{-1}$

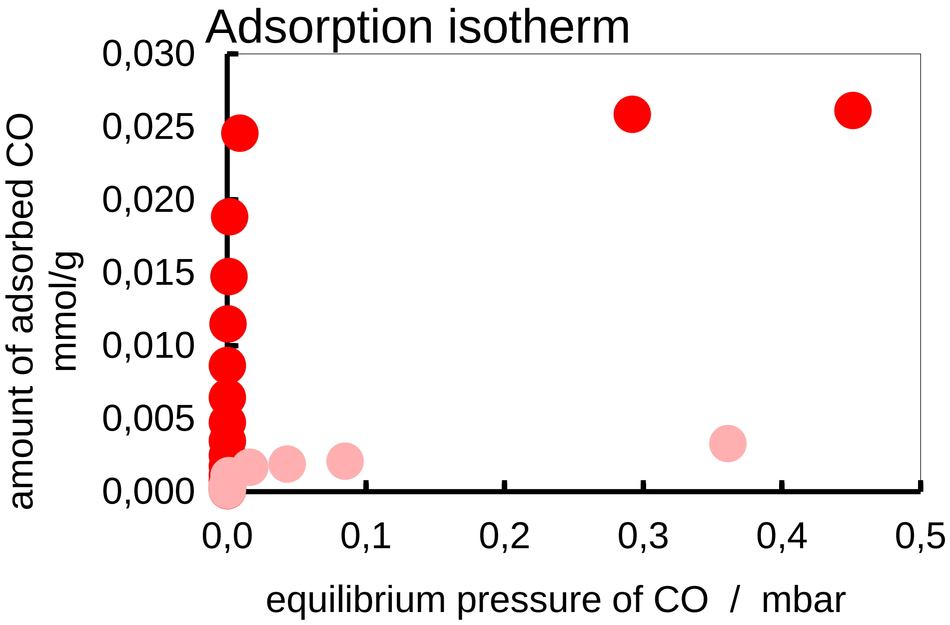
$K_{ads} = 10851\ \text{mbar}^{-1}$

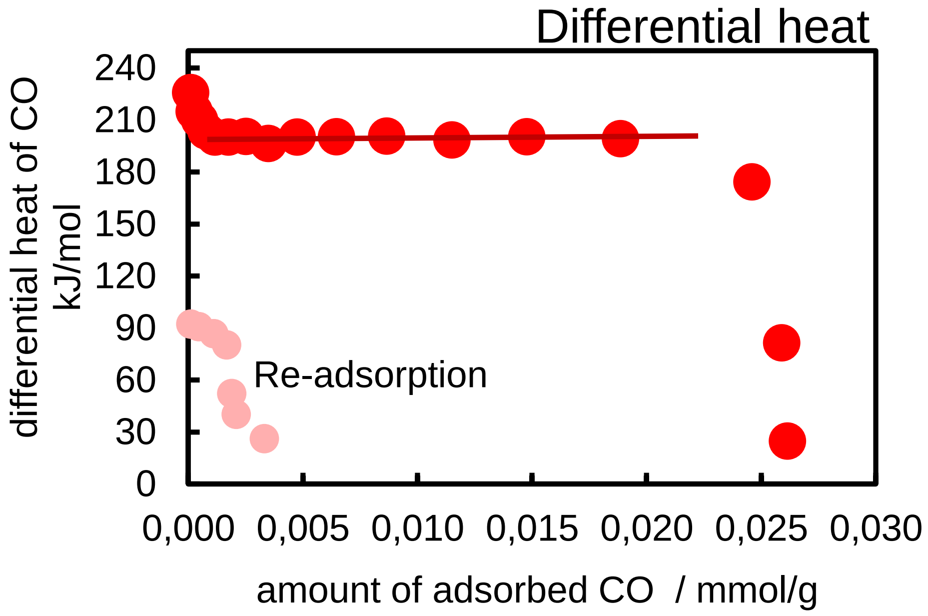
$\Delta H_{ads.} = 215 \pm 4\ \text{kJ} \cdot \text{mol}^{-1}$

$S_{Pt} \approx 1.0\ \text{m}^2 \cdot \text{g}^{-1}$

CO adsorption on $Pt_{H2\text{-}673K\text{-}2h}/Al_2O_3$ *Quantachrome* at 40°C

CO adsorption on $Pt_{H2\text{-}673K\text{-}2h}/Al_2O_3$ *Quantachrome* at 40°C


Adsorption isotherm


Differential heat

Heat plateau: homogeneously distributed and **energetically uniform** adsorption sites

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

q_{diff} = 200 kJ/mol : chemisorption ! **$\Delta_C H$ = 200 kJ/mol**

Pt-CO	terminal CO	$\Delta_C H$= 209 kJ/mol	$\nu_{CO} \sim 2055\ cm^{-1}$
$(Pt)_{n;\ n>1}$ -CO	bridged CO	$\Delta_C H$= 94 kJ/mol	$\nu_{CO} \sim 1822\ cm^{-1}$

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

higher order Langmuir model for activated adsorption

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

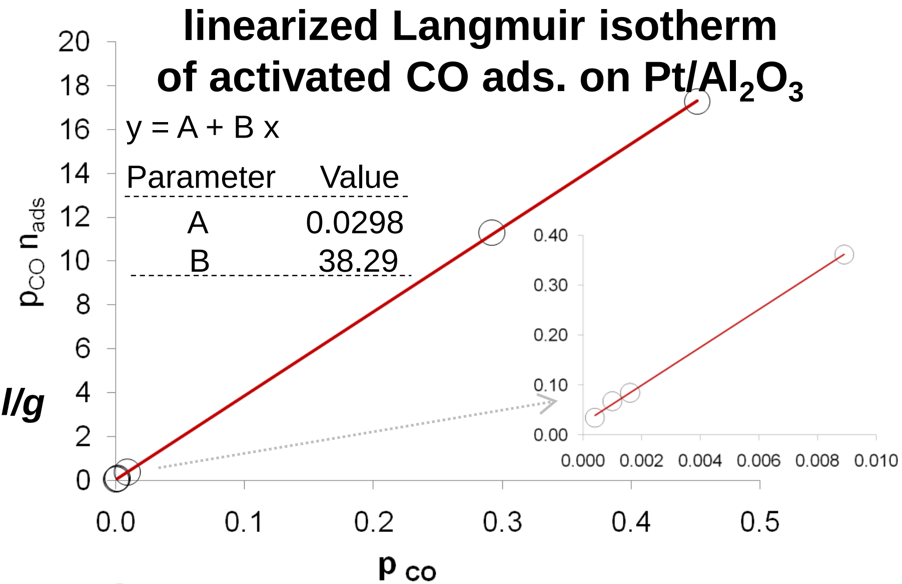
CO adsorption on $Pt_{H2\text{-}673K\text{-}2h}/Al_2O_3$ *Quantachrome* at 40°C

Linearization

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

$$1/(n_{mono}K_{ads}^{1/n}) + (1/n_{mono})\, p_{CO} = p_{CO} / n_{ads}$$

$1/n_{mono} = 38.29$ *g/mmol* → **$n_{mono} = 26.11 \times 10^{-3}$ *mmol/g***



Parameter	Value
A	0.0298
B	38.29

$1/(n_{mono}K_{ads}^{1/n}) = 0.0298$ *mbar·g/mmol* → $K_{ads} = (1/n_{mono}\, A)^{n}$

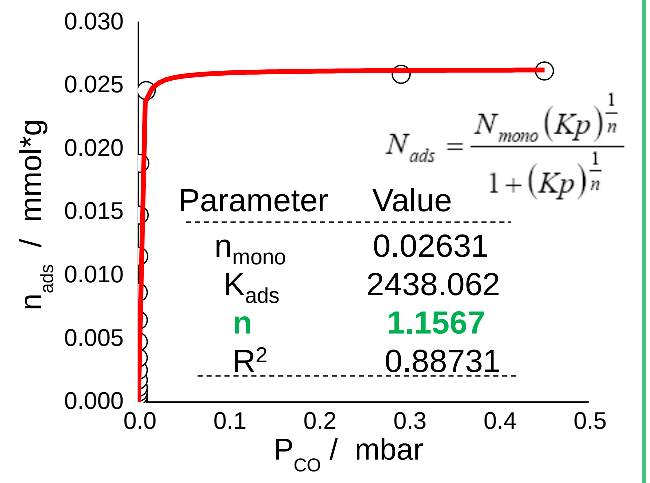
K_{ads} = = (1 *g mmol* / 26.11×10^{-3} *mmol* 0.0298 *mbar g* $)^{1.1567}$

K_{ads} = 3945,96 *mbar⁻¹*

S_{Pt} = 10563 cm²/g ≈ 1.1 m²/g ;

$S_{Pt\text{ ; certified by Quantachrome}}$ = 1.146 m²/g

Adsorption order ?



Parameter	Value
n_{mono}	0.02631
K_{ads}	2438.062
n	1.1567
R^2	0.88731

Comparison

Kinetic parameters determined for the CO ads. on Pt/Al_2O_3

n_{mono} = $26 * 10^{-6}$ $mol \cdot g^{-1}$
K_{ads} = 3946 $mbar^{-1}$
$\Delta H_{ads.}$ = 200 ±4 $kJ \cdot mol^{-1}$
S_{Pt} ≈ 1.1 $m^2 \cdot g^{-1}$

Kinetic parameters determined for the H_2 ads. on Pt/Al_2O_3

n_{mono} = $24 * 10^{-3}$ $mmol \cdot g^{-1}$
K_{ads} = 10851 $mbar^{-1}$
$\Delta H_{ads.}$ = 215 ±4 $kJ \cdot mol^{-1}$
S_{Pt} ≈ 1.0 $m^2 \cdot g^{-1}$

Validation

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

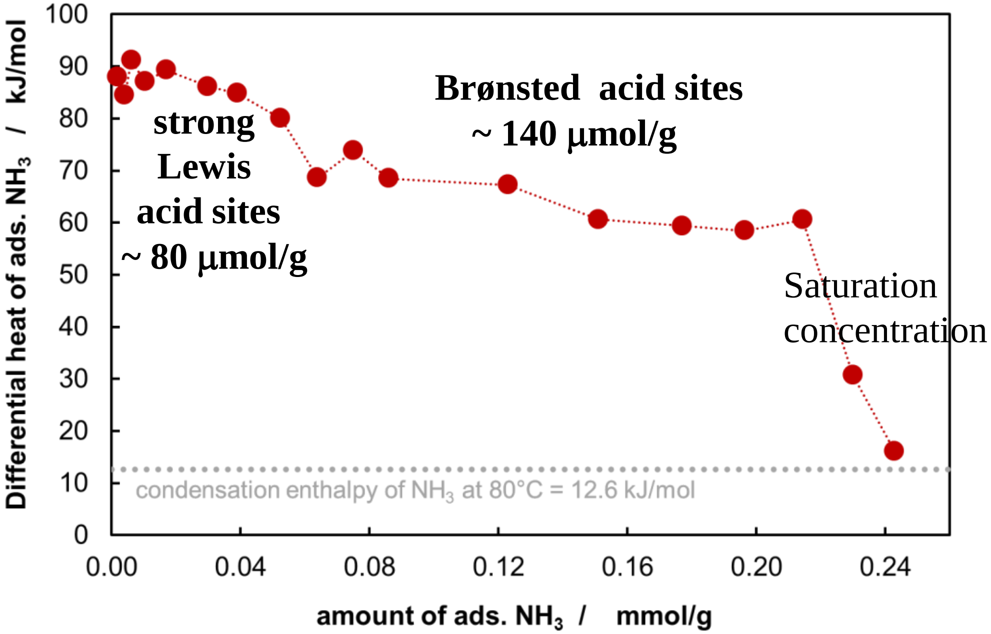
J. Therm. Anal. Cal., 82 (2005)105 : Pt-CO $\Delta_C H$ = 209 kJ/mol
S_{Pt} ; certified by Quantachrome = 1.146 m^2/g

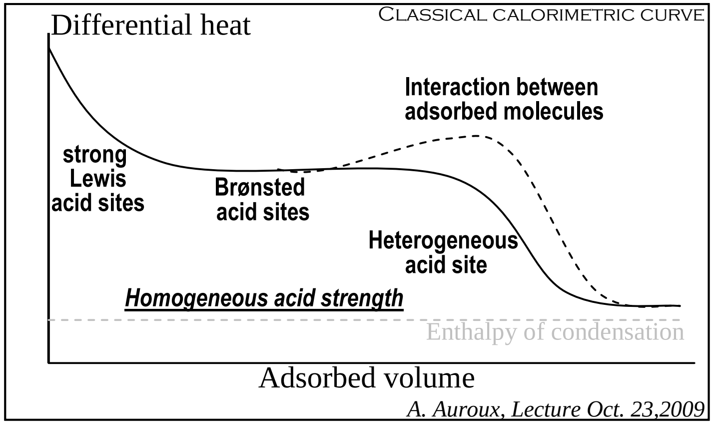
→

$\Delta_C H$ = 200 ±4 kJ/mol *(Dept. AC FHI)*
S_{Pt} = 1 ±0.1 m^2/g

Titration of acid sites
on the surface of MoVTeNb oxide catalyst #6059
using NH_3 at 80°C

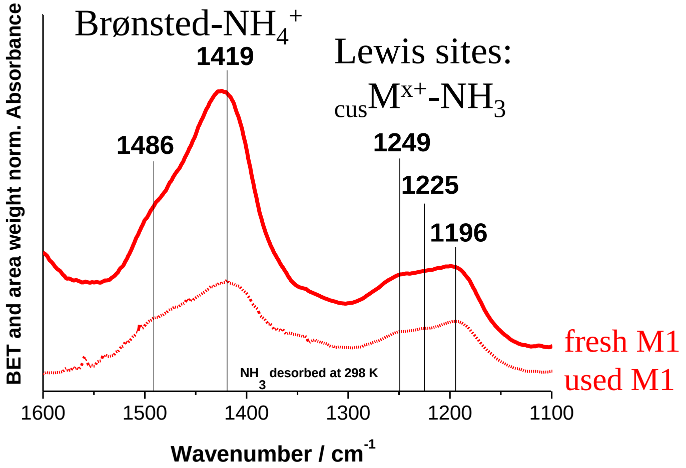
Titration of acid sites on the surface of M1 #6059 using NH_3 at 80°C





A. Auroux, Lecture Oct. 23,2009

FTIR spectra



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

Brønsted acid sites: ~ 40 µmol/g

Lewis acids sites: ~ 90 µmol/g

Development of a NEW METODE:

BasCat
UniCat BASF JointLab

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

VALIDATION via Calorimetry

NH_3 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:

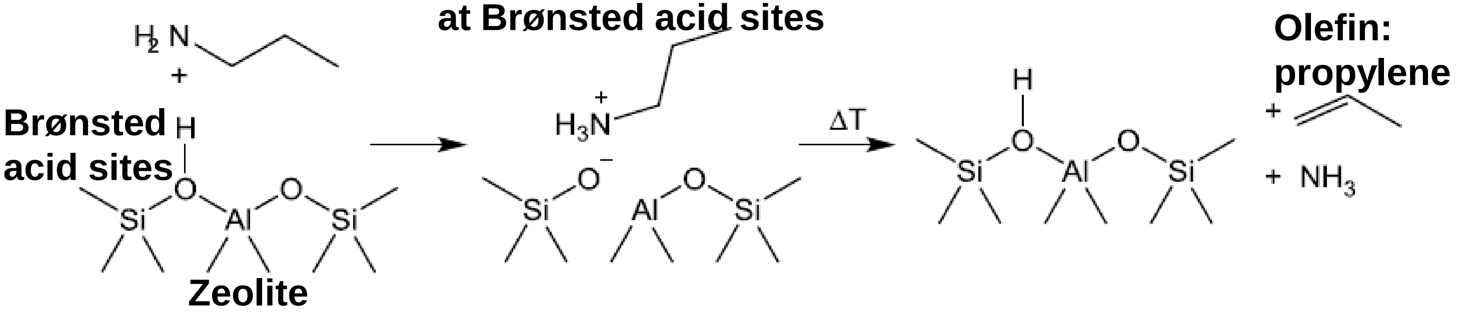
Development of a standard characterization method for the quantification of acid sites on surfaces.

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.

BasCat
UniCat BASF JointLab

Alkylamines are protonated at Brønsted acid sites



Brønsted acid sites

Zeolite

Olefin: propylene

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 SiO_2/Al_2O_3 ratio of 30)
- H-ZSM5-80 (H-ZSM5 zeolite with a SiO_2/Al_2O_3 ratio of 80)

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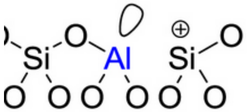
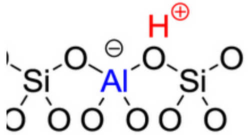
[1] *R. J. Gorte, Catal. Today 1996, 28, 405–414.*

Microcalorimetry
Differential heat of ads. NH_3 at 80°C

Lewis acid sites



Brönsted acid sites



H-ZSM5-30

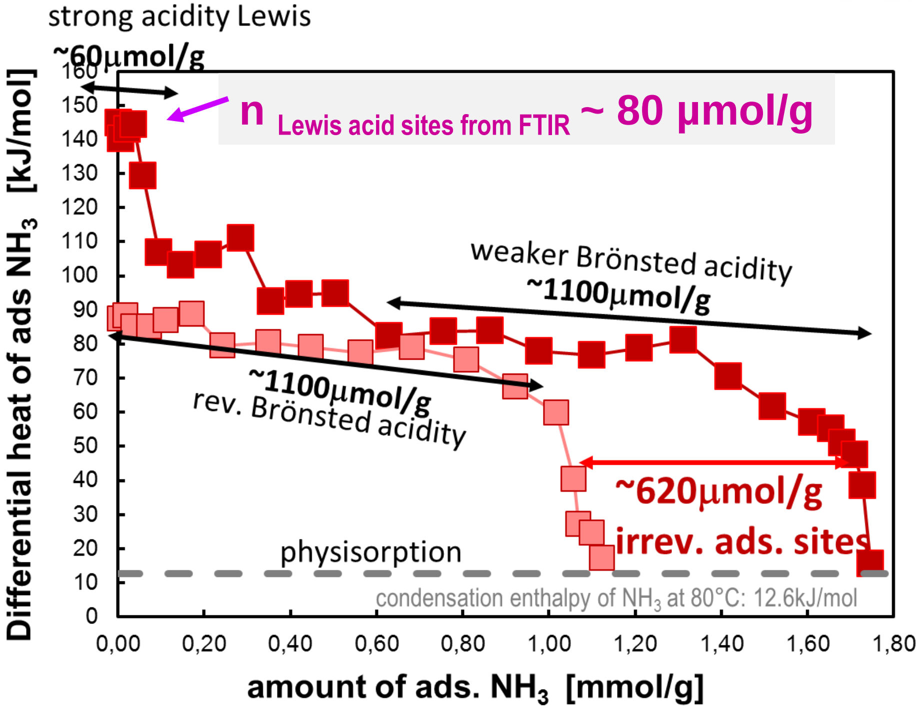
SiO_2/Al_2O_3 ratio of 30

$n_{\text{Brønsted acid sites}}$ = **560µmol/g**

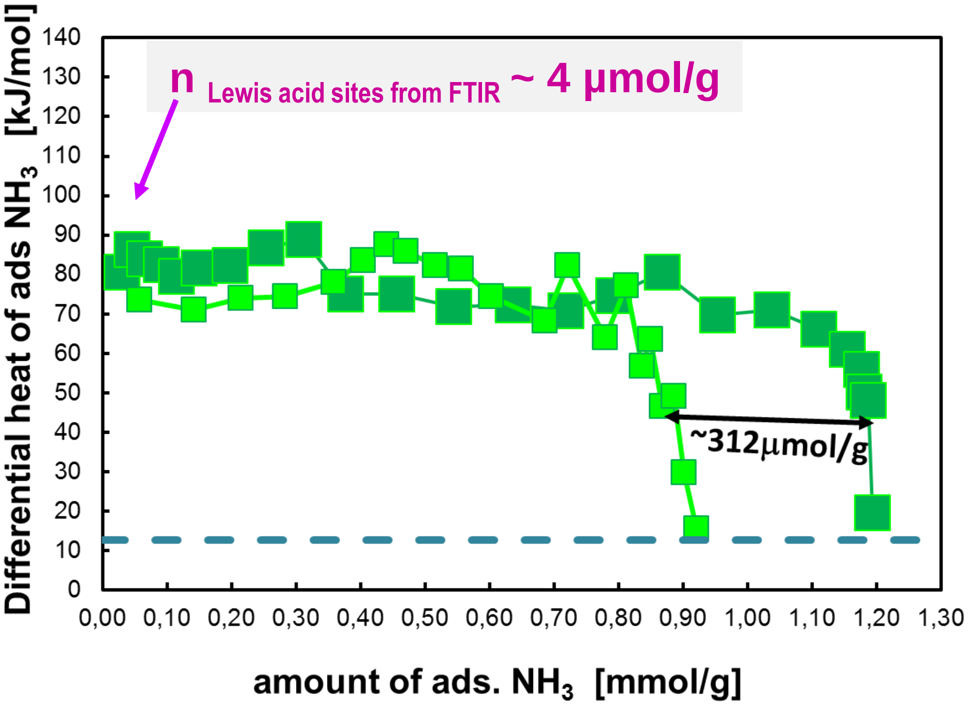
H-ZSM5-80

SiO_2/Al_2O_3 ratio of 80

$n_{\text{Brønsted acid sites}}$ = **312µmol/g**



$n_{\text{Lewis acid sites from FTIR}}$ ~ 80 µmol/g

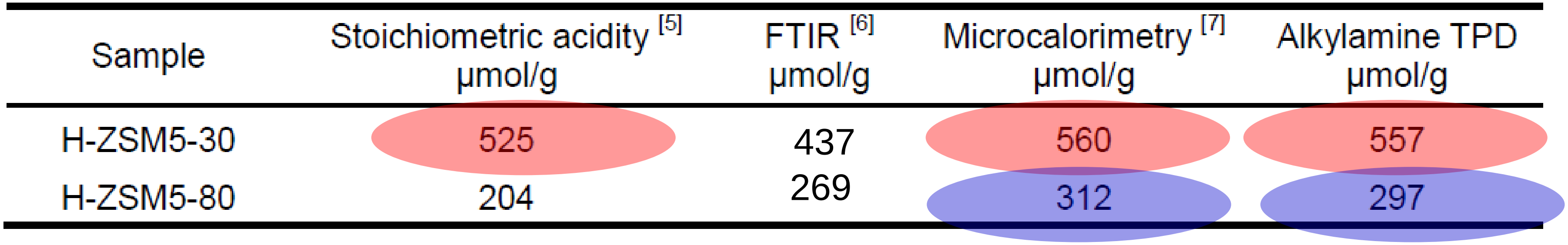


$n_{\text{Lewis acid sites from FTIR}}$ ~ 4 µmol/g

$$n_{\text{relevant Brønsted acid sites}} = n_{\text{irrev. ads sites}} - n_{\text{Lewis acid sites}}$$

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

Quantification of Brønsted Acid Sites



Sample	Stoichiometric acidity [5] µmol/g	FTIR [6] µmol/g	Microcalorimetry [7] µmol/g	Alkylamine TPD µmol/g
H-ZSM5-30	525	437	560	557
H-ZSM5-80	204	269	312	297

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

[5] *A. S. Al-Dughaither, H. de Lasa, Ind. Eng. Chem. Res. 2014, 53, 15303–15316.*

[6] *O. Bortnovsky, Z. Melichar, Z. Sobalík, B. Wichterlová, Micropor.Mesopor. Mat. 2001, 42, 97–102.*

[7] *S. Wrabetz, X. Yang, G. Tzolova-Müller, R. Schlögl, F. C. Jentoft, J. Catal. 2010, 269, 351–358.;* Klaus Dieter Friedel Ortega, Dissertation, „6.3.4. Investigation of gas-phase acidity by NH3 microcalorimetry and NH3-TPD„ S. Wrabetz, page102.

Titration of basic sites on the surface of ceria using CO_2 at 40°C

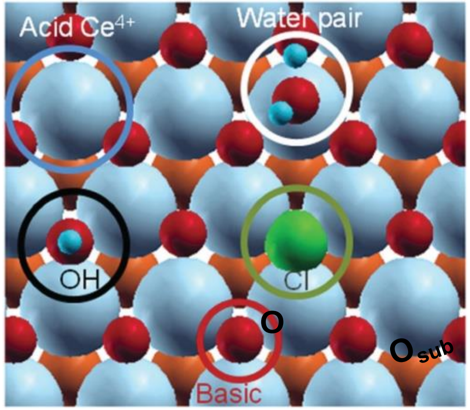
Titration of basic sites on the surface of supported ceria using acidic CO_2 at 40°C [3]

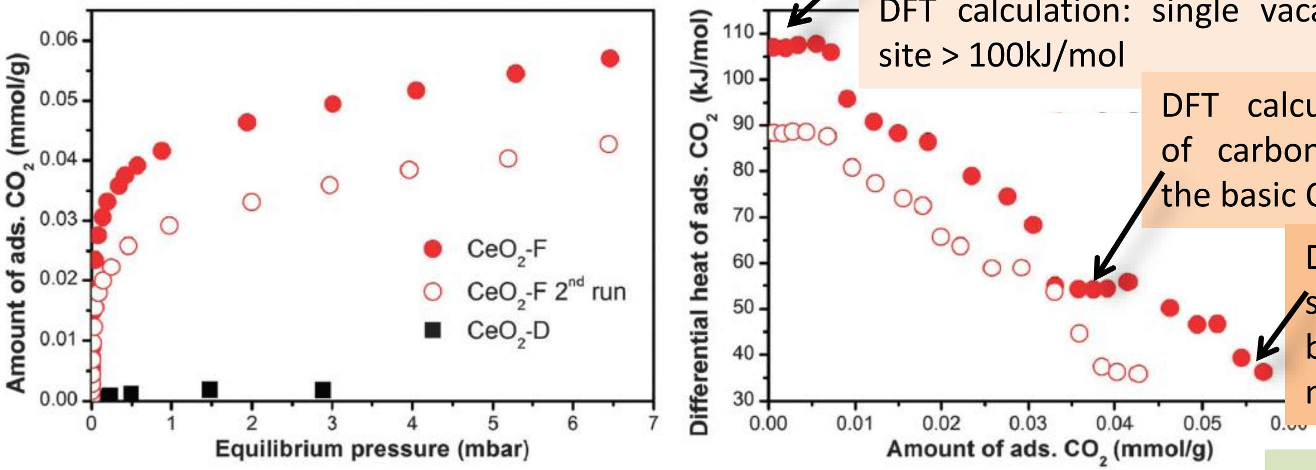
DEACON reaction

$$4\ HCl\ +\ O_2 \xrightarrow[T\ =\ 430°C,\ HCl/O_2/N_2,\ 100ml/min]{\text{Oxidation of HCl to } Cl_2 \text{ over } CeO_2} 2\ Cl_2\ +\ 2\ H_2O$$

Intention: Understanding CeO_2 as a Deacon catalyst, characterize ceria in its fresh **CeO_2-F** and post-reaction states **CeO_2-D**

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: single vacancy site > 100kJ/mol

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 CO2 molecules 18kJ/mol

- 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.

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

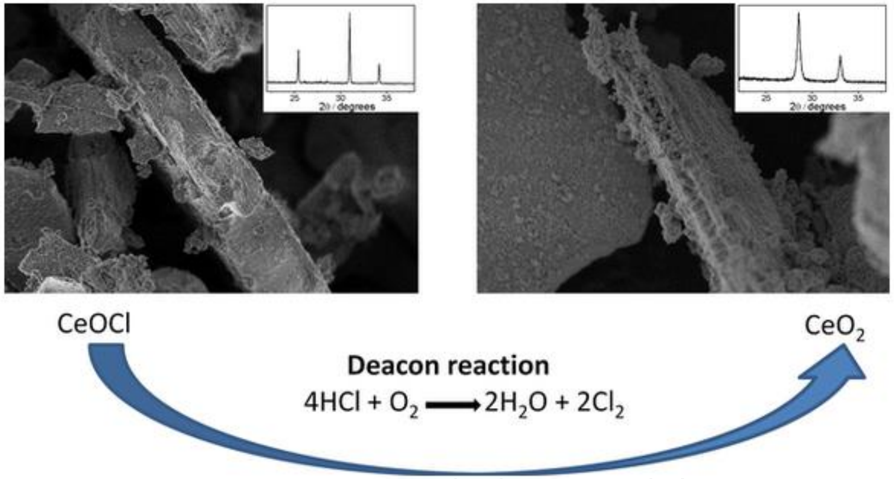
(1) G. N. Vayssilov, M. Mihaylov, P. S. Petkov, K. I. Hadjiivanov and K. M. Neyman, J. Phys. Chem. C, 2011, 115, 23435–23454.
(2) M. Nolan, S. C. Parker and G. W. Watson, Phys. Chem. Chem. Phys., 2006, 8, 216–218.
(3) Farra, R., Wrabetz, S., Schuster, M. E., Stotz, E., Hamilton, N., Amrute, A. P., Pérez-Ramírez, J., López, N., Teschner, D., Phys. Chem. Chem. Phys.,15 (2013) 3454 - 3465 .

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

Investigation of the oxidation process:

Oxidation of HCl to Cl_2 over bare and supported CeO_2

Oxidation of HCl to Cl_2 over bare and supported CeO_2 DEACON reaction

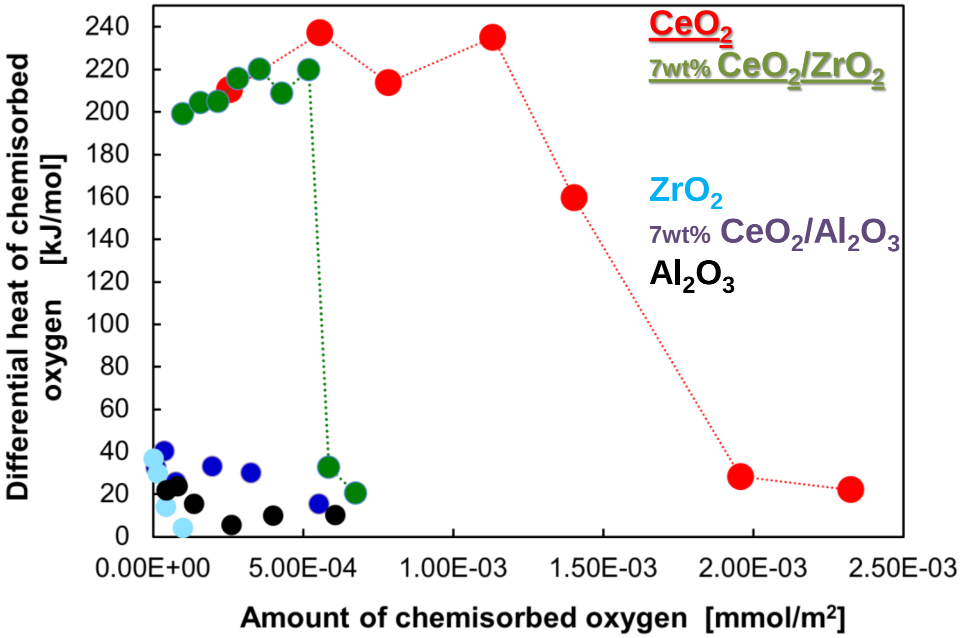


T = 430°C, $HCl/O_2/N_2$, 100ml/min

- **Best reactivity** **was obtained from bare CeO_2 and CeO_2 /ZrO_2.**
- One essential parameter seems to be the **reducibility** of the catalyst in order to create catalytically important oxygen vacancies.

Heat of adsorption of O_2 at 200° C / HT1000

Pretreatment: H_2 reduction at 200° C



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

Farra, R., Wrabetz, S., Schuster, M. E., Stotz, E., Hamilton, N., Amrute, A. P., Pérez-Ramírez, J., López, N., Teschner, D., Phys. Chem. Chem. Phys.,15 (2013) 3454 - 3465 .
M. Mosera C. Mondellia T. Schmidtb F. Girgsdiesc M.E. Schusterc R. Farra, L. Szentmiklósi, D. Teschner, J. Pérez-Ramírez, Applied Catalysis B: Environmental 132– 133 (2013) 123– 131.

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

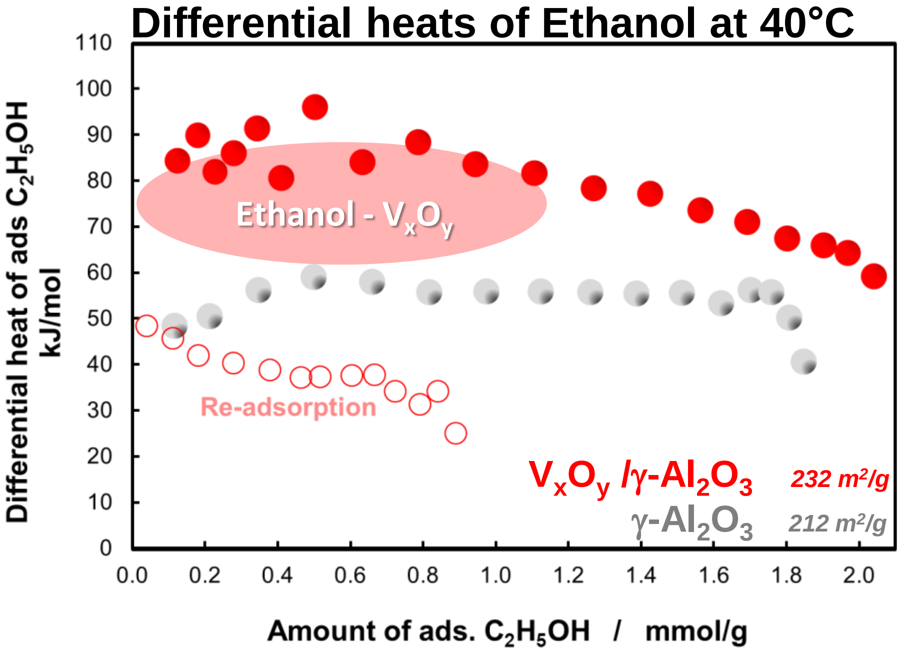
Oxidation of alcohol over vanadium supported Al_2O_3

Oxidation of alcohol over vanadium supported Al_2O_3

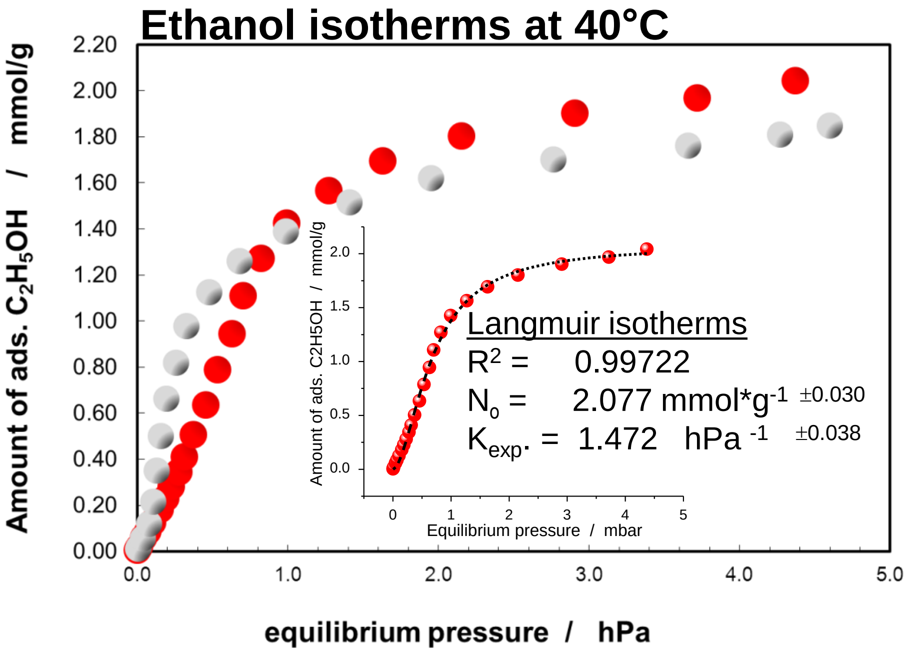
$$C_2H_5OH + \tfrac{1}{2}O_2 \longrightarrow C_2H_4O + H_2O \quad \Delta_R H = -178{,}5\,\mathrm{kJ/mol}$$

Catalyst: $V_xO_y / \gamma\text{-}Al_2O_3$
$T_{reaction}$ = 140 - 200 °C

<u>Intention:</u> Determination of kinetic data: N_{ads}, K_{ads} and $_{\Delta}H_{ads}$ of Ethanol on V_xO_y/Al_2O_3



Differential heats of Ethanol at 40°C



Ethanol isotherms at 40°C

<u>Langmuir isotherms</u>
R^2 = 0.99722
N_o = 2.077 mmol*g^{-1} ±0.030
$K_{exp.}$ = 1.472 hPa $^{-1}$ ±0.038

Kinetic parameters determined for the ethanol ads. on V_xO_y/Al_2O_3

N_{mono} = 2.077 mmol*g^{-1}
$K_{ads.}$ = 1.47 hPa^{-1}
$\Delta H_{ads.}$ = 90 ±10 kJ*mol^{-1}

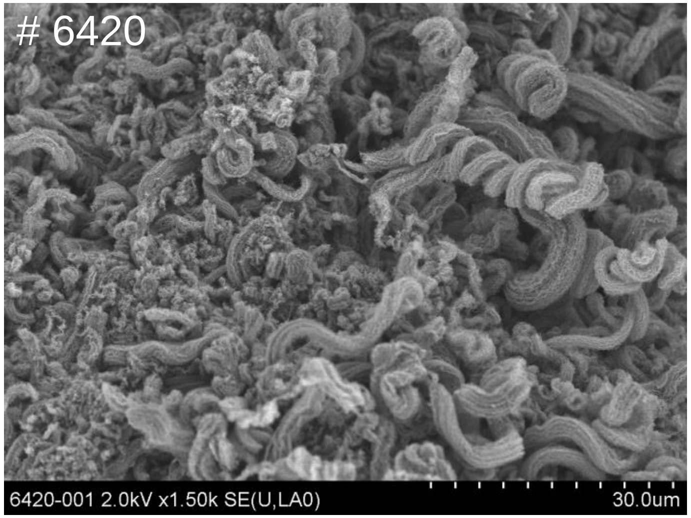
A. Dinse, S. Khennache, B. Frank, C. Hess, R. Herbert, S. Wrabetz, R. Schlögl and R. Schomäcker, J.of Mol. Catal. A: Chem. 307 (2009) 43-50.

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

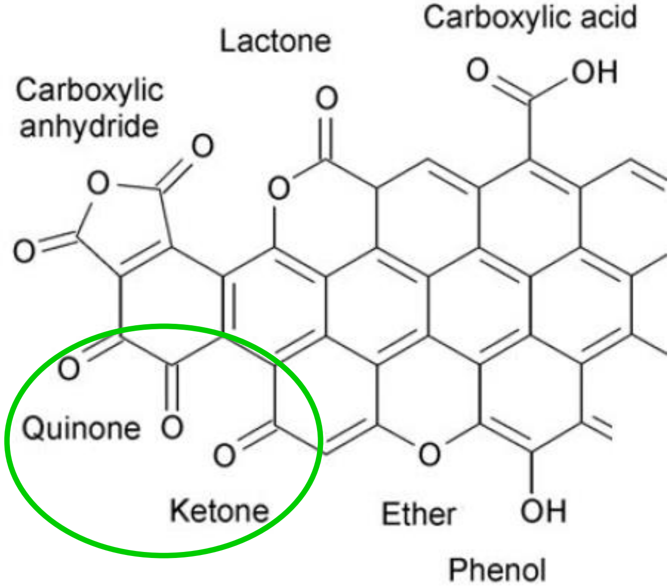
New insights on active sites of oxygen functionalized carbon nanotube *(oCNT)* for oxidative dehydrogenation *(ODH)*

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).

Catalytic Performance

We choose the ODH of propane and ethylbenzene (EB) as the model reactions.

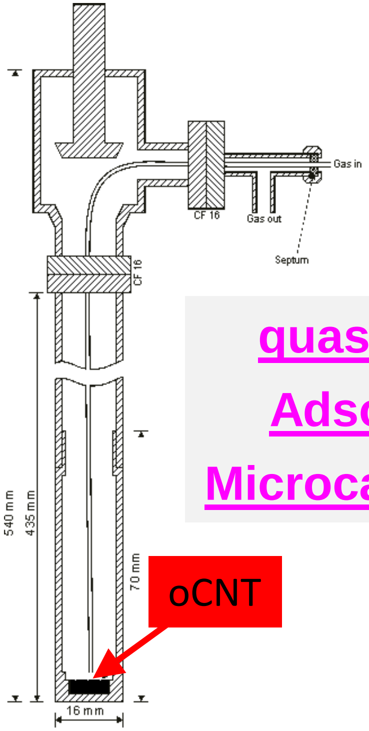
Model reaction

propane
C–H bond strength
410.5 kJ mol^{-1}

$\xrightarrow[\text{over } \textbf{oCNT}]{\underline{400\ °C}\text{, 50 ml min}^{-1}\ \ C_3H_8/O_2/He = 10/5/85}$ **propylene**

ethylbenzene
C–H bond strength
357.3 kJ mol^{-1}

$\xrightarrow[\text{over } \textbf{oCNT}]{\underline{300\ °C}\text{, 50 ml min}^{-1}\ \ C_8H_{10}/O_2/He = 2/1/97}$ **styrene**



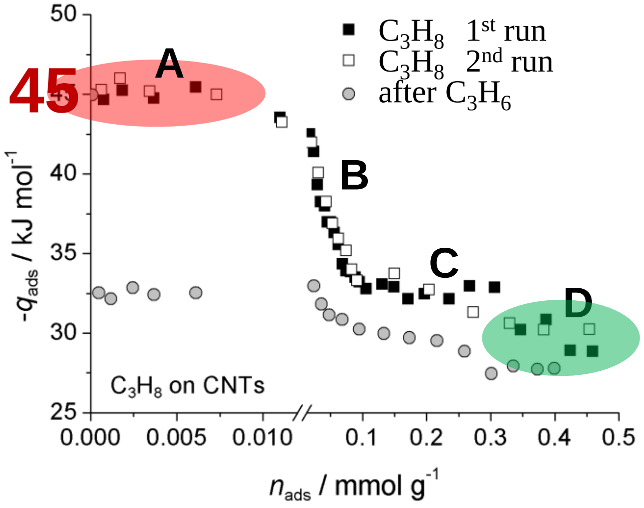
quasi *in situ*
Adsorption
Microcalorimetry

★ probe molecule: propane, propylene and ethylbenzene
★ $T_{adsorption}$=313K < 673K=$T_{reaction}$
★ selected catalyst: 370mg used MW oCNT$_{\#6420}$

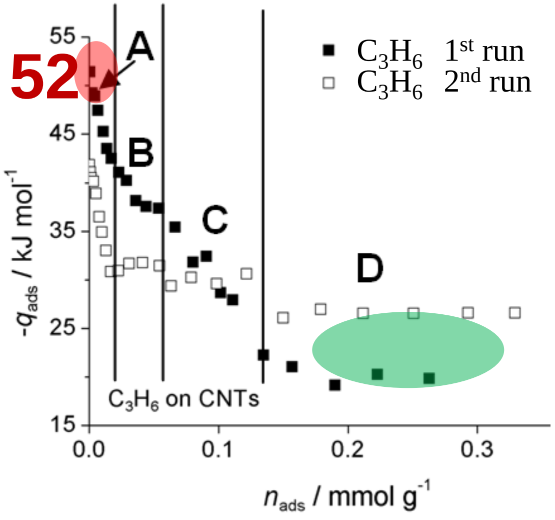
B. Frank, S. Wrabetz, O.V. Khavryuchenko, R. Blume, A. Trunschke, R. Schlögl, ChemPhysChem 12 (2011) 2709.

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

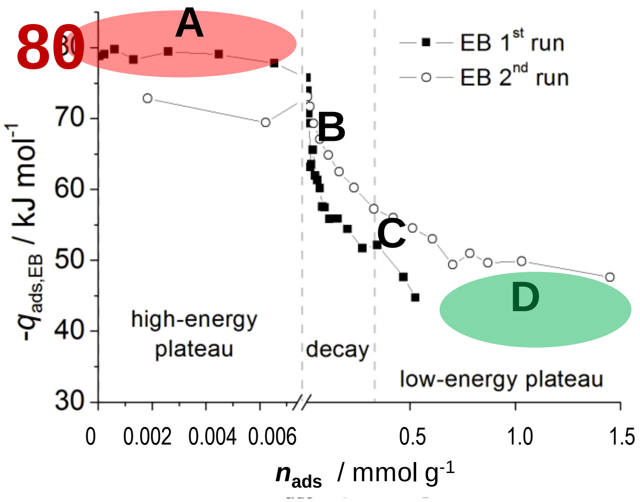
Propane



Propene



Ethylbenzene



- ~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

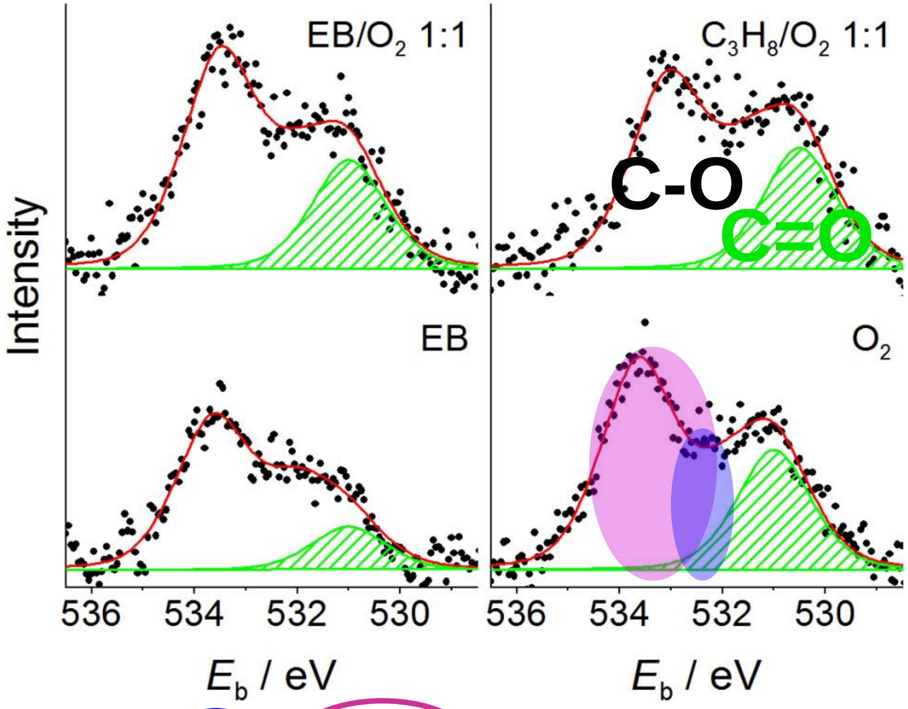
---

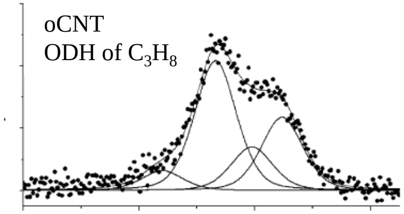
[1] B. Frank, S. Wrabetz, O.V. Khavryuchenko, R. Blume, A. Trunschke, R. Schlögl, ChemPhysChem 12 (2011) 2709.

[2] B. Frank, J. Zhang, R. Blume, R. Schlögl, D. S. Su, Angew. Chem. 2009,121, 7046– 7051; Angew. Chem. Int. Ed. 2009, 48, 6913 –6917.

O1s ranges of XP spectra

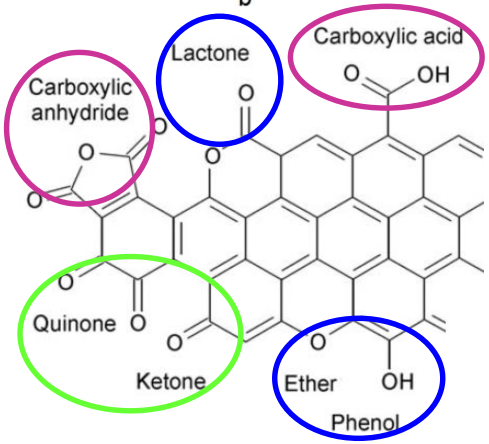
MW oCNT catalyst under different atmospheres @ 350°C.





Atmosphere	$I_{C=O}$ / I_{C-O}
EB	0.168
EB/O_2	0.283
C_3H_8/O_2	0.313
O_2	0.315

REACTIVITY

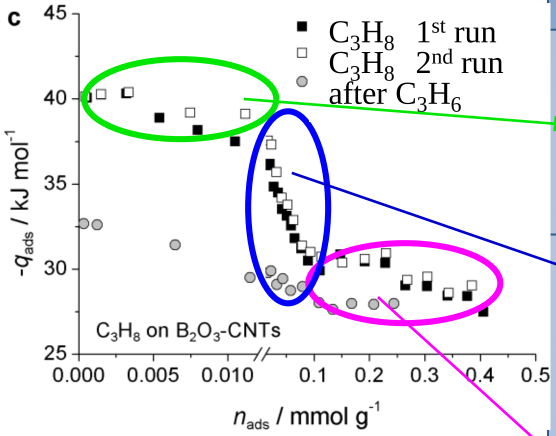


nucleophilic oxygen
ketones & quinones

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]



ODH substrate		C_3H_8 [1]	EB [2]
	-q_{ini} (kJ mol^{-1})	45	**80**
nucleophilic oxygen *ketones & quinones* **high energy plateau**	n_{ads} (µmol g^{-1})	0 - 8	**0 - 8**
	-q_{ads} (kJ mol^{-1})	45±0.5	**80±0.5**
quasi neutral oxygen lactone/ester, ethers, phenols **steady decay range**	n_{ads} (µmol g^{-1})	10 - 120	**10 - 110**
	-q_{ads} (kJ mol^{-1})	45 - 33	**80 - 55**
electrophilic oxygen *carboxylic anhydrides,* carboxylic acid **low energy plateau**	n_{ads} (µmol g^{-1})[a]	-	**-**
	-q_{ads} (kJ mol^{-1})[b]	33	**55**
capacity at 40 mbar	**$n_{ads,total}$ (µ**	**220**	**0**

$S_{propane}$=51 m^2 g^{-1}

S_{EB}=122 m^2 g^{-1}

BET$_{used\ oCNT}$ = 544 m^2 g^{-1}

[a] could not be determined

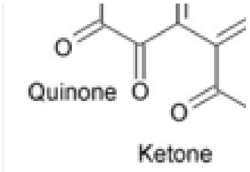
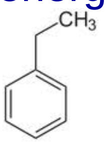
[b] Maximum differential adsorption heat.

[1] B. Frank, S. Wrabetz, O.V. Khavryuchenko, R. Blume, A. Trunschke, R. Schlögl, ChemPhysChem 12

[2] Benjamin Frank, Raoul Blume, Oleksiy V. Khavryuchenko, Pierre Kube, Sabine Wrabetz, Jian Zhang,
"A Unifying Concept of Hydrocarbon Oxidative Dehydrogenation over Carbon-Based Catalysts", in prog

Adsorption Isotherm 40°C

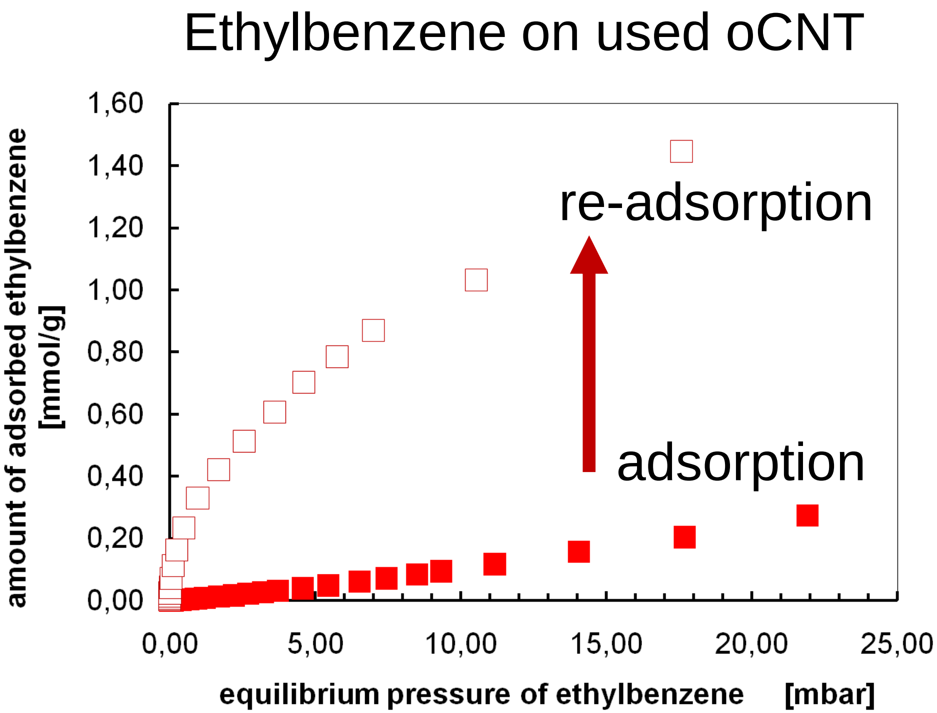
Explanation:

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

→ formation of H_2O 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 H_2O

→ more weak ads. sites available for EB

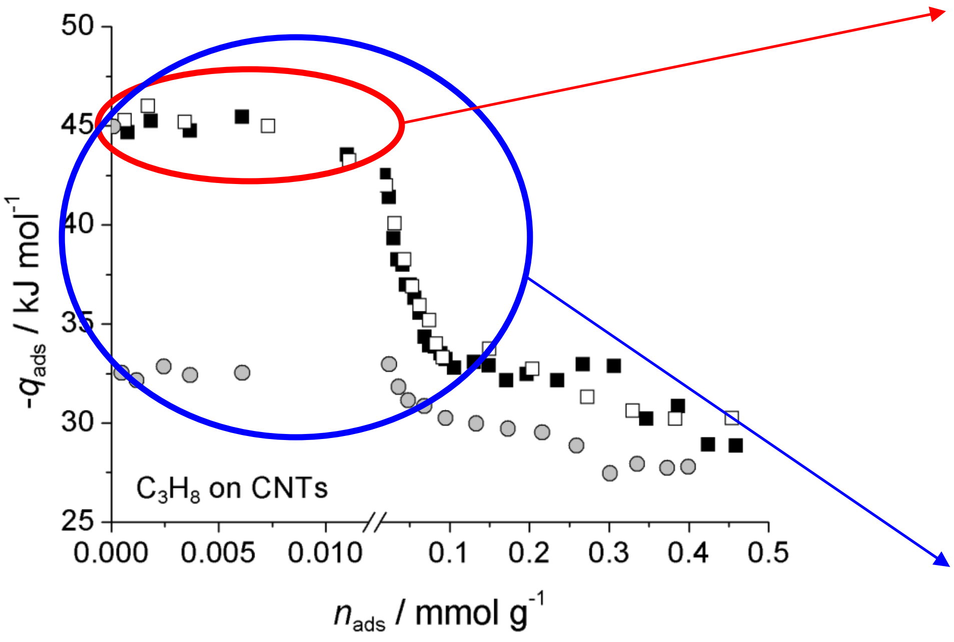


Ethylbenzene on used oCNT

➢2nd run of EB ads. reveals a drastic increase of the total adsorption capacity

Analyzing of Adsorption Isotherm 40°C

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

$$\theta = \frac{K\ p}{1 + K\ p}$$ K: Langmuir adsorption constant

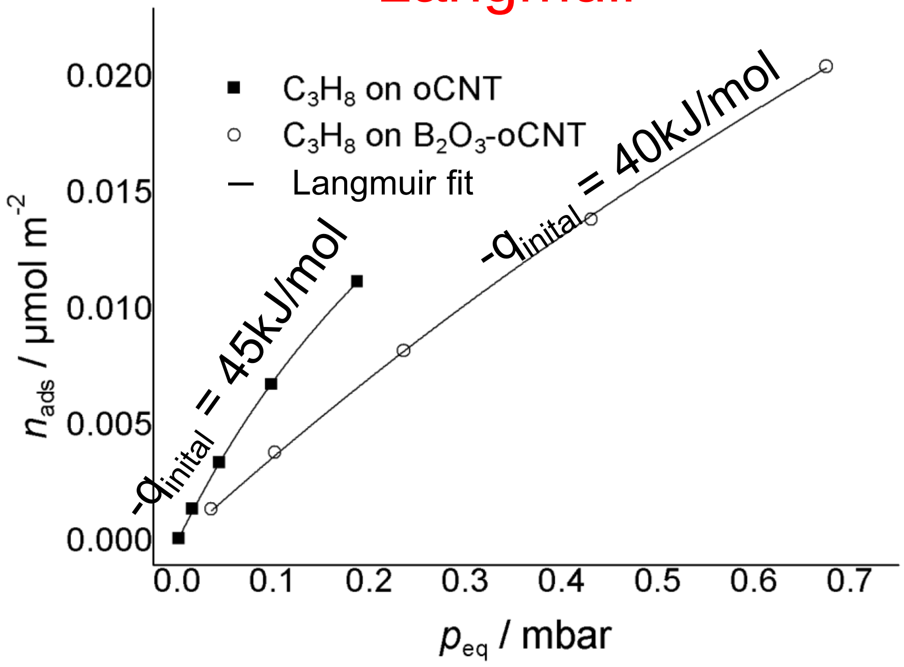
$$\theta = \frac{R\,T}{q_{ads}^{(\theta=0)} - q_{ads}^{(\theta=1)}} \ln\left(\frac{1 + \frac{p}{p^*} \exp \frac{q_{ads}^{(\theta=0)}}{R\,T}}{1 + \frac{p}{p^*} \exp \frac{q_{ads}^{(\theta=1)}}{R\,T}} \right)$$

p*: is a constant combining surface and molecular properties

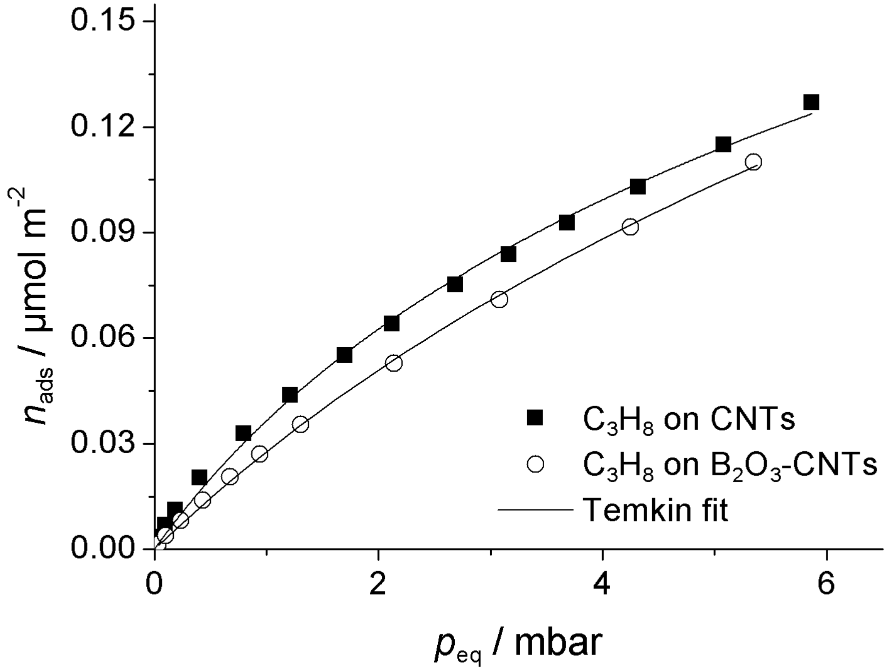
Energetically non-uniform sites (decay of q_{ads} with increasing coverage) → Temkin model

Analyzing of Adsorption Isotherm 40°C

Langmuir



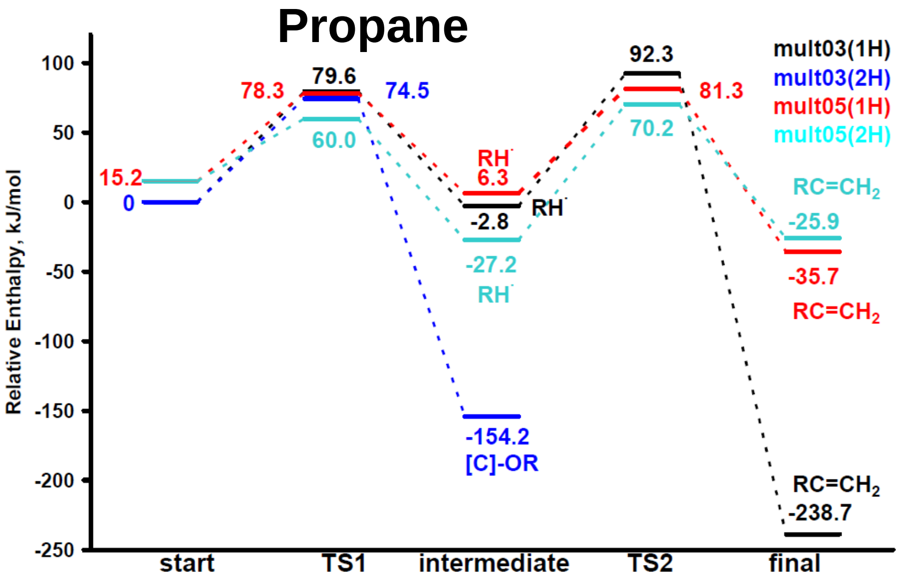
Temkin

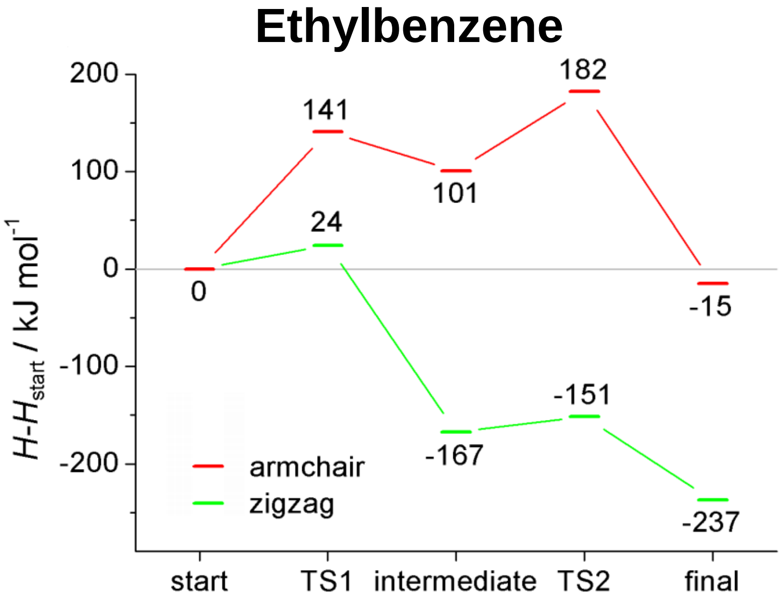


	K **(Langmuir adsorption constant)**	***p**** **(Temkin factor, combining surface and molecular properties)**
oCNT	2250 bar^{-1} (45kJ/mol)	0.0065 bar
B_2O_3-oCNT	370 bar^{-1} (40kJ/mol)	0.048 bar

Electronic structure theory calculations by DFT [1]

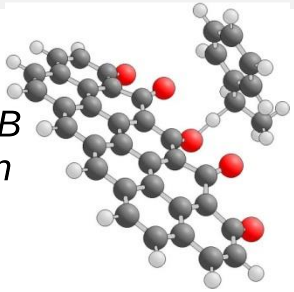
Energy Diagram for ODH of propane and EB (1st H-abstraction) over zigzag-termination of the carbon cluster





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

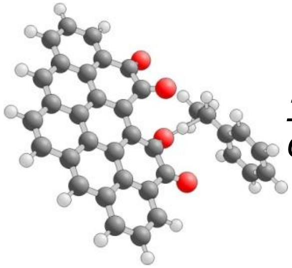
1st H-abstraction from EB over zigzag-termination



Quinones

Hydrogen

Carbon



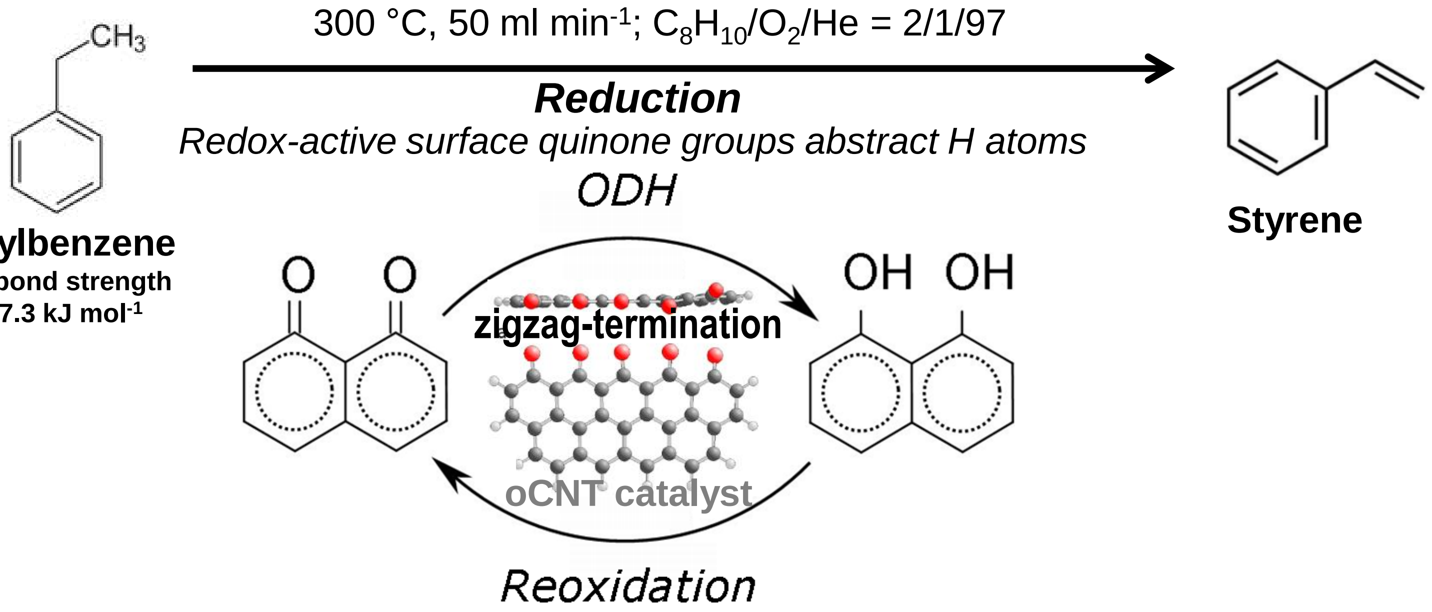
1st H-abstraction from EB over armchair-termination

[1] *O. V. Khavryuchenko, B. Frank, A. Trunschke, K. Hermann, R. Schlögl, J. Phys. Chem. C 117 (12) (2013) 225*

Conclusion

- Classification and quantification of the 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:



300 °C, 50 ml min^{-1}; $C_8H_{10}/O_2/He = 2/1/97$

Reduction

Redox-active surface quinone groups abstract H atoms

ODH

Ethylbenzene

C–H bond strength
357.3 kJ mol^{-1}

Styrene

zigzag-termination

oCNT catalyst

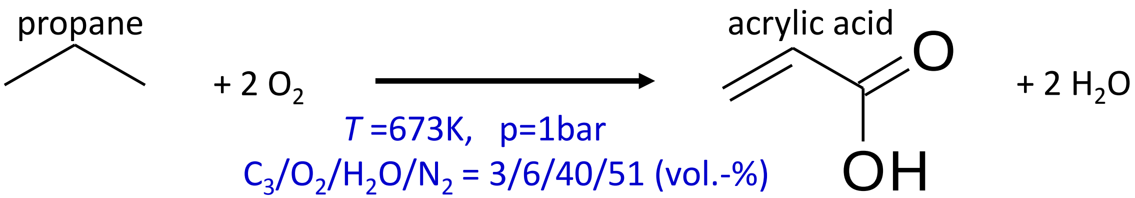
Reoxidation

- 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 m^2 g^{-1}, 8 μmol/g, 3-5% $_{\text{Calo/XPS}}$) 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

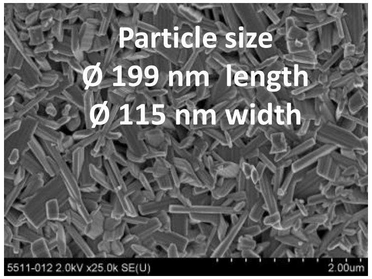
Selective oxidation of propane to acrylic acid over M1 [1,2]



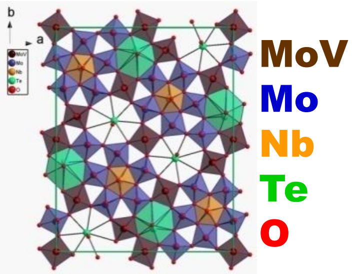
T =673K, p=1bar

$C_3/O_2/H_2O/N_2$ = 3/6/40/51 (vol.-%)

Catalyst: **Highly crystalline MoVTeNb oxide catalyst**



Particle size
Ø 199 nm length
Ø 115 nm width



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 Microcalorimetry :

- ★ propane as probe molecule
- ★ $T_{adsorption}$=313K < 673 K=$T_{reaction}$
- ★ selected catalysts: different selective catalysts

pure-phase MoVTeNb	**S_{aa} = 53%**
modified MoVTeNb by an oxidizing agent	**S_{aa} = 37%**
MoV oxide	**S_{aa} = 1.8 %**

---

[1] Botella, P., et al., The preparation, characterization, and catalytic behavior of MoVTeNbO catalysts prepared by hydrothermal synthesis. Journal of Catalysis, 2002. 209(2): p. 445-455.

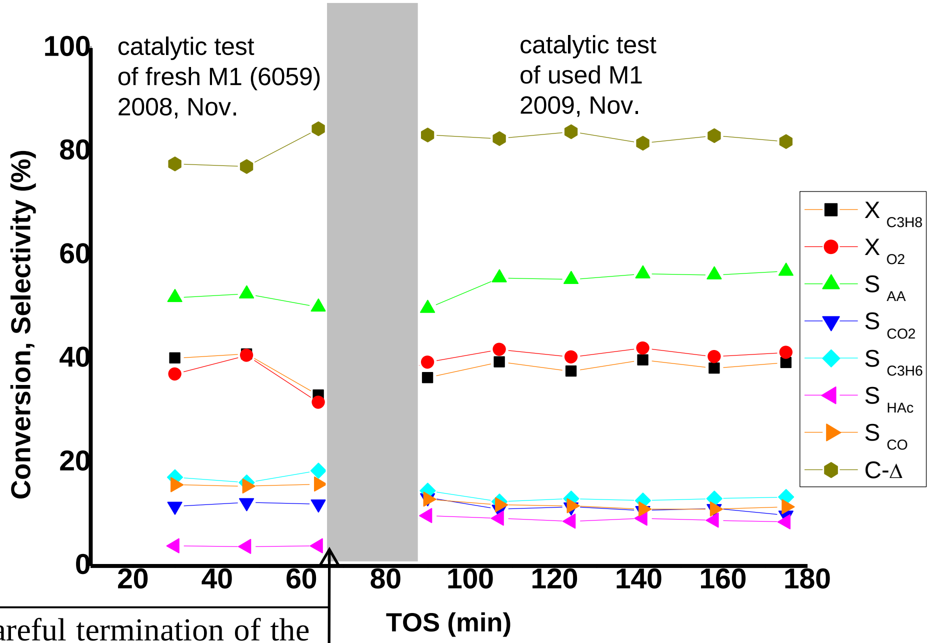
[2] Ueda, W., et al., Structural organization of catalytic functions in Mo-based oxides for propane selective oxidation. Catalysis Today, 2004. 96(4): p. 235-240.

Active catalyst surface stable under ambient conditions ?

CATALYTIC TEST (fresh/used catalyst)

propane oxidation data obtained from fresh and used MoVTeNb catalyst

used M1 (6059) has been stored for 1 year under ambient conditions

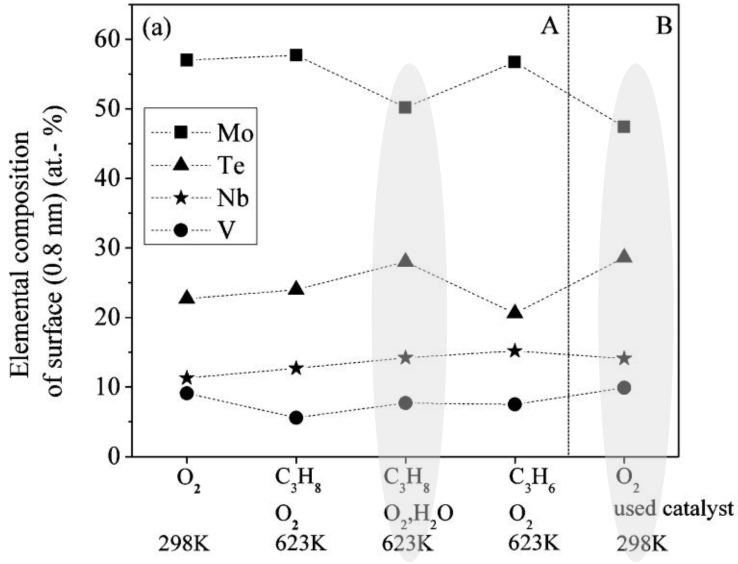

catalytic test of fresh M1 (6059) 2008, Nov.

catalytic test of used M1 2009, Nov.

Careful termination of the reaction under steam and N_2 with a cooling rate of 5 K/min.

SURFACE STUDY (fresh/used catalyst)

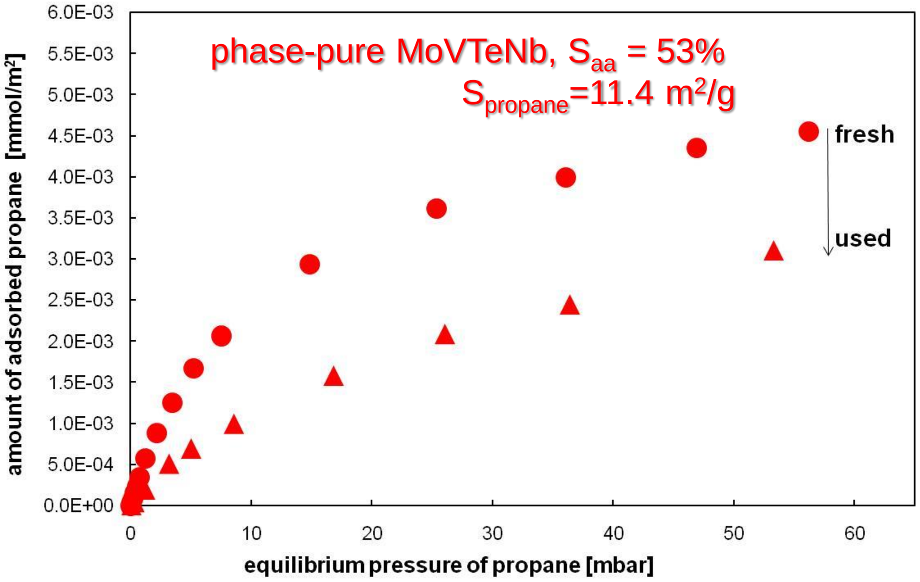
in situ XPS: surface element composition during and after PO over MoVTeNb catalyst

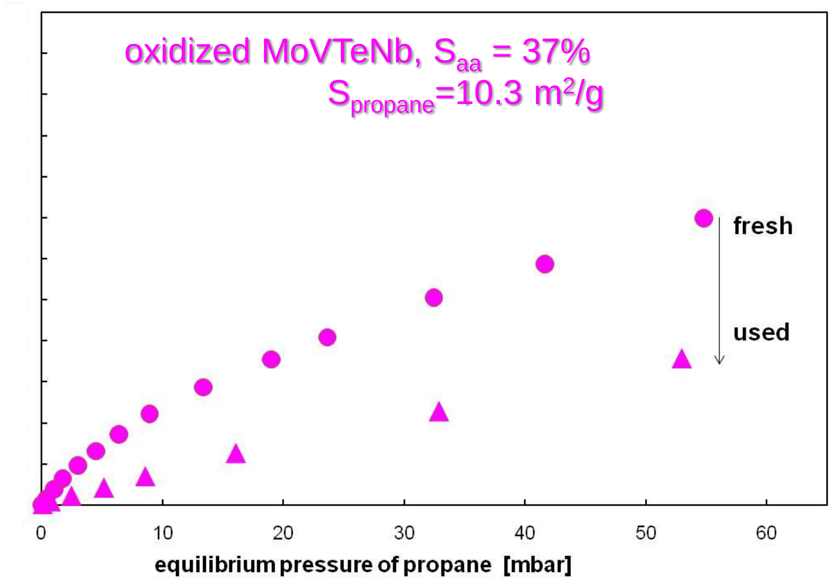


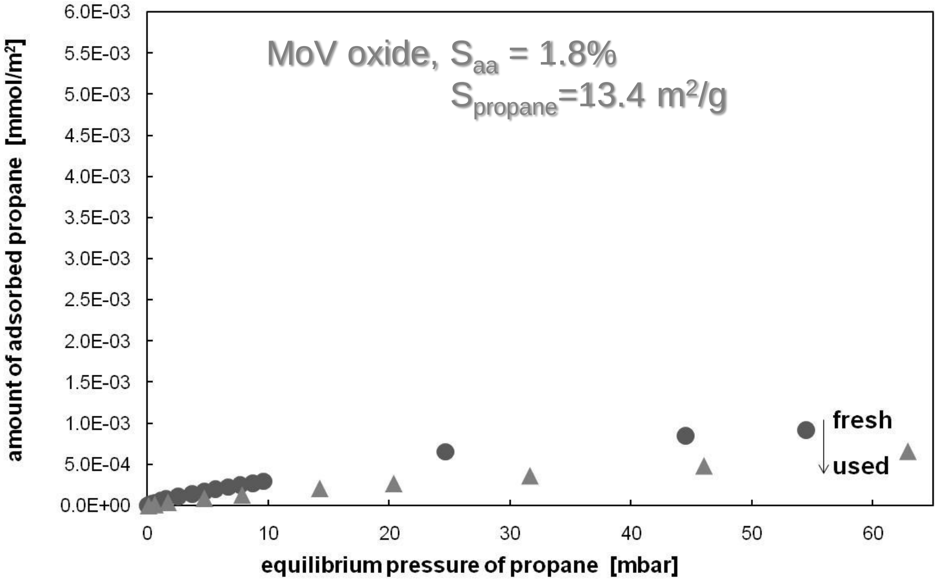
Surface composition of the used M1 is similar to the composition measured in the *in situ* experiment in the presence of steam.
[A.Celaya Sanfiz et.al., J. Phys. Chem. C, 2010, 114, pp 1912]

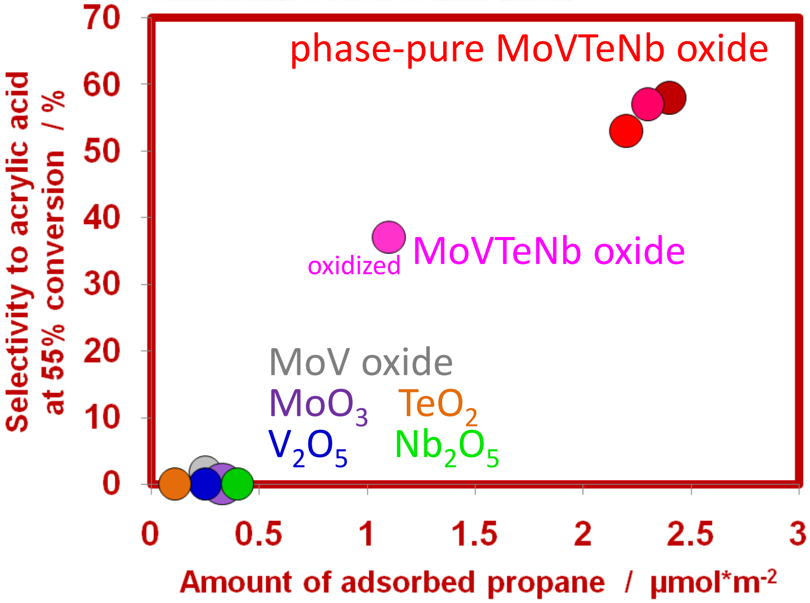
***ex situ* surface analysis of the used catalyst can be done**

Propane adsorption isotherms of different selective catalysts

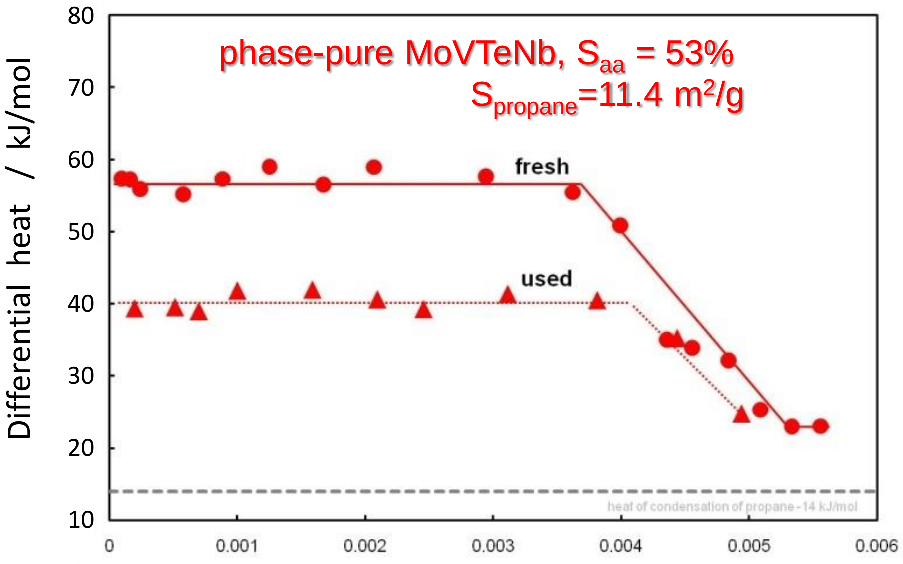


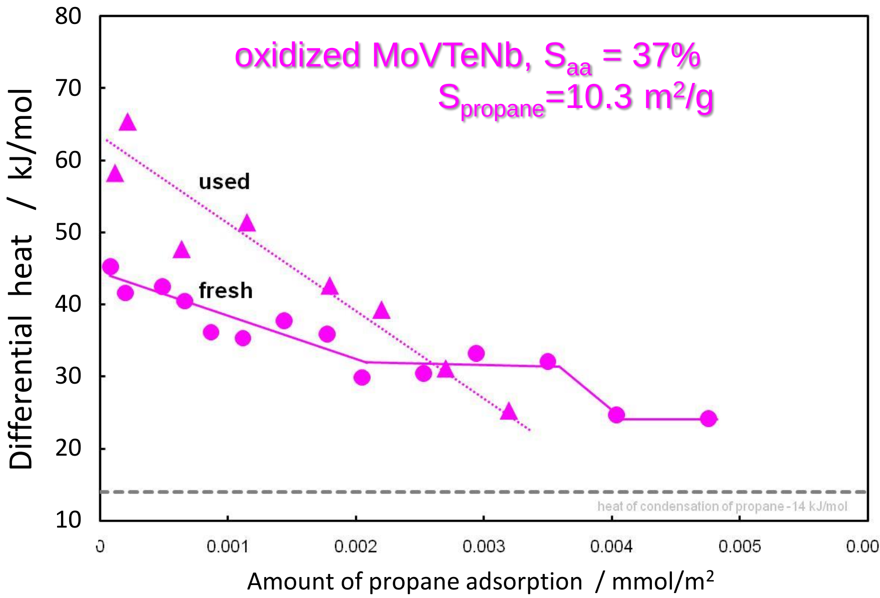


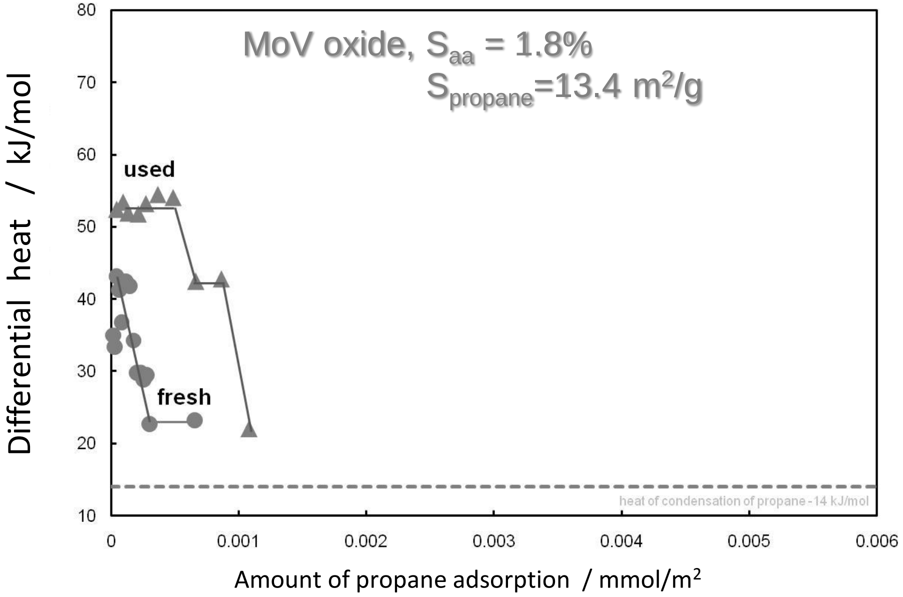




Differential heats of adsorbed propane of different selective catalysts







★ 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.

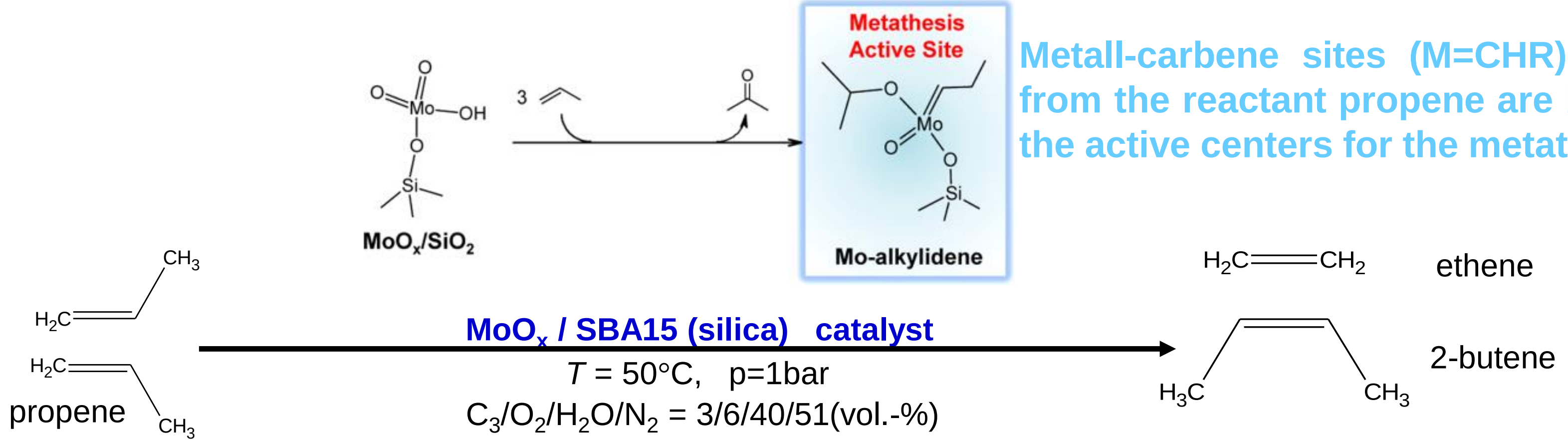
M. Hävecker, S. Wrabetz , A. Trunschke, R. Schlögl et.al. ; Journal of Catalysis, 258(1) (2012) 48 -60.

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

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



MoO$_x$ / SBA15 (silica) catalyst

T = 50°C, p=1bar

$C_3/O_2/H_2O/N_2$ = 3/6/40/51(vol.-%)

Intention: Studying of the catalytically active surface sites - quantification

Adsorption

Microcalorimetry :

- ★ propylene as probe molecule
- ★ $T_{adsorption}$= 50°C = $T_{reaction}$
- ★ selected catalysts: different activity

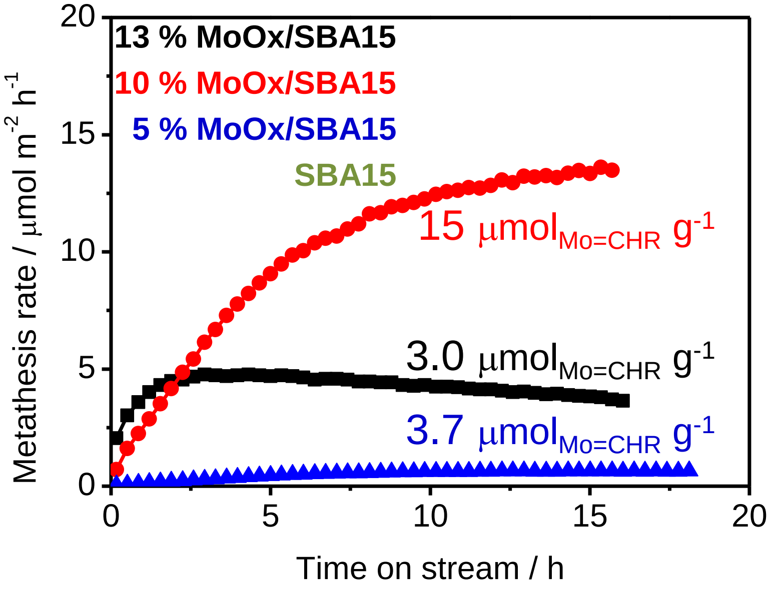
13 % MoOx/SBA15	Metathesis rate = **3.0** µmol/m^2*h
10 % MoOx/SBA15	Metathesis rate = **13.0** µmol/m^2*h
5 % MoOx/SBA15	Metathesis rate = **1.5** µmol/m^2*h
SBA15	Metathesis rate = **0.0** µmol/m^2*h

K. Amakawa, S. Wrabetz, R. Schlögl et.al. ; J. Am. Chem. Soc., 134 (28) (2012) 11462-11473.

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

Propene Metathesis Activity

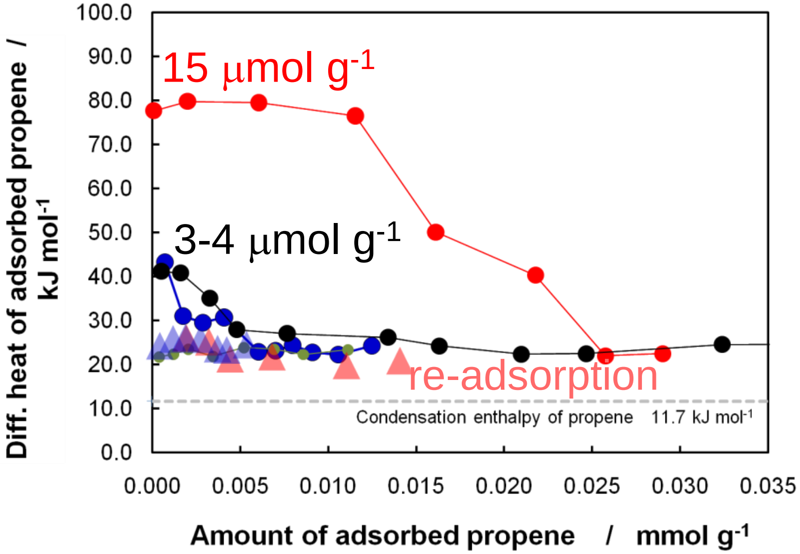
T = 50 °Cc



Microcalorimetry

Differential heat of propene adsorbed on MoOx/SBA15

$T_{reaction}$ = 50°C



- Activity strongly depends on the Mo loading

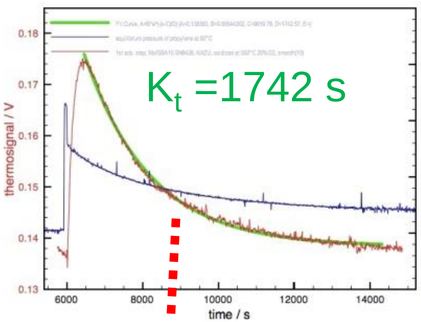
- Correlation between amount & strength of C_3H_6 adsorption sites and catalytic activity.

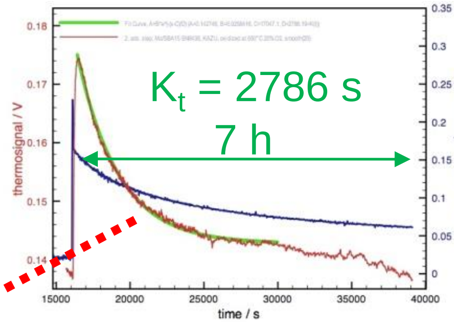
<u>Post-reaction carbene titration</u>

Active site counting was performed after metathesis using post-reaction ethene-*d₄* ($CD_2=CD_2$) metathesis to titrate the formed metal-carbene ($Mo=CH-CH_2$) sites.

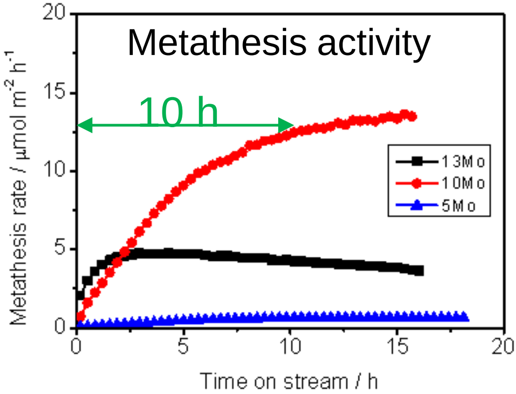
$Mo=CH-CH_3 + CD_2=CD_2 \rightarrow Mo=CD_2 + CD_2=CH_2-CH_3$

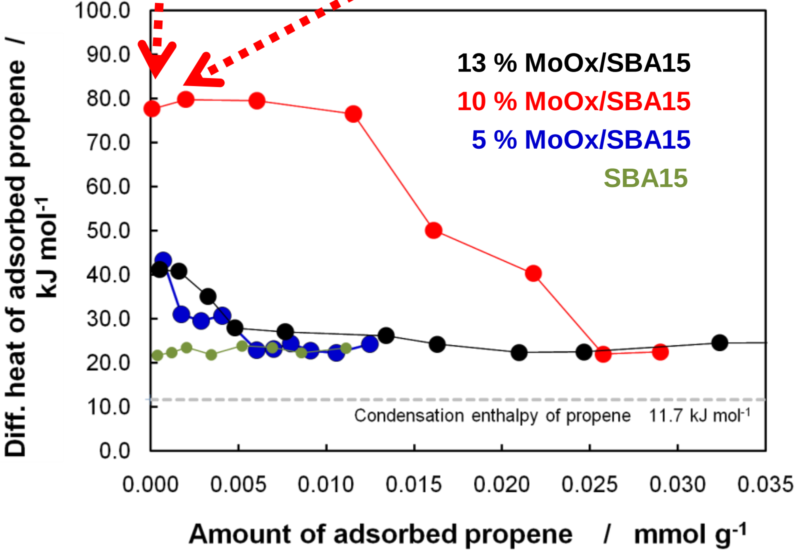
Active Site Quantification on Propylene Metathesis over MoOx/SBA-15



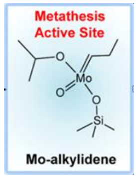


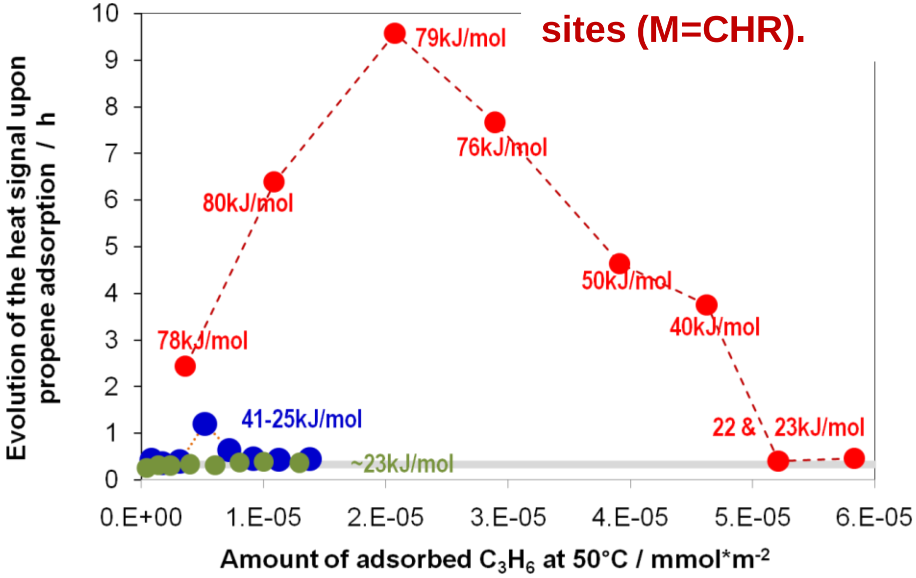
A long decay time and fine structure in the exothermic signal indicate reactive adsorption.





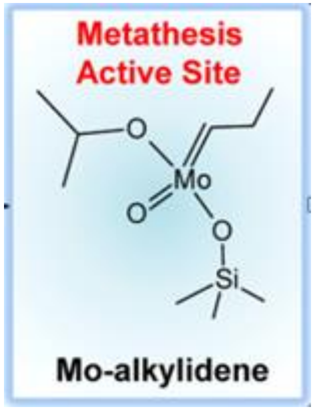
Generation of the active Metall-carbene sites (M=CHR).





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

- 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


Metathesis Active Site

Mo-alkylidene

Σ

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

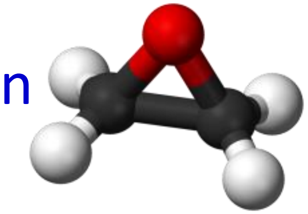
- ca. 1% of Mo atoms formed active sites

Amakawa, K., Wrabetz, S., Kröhnert, J., Tzolova-Müller, G., Schlögl, R., Trunschke, A.; J. Am. Chem. Soc., 134 (28) (2012) 11462-11473.

Study of catalytic relevant sites via calorimetry under reaction conditions:

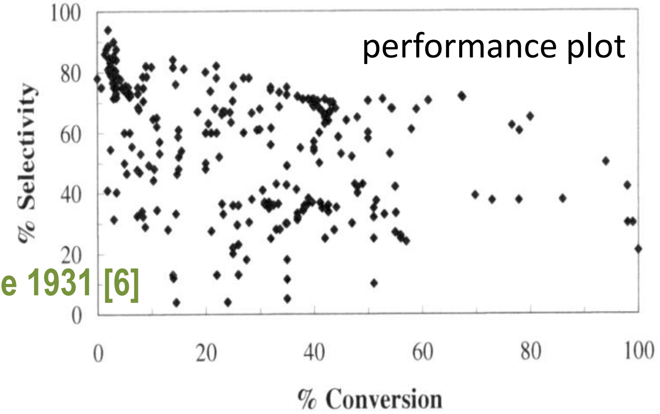
Silver as a catalyst for the ethylene epoxidation

- 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.



EO epoxidation over Ag; since 1931 [6]

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

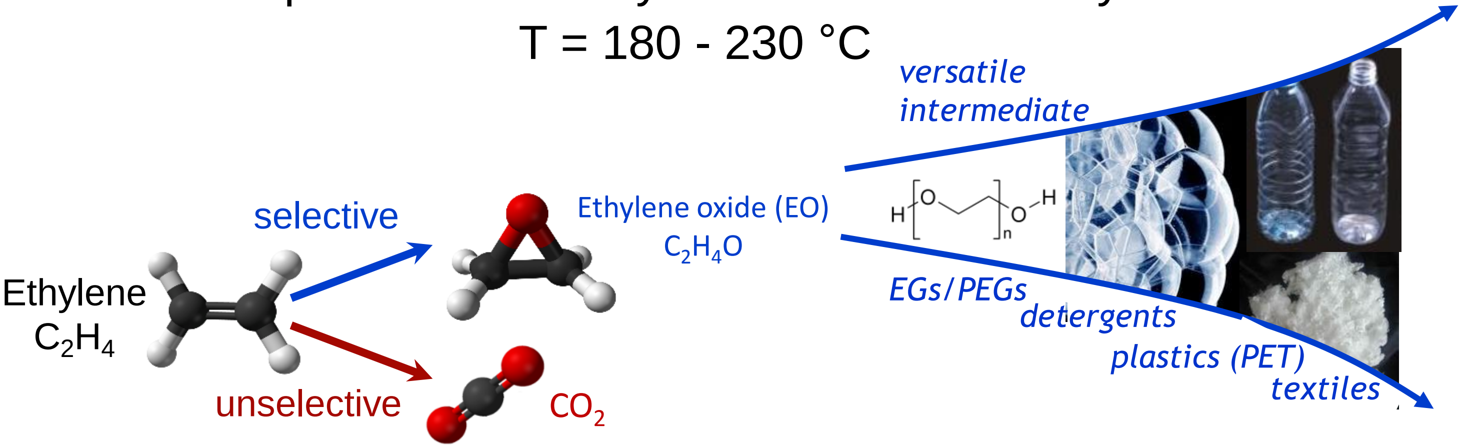
- Final goal is to safely **translate the electronic signatures** obtained by X-ray spectroscopies **into structural information**, which can be used to construct reaction mechanisms [4,5] .

[1] C. Hess, R. Schlögl, A. T. Bell, A. Trunschke, A. Knop-Gericke, Nanostructured Catalysts: Selective Oxidations, Royal Society Of Chemistry, 2011.
[2] T. C. R. Rocha, A. Knop-Gericke, R. Schlögl, The Journal of Physical Chemistry C 2012, 116, 11408−11409.
[3] R. Reichelt, S. Gunther, J. Wintterlin, Journal of Physical Chemistry C 2011, 115, 17417–17428.
[4] T. C. R. Rocha, A. Oestereich, D. V Demidov, M. Hävecker, S. Zafeiratos, G. Weinberg, V. I. Bukhtiyarov, A. Knop-Gericke, R. Schlögl, Phys. Chem. Chem. Phys. 2012, 14, 4554–64.
[5] V. I. Bukhtiyarov, M. Hävecker, V. V. Kaichev, A. Knop-Gericke, R. W. Mayer, R. Schlögl, Phys. Rev. B 2003, 67, 235422.
[6] B. K. Hodnet, Heterogeneous Catalytic Oxidation, John Wiley & Sons, New York, 2000.

The Ag-O system in catalysis

epoxidation of ethylene over silver catalyst

T = 180 - 230 °C



versatile intermediate

selective

Ethylene oxide (EO)
C_2H_4O

Ethylene
C_2H_4

unselective

CO_2

EGs/PEGs

detergents

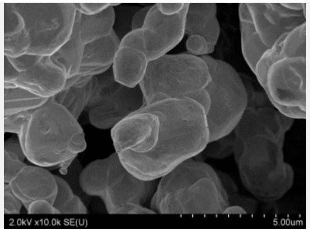
plastics (PET)

textiles

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:
Microcalorimetry

- ★ Oxygen
- ★ $T_{reaction}$ = 230 °C
- ★ selected catalyst: Ag powder <45micron

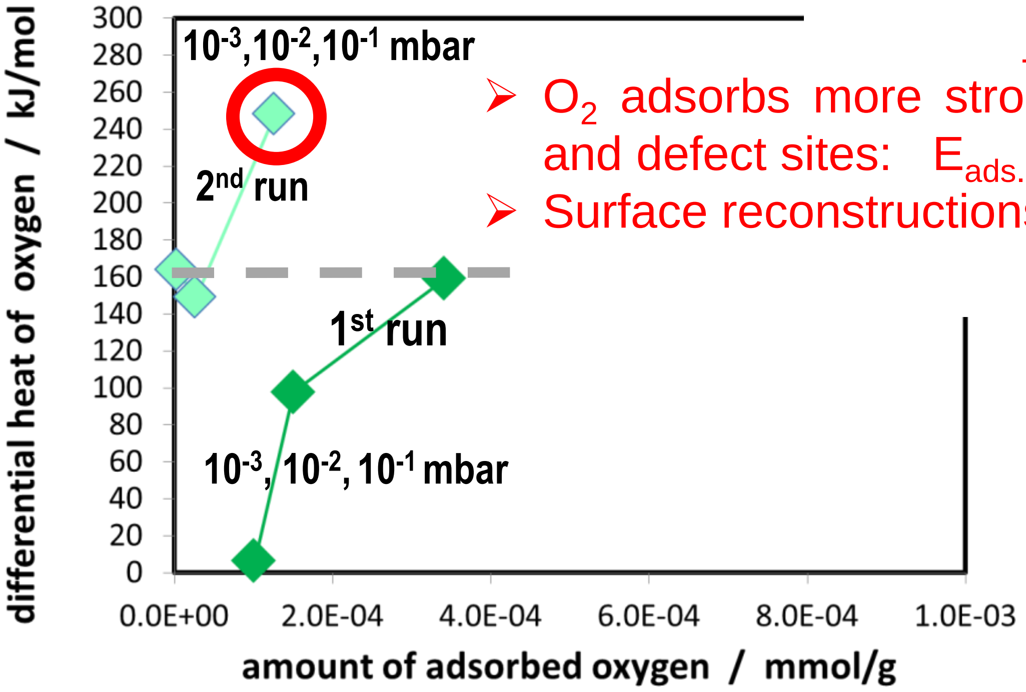


The Ag-O system in catalysis

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_{sub} and defect sites: $E_{ads.} = 180 – 240$ kJ/mol
- Surface reconstructions: $E_{ads.} = 120 – 160$ kJ/mol

$q_{diff}\uparrow$ 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

4] *Auroux, A. & Gravelle, P.C., 1981. Comparative study of the bond energy of oxygen at the surface of supported silver catalysts and of the activity of these catalysts for ethylene epoxidation. Thermochimica Acta, 47, pp.333–341.*

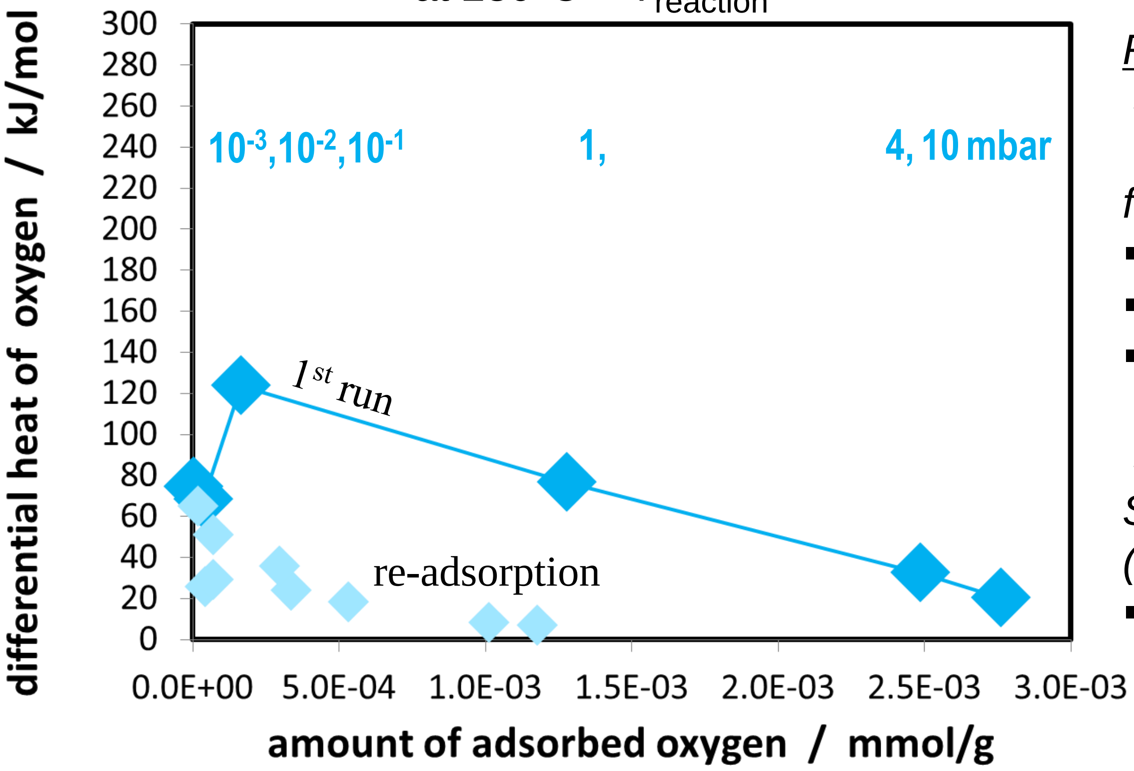
[5] *Anderson, K.L., Plischke, J.K. & Vannice, M., 1991. Heats of Adsorption of Oxygen , Ethylene , and Butadiene on Al_20_3- Supported Silver. J. of Catalysis, 160, pp.148–160.*

[6] *Anderson, K.L., Plischke, J.K. & Vannice, M., 1991. Heats of Adsorption of Oxygen , Ethylene , and Butadiene on Al203- Supported Silver. Journal of Catalysis, 160, pp.148–160.]*

The Ag-O system in catalysis

Steady State

Differential heat of O_2 ads. on the clean Ag surface
at 230°C = $T_{reaction}$



References:

[12]

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

- *$O_{ads.}$: H = −63.0 kJ/mol*
- *$O_{2\ ads.}$: H = −44.5 kJ/mol*
- *$O_{ads.}$ / $O_{surface}$: H = −103.0 kJ/mol*

[13]

Standard enthalpies of formation at 298 K (ΔH^{o}_{f}) of O adatoms on Pt(111):

- *109 – 99 kJ/mol*

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

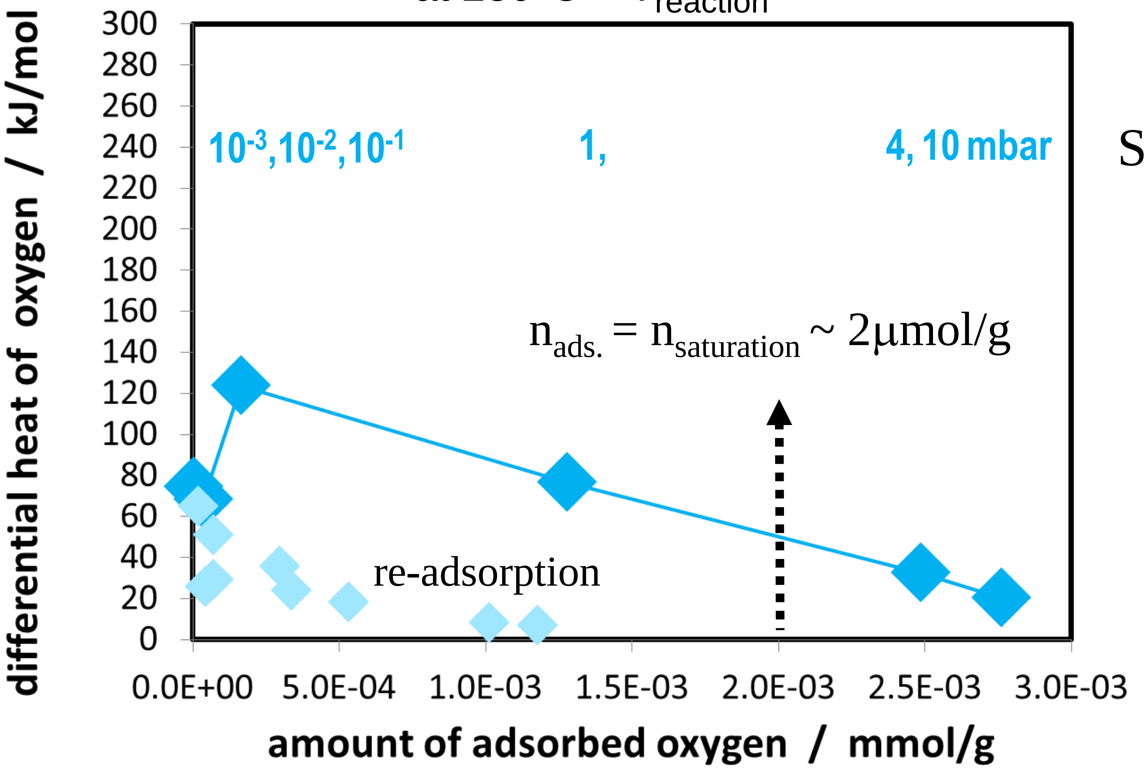
---

[12] C. Stegelmann, N.C. Schiødt, C.T. Campbell, and P. Stoltze, J. Of Catal. 221 (2004) 630-649.
[13] Eric M. Karp, Charles T. Campbell , Felix Studt, Frank Abild-Pedersen and Jens K. Nørskov; SLAC-PUB-15339.

The Ag-O system in catalysis

Steady State

Differential heat of O_2 ads. on the clean Ag surface
at 230°C = $T_{reaction}$



Specific surface area of Ag for O_2
at $T_{reaction}$ = 230°C

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

$$\frac{2 \cdot 10^{-6}\ \text{mol} \cdot 6.022 \cdot 10^{23}\ \text{particles} \cdot \text{cm}^2}{\text{g} \cdot 1.4 \cdot 10^{15}\ \text{atoms} \cdot \text{mol}}$$

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

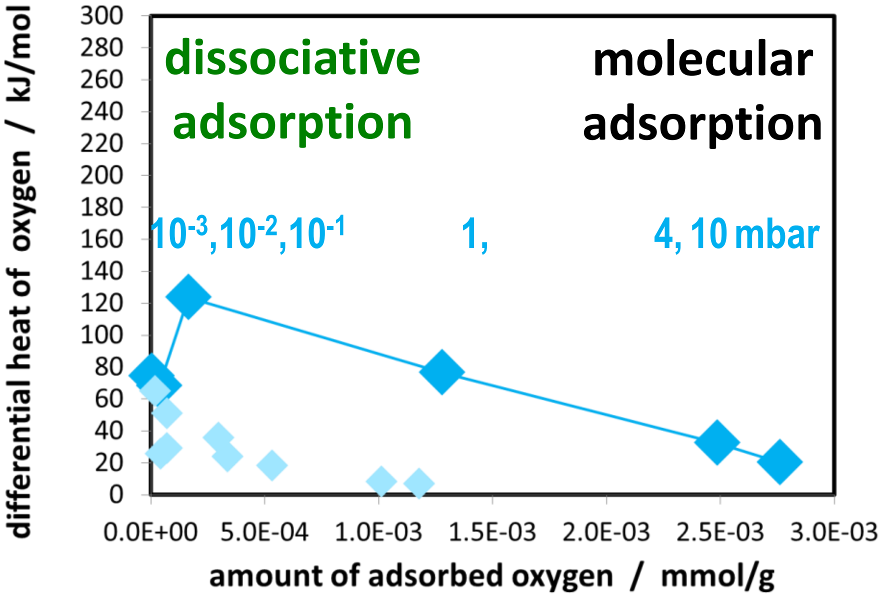
$BET_{N2,\ 77K}$ = 0.72 m^2/g

ΔS = 0.14 m^2/g

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

The Ag-O system in catalysis

Experiment



Theory

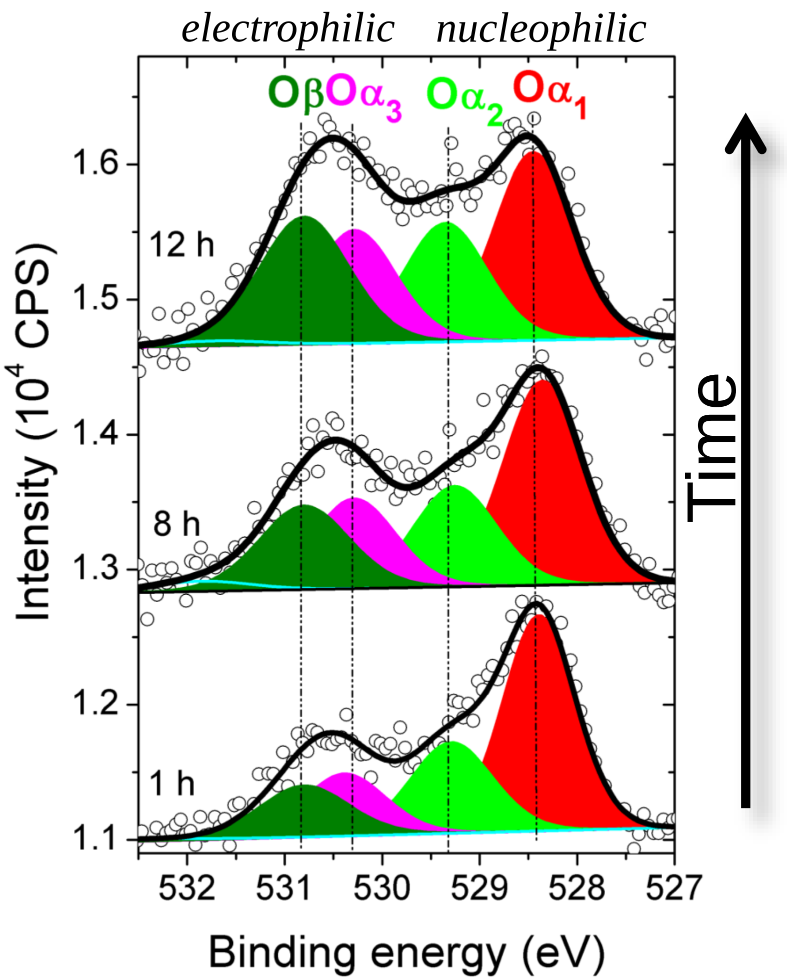
DFT calculations

system	Eads per 1/2 O_2 [kJ/mol]	Eads per O_2 [kJ/mol]
reconstructions O_{ads} stronger on Ag(110)	**60-80**	120-160
unreconstructed O_{ads} on hollow sites of Ag(111)	40-60	80-120
on subsurface O	**110-120**	220-240
surface defects	**90-120**	180-240
subsurface	<10	10
grain boundaries	10-20	**20-40**
O2 clean surface	5-10	10-20
O2 on sub O	10-20	**20-40**
O2 on defects	20-30	**40-60**

The Ag-O system in catalysis

O1s XPS spectra for Ag powders

measured in situ under 0.5 mbar O_2 at 180 °C

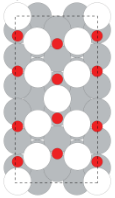
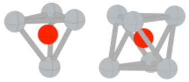
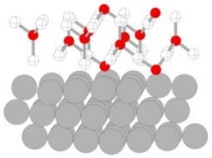
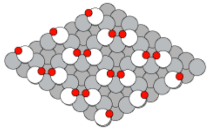
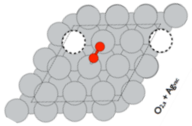


The **distribution of O species** on the Ag surface dynamically **changes with time** as the catalyst surface equilibrates with the gas phase at mbar pressure and temperatures typical of alkene (180-230 °C).

→ Dynamics at 180 °C

Ag-O dynamics depend on time / temperature and pressure

Summary

T °C	p_{O2} mbar	n ads. $\mu mol_{O2}/g_{Ag}$	q diff kJ/mol	Ag-O dynamics	DFT ○ Ag_{surf} ● Ag_{sub} ● O
$T_{cleaning}$ 150	$< 10^{-1}$	0.5	>120 - 260	➢ dissociative adsorption ➢ cleaning the surface from CH_x/CO_3 ➢ initial formation of the surface reconstructions	c(6x2) Ag(110)reconstruction 
$T_{reaction}$ 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 ***	 
$T_{reaction}$ 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.

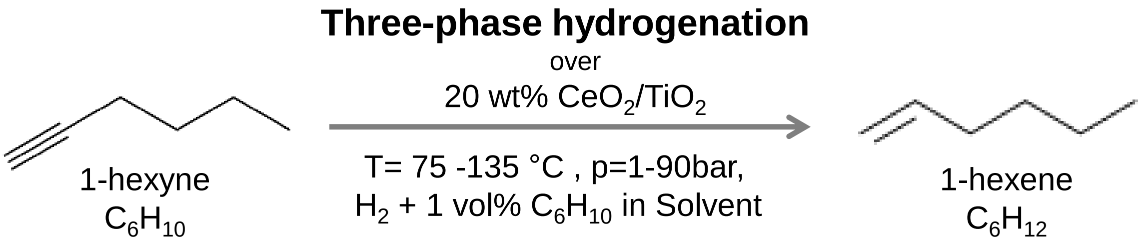
**** Proposed by theory and calorimetry. In this case the time/temperature dependence is related to the defect formation.

***** 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 $T_{react.}$ on supported ceria ,
being unexpectedly active in the hydrogenation of 1-hexyne

1-hexyne adsorption at $T_{react.}$ = 80°C on supported ceria

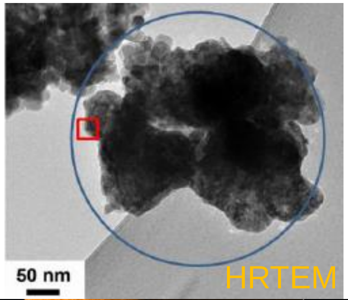


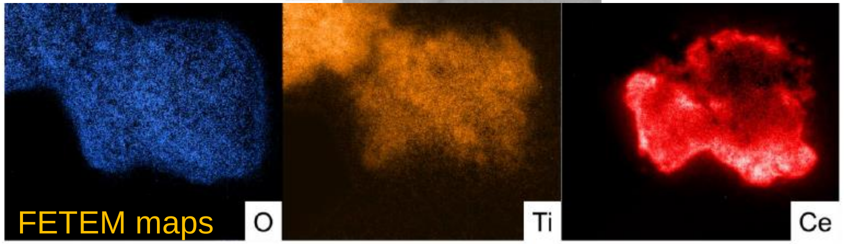
1-hexyne
C_6H_{10}

Three-phase hydrogenation
over
20 wt% CeO_2/TiO_2

T= 75 -135 °C , p=1-90bar,
H_2 + 1 vol% C_6H_{10} in Solvent

1-hexene
C_6H_{12}





Intention: Does calorimetry offers the possibility to distinguish between catalysts of similar characteristic properties$_{\text{IR, XRD,TEM,XPS,BET)}}$, but different catalytic activity?

Adsorption Microcalorimetry :

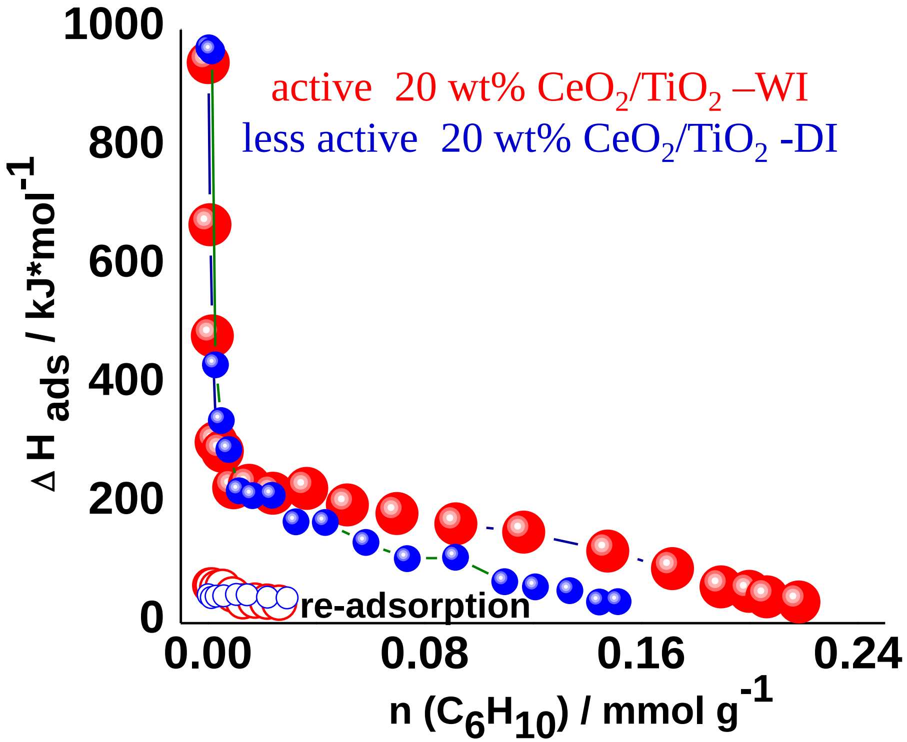
- 1-hexyne as probe molecule
- $T_{adsorption}$ = 80°C ← *as the Arrhenius plot of 1-hexyne hydrogenation is smooth in the whole 75 - 135 °C range*
- selected catalysts: different active catalysts

20 wt% CeO_2/TiO_2 -WI	very active	(wet impregnation; # 17380)
20 wt% CeO_2/TiO_2 -DI	less active	(dry impregnation; # 17378)

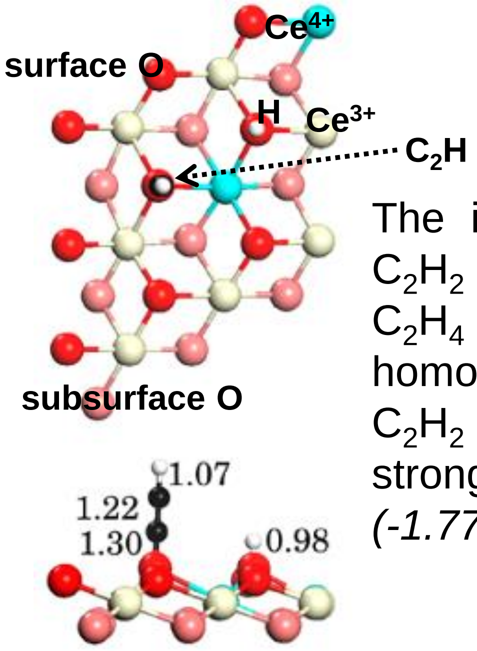
Vilé, G., Wrabetz, S., Floryan, L., Schuster, M. E., Girgsdies, F., Teschner, D., et al., ChemCatChem, 6(7) (2014) 1928-1934.

1-hexyne adsorption at $T_{react.}$ = 80°C on supported ceria

Differential heats



DFT calculations [1]



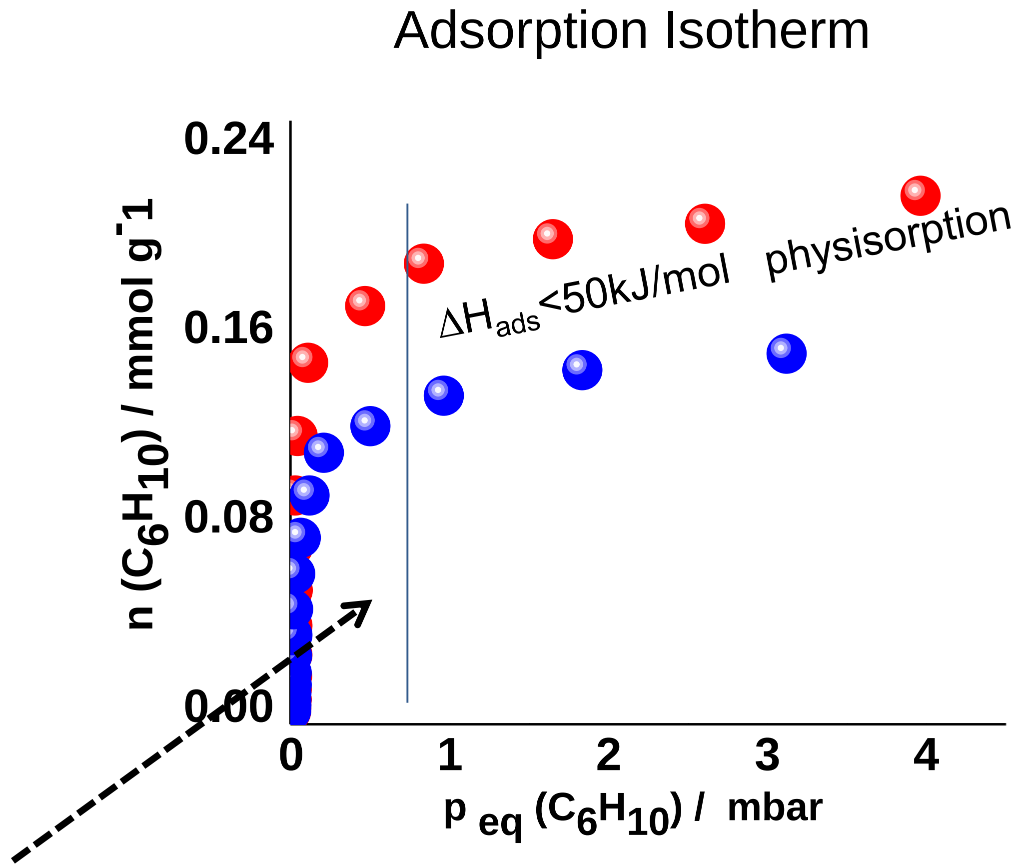
The initial step of the C_2H_2 hydrogenation to C_2H_4 is the dissociative homolytic adsorption of C_2H_2 . This process is strongly exothermic. *(-1.77eV)*

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

$\Delta H_{ads.\ ,\ plateau}$ **<u>~ 200 kJ/mol</u>** 60µmol/g → dissociative homolytic adsorption of C_6H_{10}
→ single dehydrogenation step [1]

[1] J. Carrasco, G. Vilé, D. Fernández-Torre, R. Pérez, J. Pérez-Ramírez, M. V. Ganduglia-Pirovano, J. Phys. Chem. C 2014, 118, 5352.
[2] Claire L. Pettiette-Hall, Donald P. Land, Robert T. McIver, Jr.,* and John C. Hemminger, J. Am. Chem. SOC. 1991, 113, 2755-2756 .

1-hexyne adsorption at $T_{react.}$ = 80°C on supported ceria



ΔH_{ads} > 50kJ/mol - chemisorption

very active 20 wt% CeO_2/TiO_2 –WI → 190 µmol/g reacted 1-hexyne molecules

less active 20 wt% CeO_2/TiO_2 -DI → 130 µmol/g reacted 1-hexyne molecules

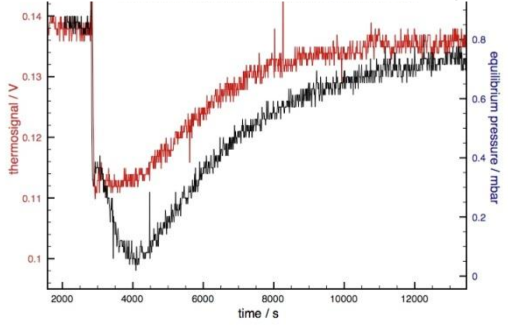
1-hexyne adsorption at $T_{react.}$ = 80°C on supported ceria

Corresponding integral heats

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

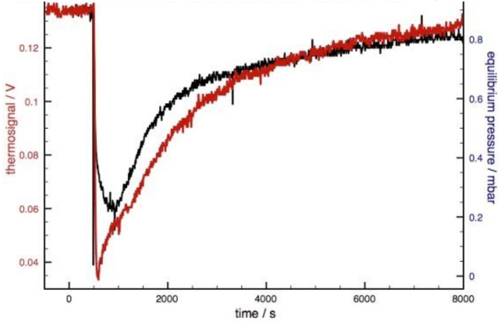
1st ads. step = 0.00023 mmol/g

1st ads. step = 0.00039 mmol/g



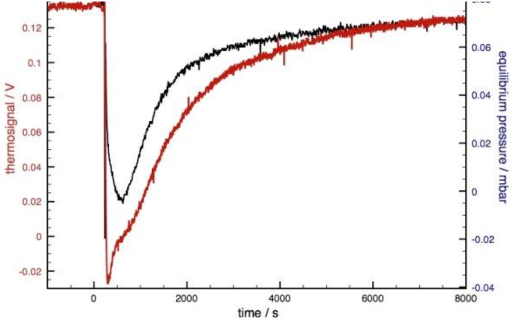
4st ads. step = 0.0031 mmol/g

3rd ads. step = 0.0029 mmol/g



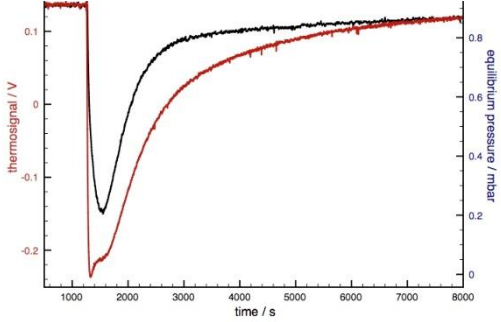
5st ads. step = 0.0053 mmol/g

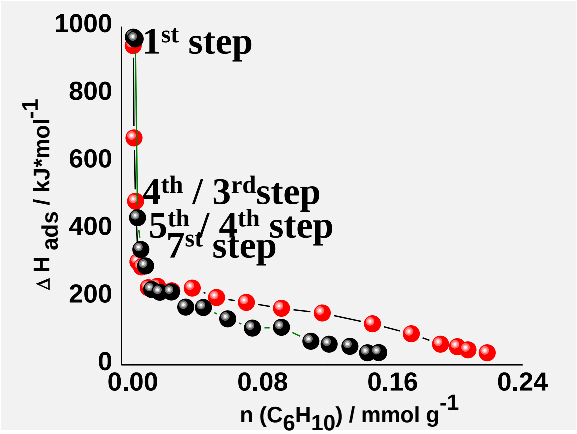
4st ads. step = 0.0050 mmol/g



7st ads. step = 0.0153 mmol/g

7st ads. step = 0.0166 mmol/g





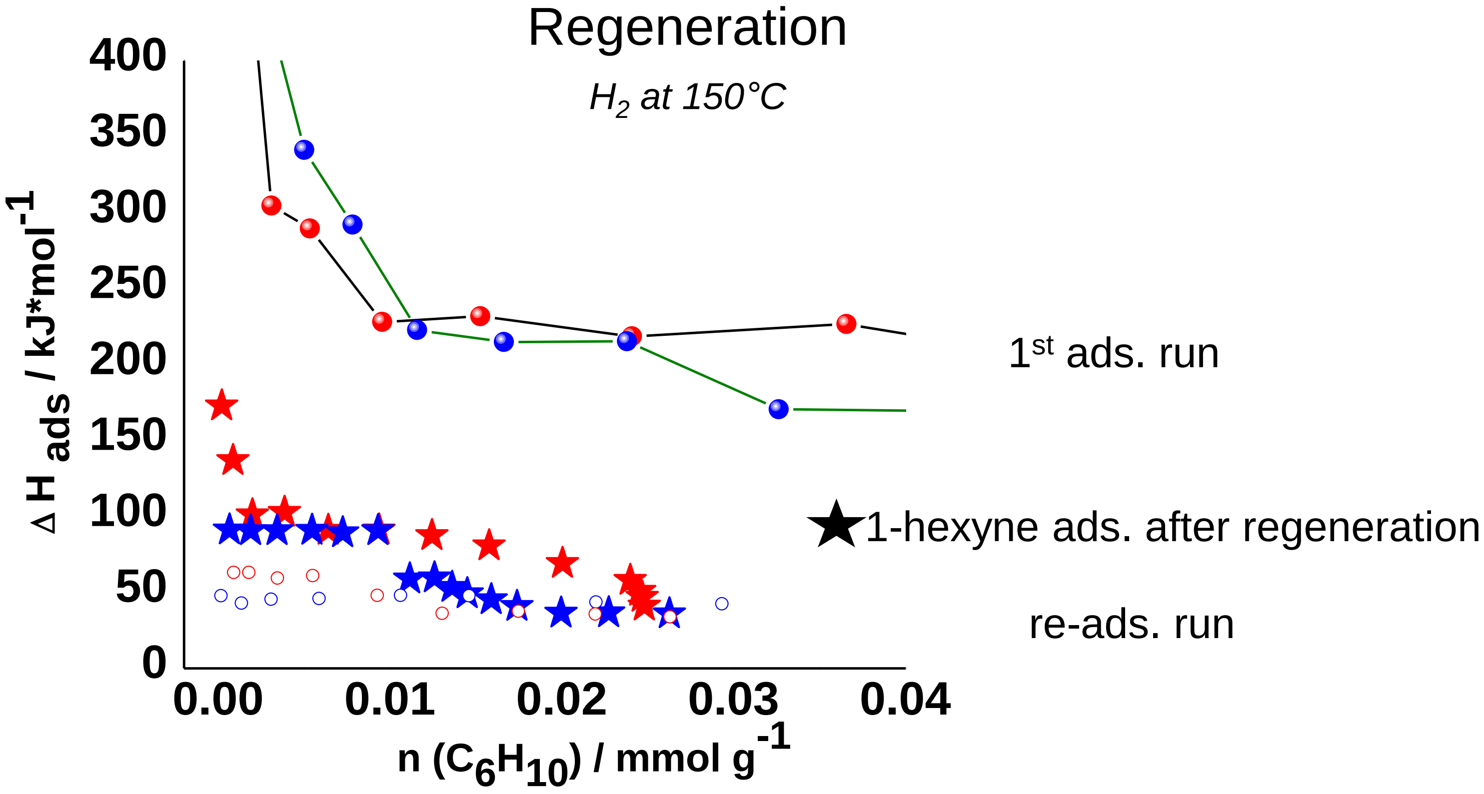
The **adsorption signature** is composed of two main contributions:

- 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.

1-hexyne adsorption at $T_{react.}$ = 80°C on supported ceria



The regeneration of the catalyst surface using H_2 (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 $T_{react.}$ 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 μmol/g
- slightly easier regeneration of the surface after 1-hexyne contact at $T_{react.}$
- pronounced trapped and phys. state of the adsorbates to find the most suitable place for reaction → dynamic surface is apparently favorable for the catalytic performance

Vilé, G., Wrabetz, S., Floryan, L., Schuster, M. E., Girgsdies, F., Teschner, D., et al., ChemCatChem, 6(7) (2014) 1928-1934.

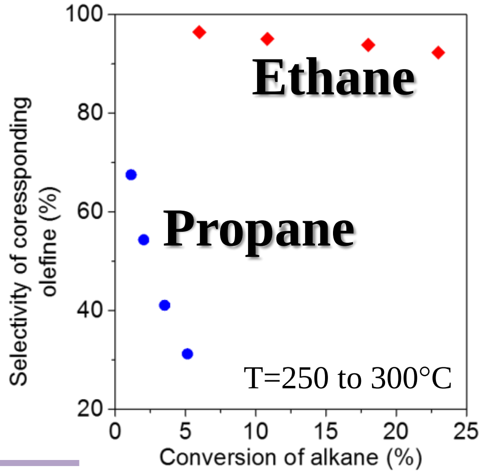
Reactants induced responses of catalyst surface:

Propane and ethane ads./des. cycles (40°C) on MoV oxide model catalyst for oxidative dehydrogenation of alkanes.

1st MoV oxide model catalyst in 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

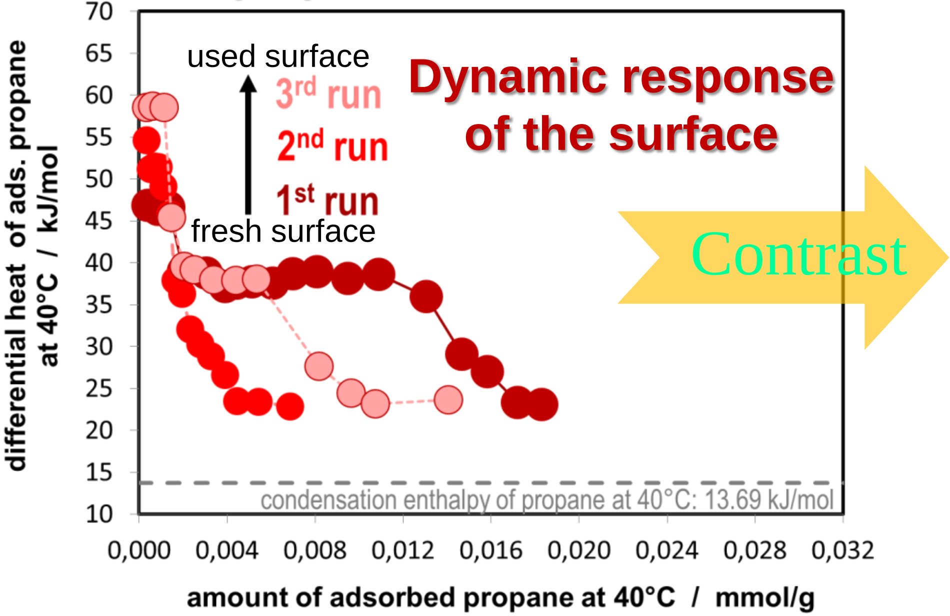


Microcalorimetry

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

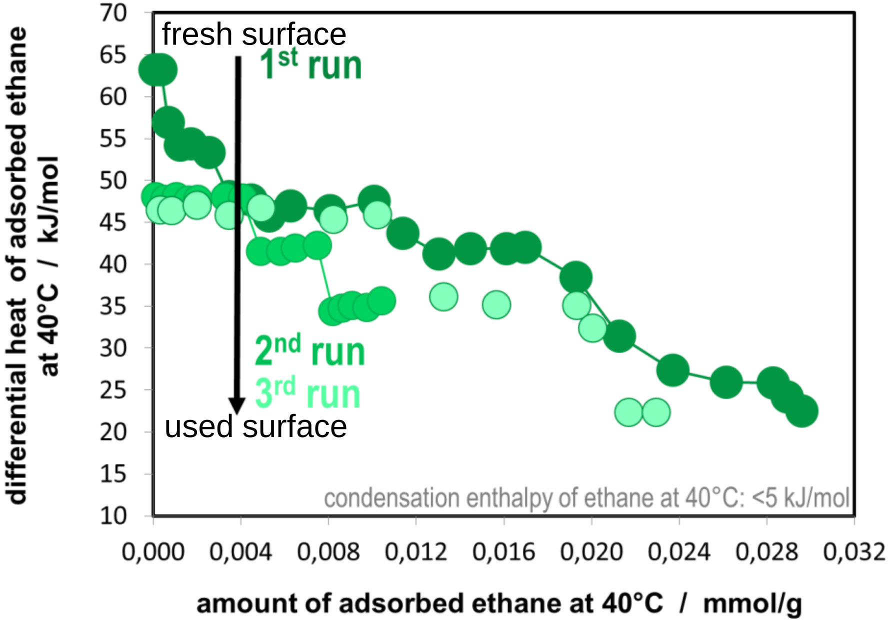
PROPANE and ETHANE adsorption on MoV oxide at 40°C

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



Dynamic response of the surface

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



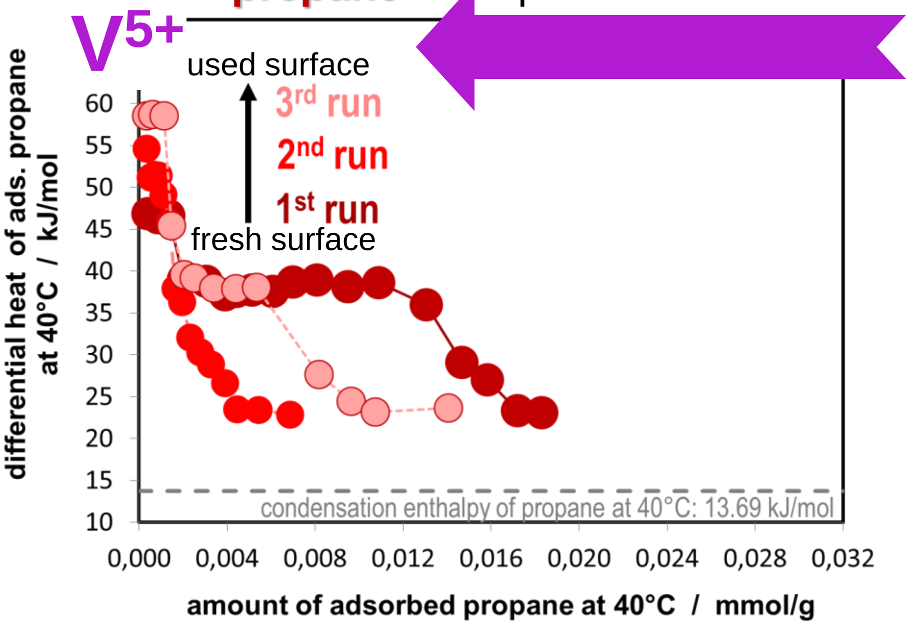
- $S_{\text{specific for propane}} \sim 3.6\ m^2/g$
  $BET = 25.52\ m^2/g$

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

$$S_{\text{MoV oxide}} = n_{\text{ads.}} \cdot \text{Avogadro const.} \cdot \underset{\text{assumed}}{S_{1:1}} \cdot \text{cross-section area}_{\substack{39Å2 \text{ for propane} \\ 22Å2 \text{ for ethane}}}$$

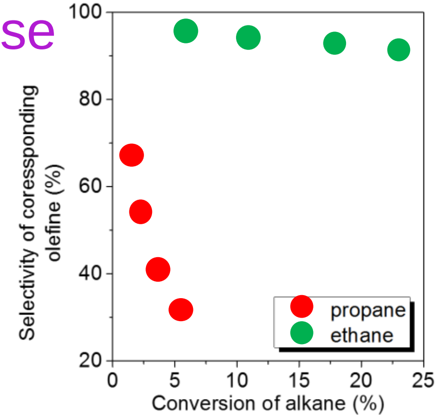
PROPANE and ETHANE adsorption on MoV oxide at 40°C

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



In-situ photoelectron spectroscopy

with TOS (presents of H_2O) 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**

Reactants induced dynamic responses of catalyst surface:

CO chemisorption cycles (30°C) on Ni/MgAl oxide catalyst for dry reforming of methane (DRM)

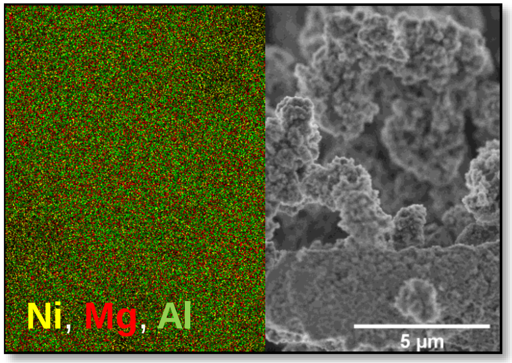
2nd Ni based catalysts for the dry reforming of methane

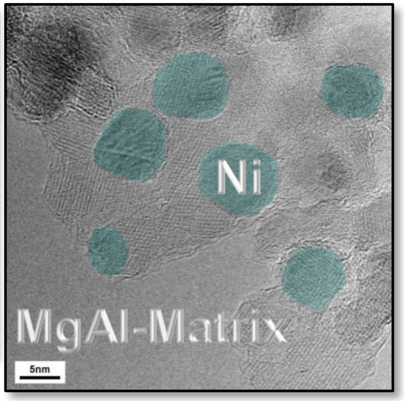
Task: study the influence of structural and compositional properties of nickel catalysts on the catalytic performance during DRM

Dry reforming (DRM): $CO_2 + CH_4 \xrightleftharpoons[900\ °C]{Ni} 2\ CO + 2\ H_2$ $\Delta H^0 = 247$ 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

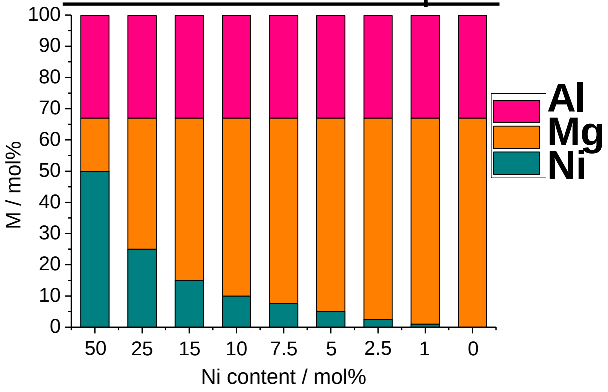




Obtained Ni/MgAl oxide catalyst

- reduction at 1000°C
- $d_{P,\ Ni}$ = 7 – 9 nm in all samples
- $d_{P,\ Ni}$ = 7 – **20** nm only in the 50wt% sample

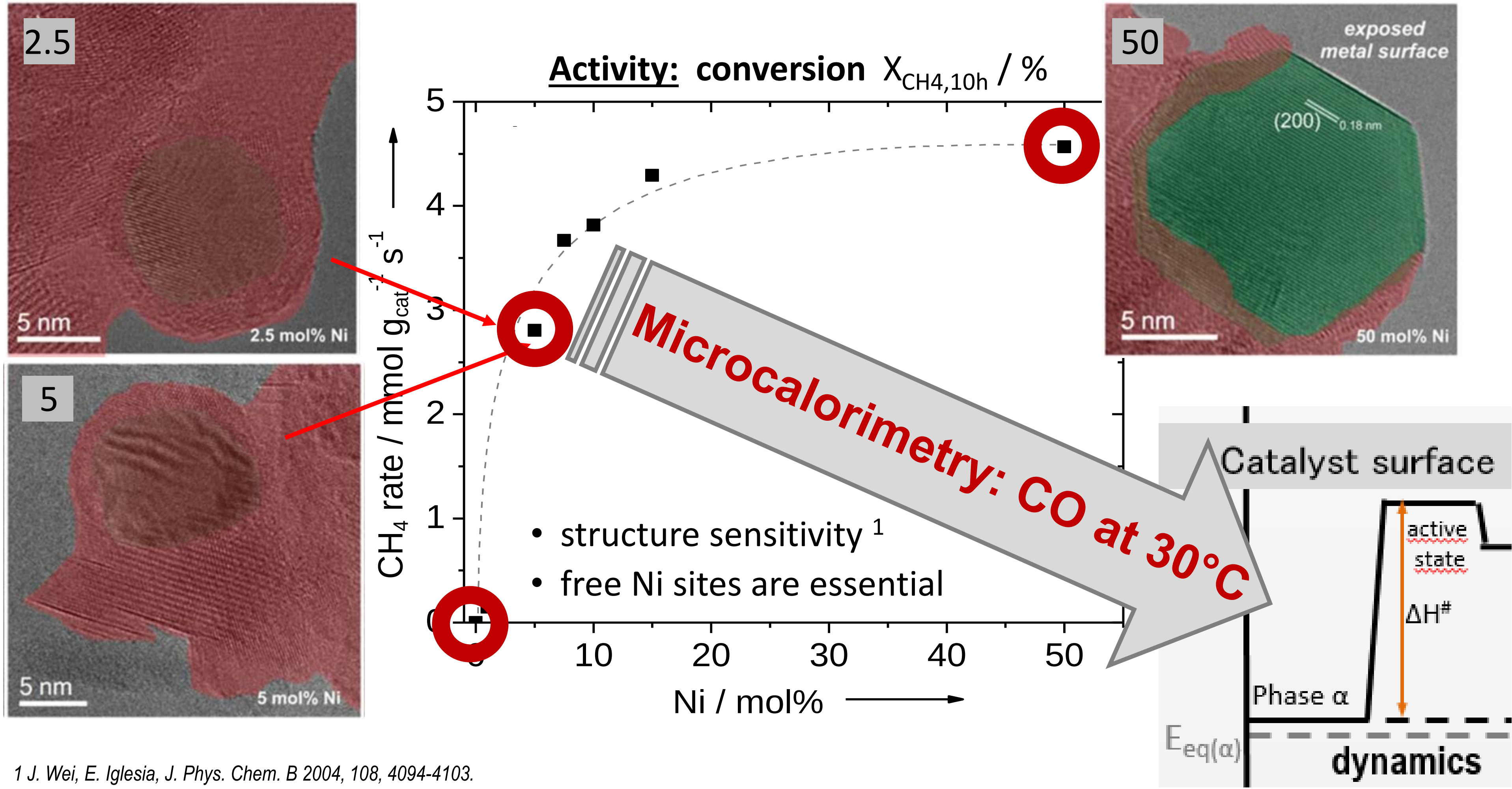
Metal ratios in samples



K. Mette, St. Kühl, A. Tarasov, M. G. Willinger, J. Kröhnert, S. Wrabetz, A. Trunschke, M. Scherzer, F. Girgsdies, H. Düdder, K. Kähler, K. Friedel Ortega, M. Muhler, R. Schlögl, M. Behrens, T. Lunkenbein, ACS Catal., 2016, 6 (10), pp 7238–7248.

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 $NiAl_2O_4$ spinel

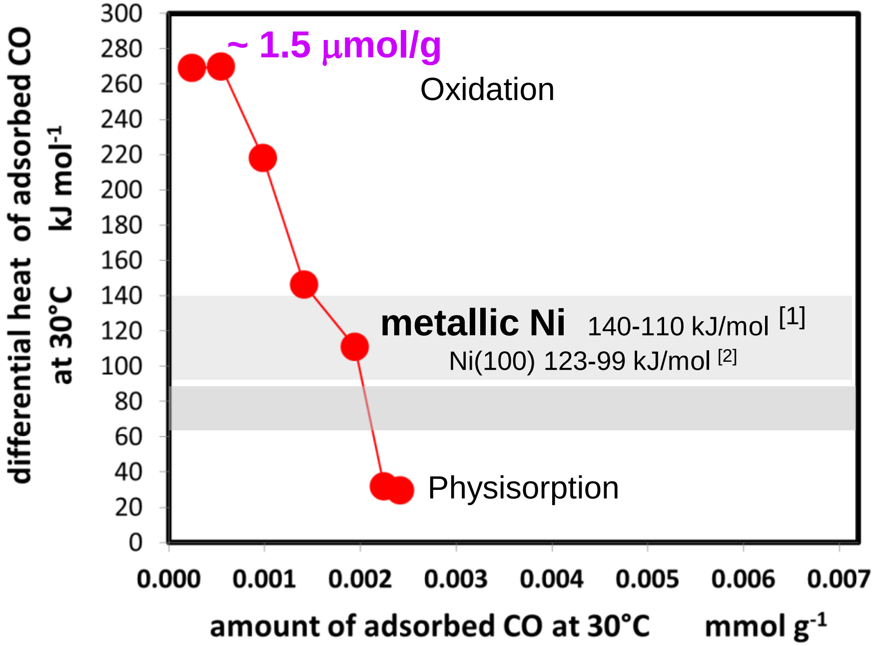


- structure sensitivity [1]
- free Ni sites are essential

[1] J. Wei, E. Iglesia, J. Phys. Chem. B 2004, 108, 4094-4103.

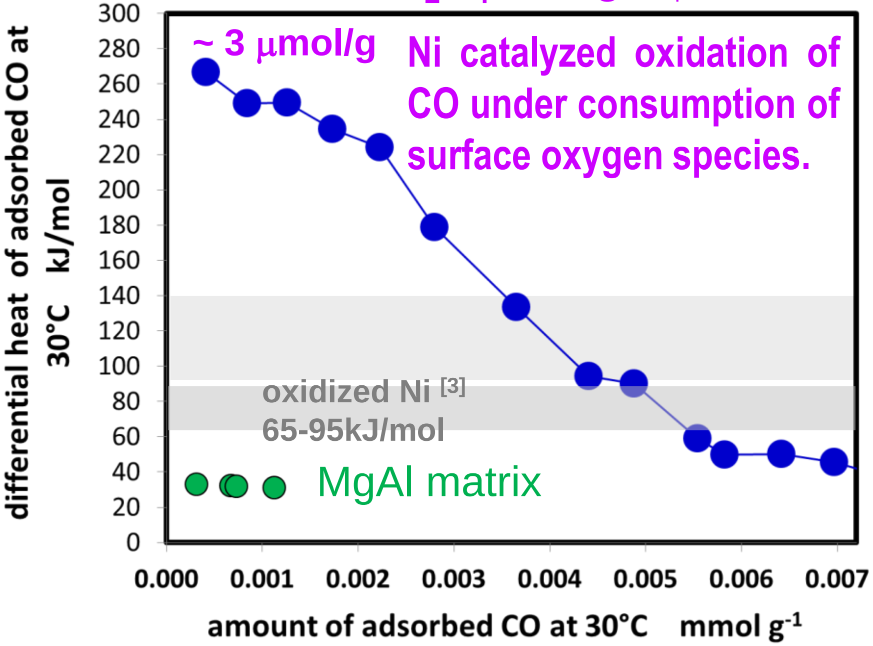
CO adsorption at 30°C using microcalorimetry

50mol% Ni/MgAl oxide
$X_{CH4,10h}$ = **73** %



5 mol% Ni/MgAl oxide
$X_{CH4,10h}$ = **50** %

$NiAl_2O_4$ + MgO ↑



Ni catalyzed oxidation of CO under consumption of surface oxygen species.

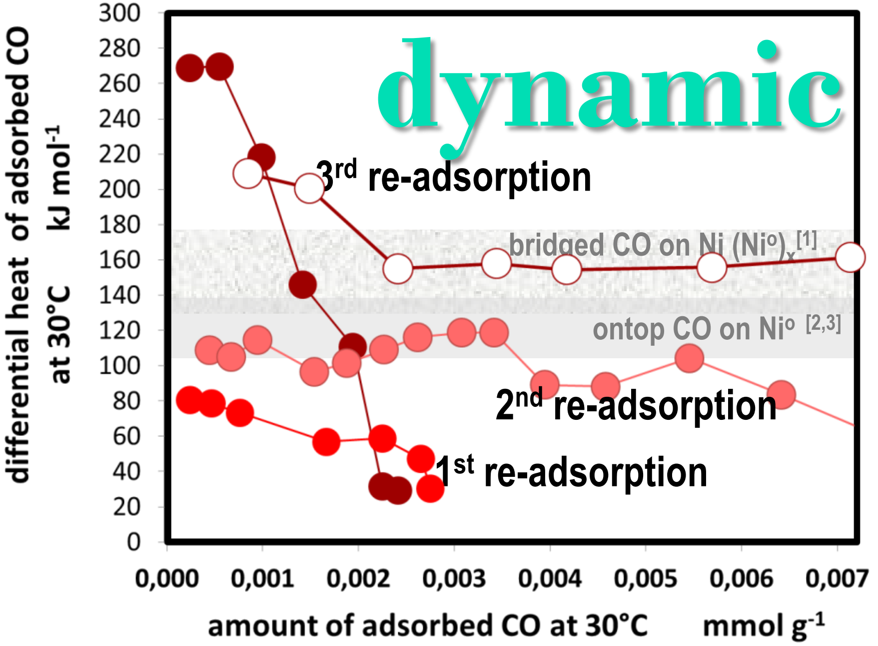
- The differential heat profiles are dominated by the presence of nickel

---

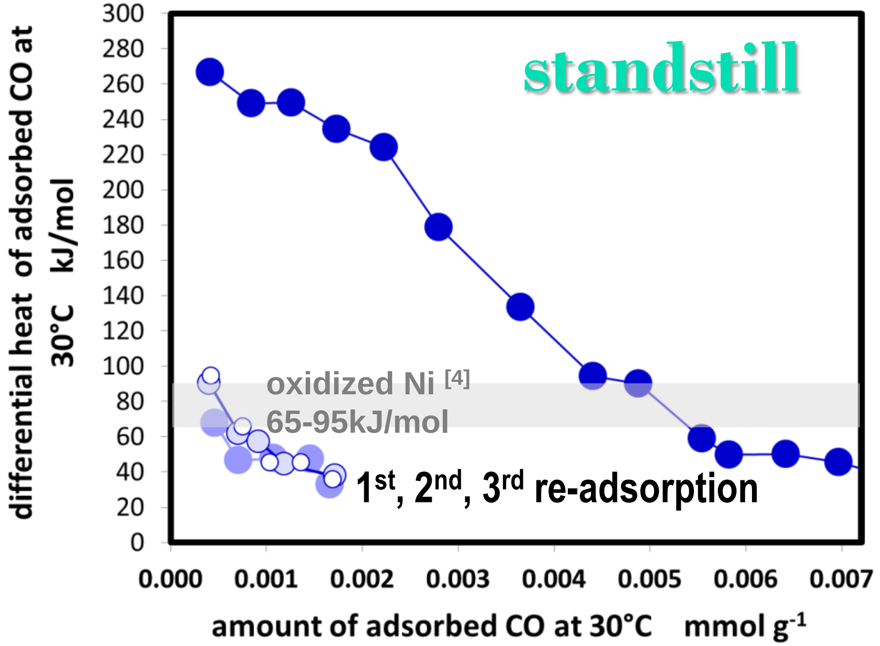
[1] A. Tanksale, J.N. Beltramini, J.A. Dumesic, G.Q. Lu, Journal of Catalysis 258 (2008) 366–377.
*[2] J. T. Stuckless, N. Al-Sarraf, C. Wartnaby, D. A. King, J. Chem. Phys. **1993**, 99, 2202-2212.*
[3] M. Cerro-Alarcó, B. Bachiller-Baeza, A. Guerrero-Ruiz, I. Rodríguez-Ramos, J. Mol. Catal. Chem. 2006, 258, 221-230.

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

50mol% Ni/MgAl oxide
$X_{CH4,10h}$ = **73** %

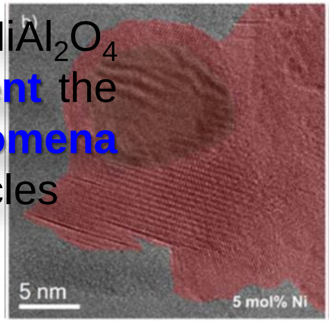


5 mol% Ni/MgAl oxide
$X_{CH4,10h}$ = **50** %



Catalytically relevant Ni^0 is back again !

- **Overgrowth** $NiAl_2O_4$ seems to **prevent** the **dynamic phenomena** on Ni nanoparticles



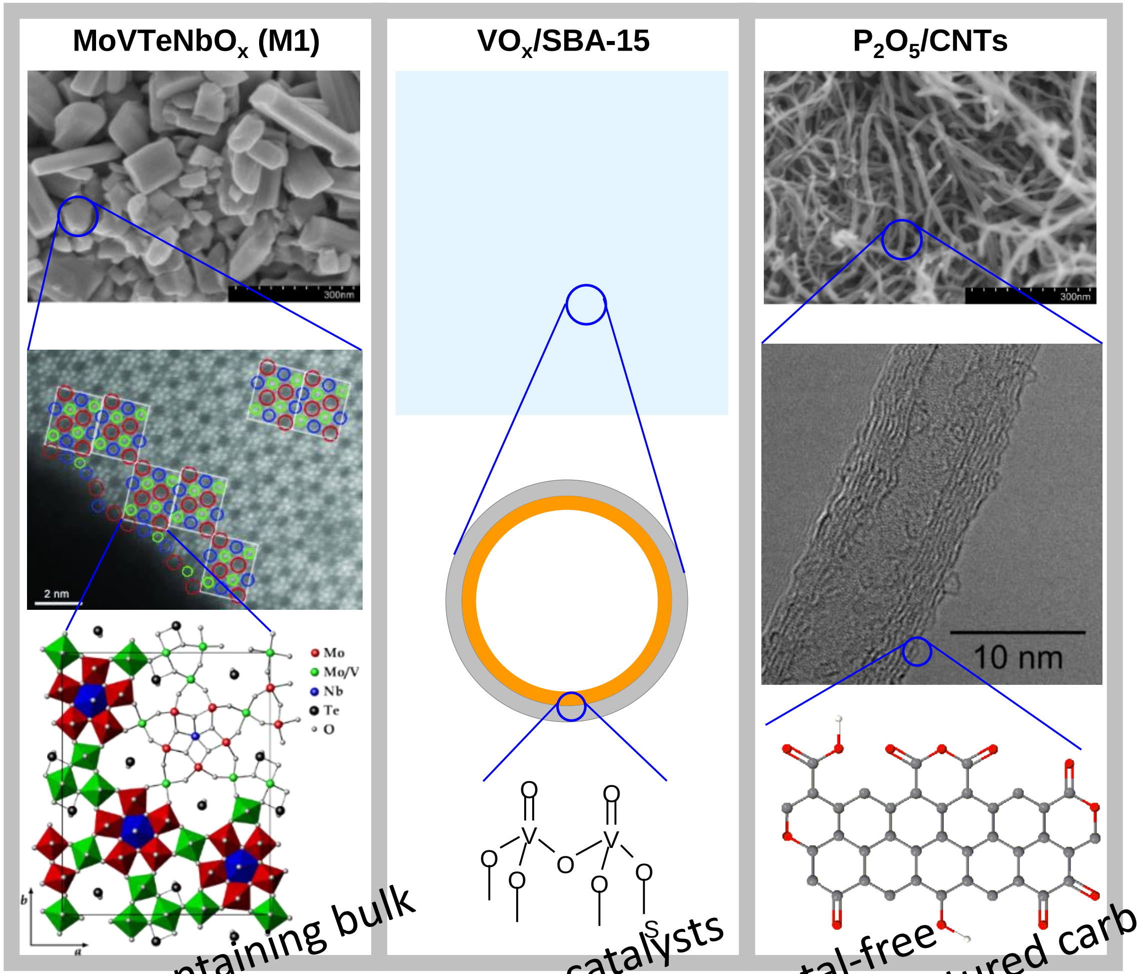
[1] R. S. Bordoli, J. C. Vickerman, J. Wolstenholme, *Surf. Sci.* **1979**, 85, 244-262.
[2] *A. Tanksale, J.N. Beltramini, J.A. Dumesic, G.Q. Lu, J. of Catalysis 258 (2008) 366–377.*
[3] *J. T. Stuckless, N. Al-Sarraf, C. Wartnaby, D. A. King, J. Chem. Phys. 1993, 99, 2202-2212*
[4] *M. Cerro-Alarcó, B. Bachiller-Baeza, A. Guerrero-Ruiz, I. Rodríguez-Ramos, J. Mol. Catal. Chem. 2006, 258, 221-230.*

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 [1]

Catalysts



vanadium-containing bulk

monolayer catalysts

metal-free nanostructured carbon

- 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

[1] P. Kube, B. Frank, S. Wrabetz, J. Kröhnert, M. Hävecker, J. Valasco-Vélez, J. Noack, R. Schlögl, A. Trunschke, ChemCatChem 9 (2017) 1-14.

Catalytic Performance

- Bulk MoVTeNb oxide, 6V/SBA-15 and P/oCNT have been compared in the ODH of C_2H_6 and C_3H_8 under identical conditions. [1]

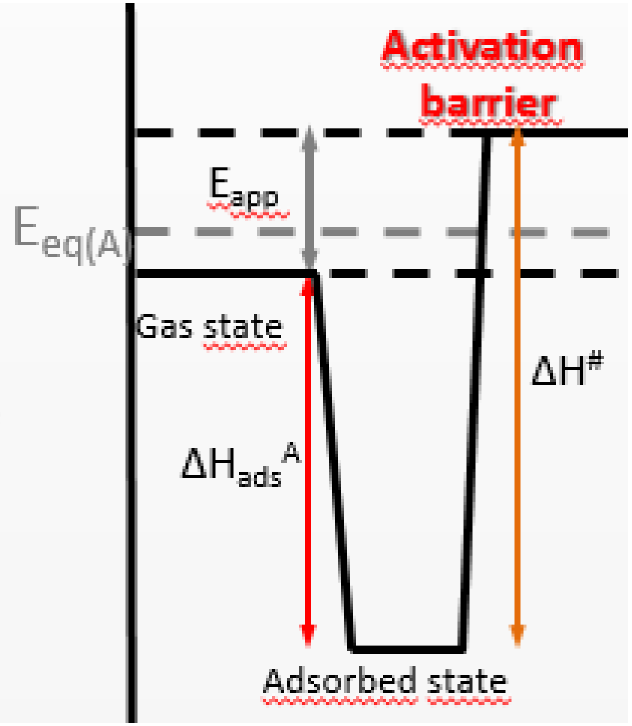
Similarities and Differences in the reaction network

Strong temperature dependence → **different transition states**

$E_{app.}$

Microcalorimetry
C_2H_6 C_2H_4 C_3H_8 C_3H_6
at 40° C

$\Delta H_{ads.}$



enthalpy of formation of the transition state

Note: $\Delta H_{ads.} \neq T_{ads.}$ [2]; *ads. in quasi-equilibrium* [3]; *intermediates occure in pseudo-steady-state*

---

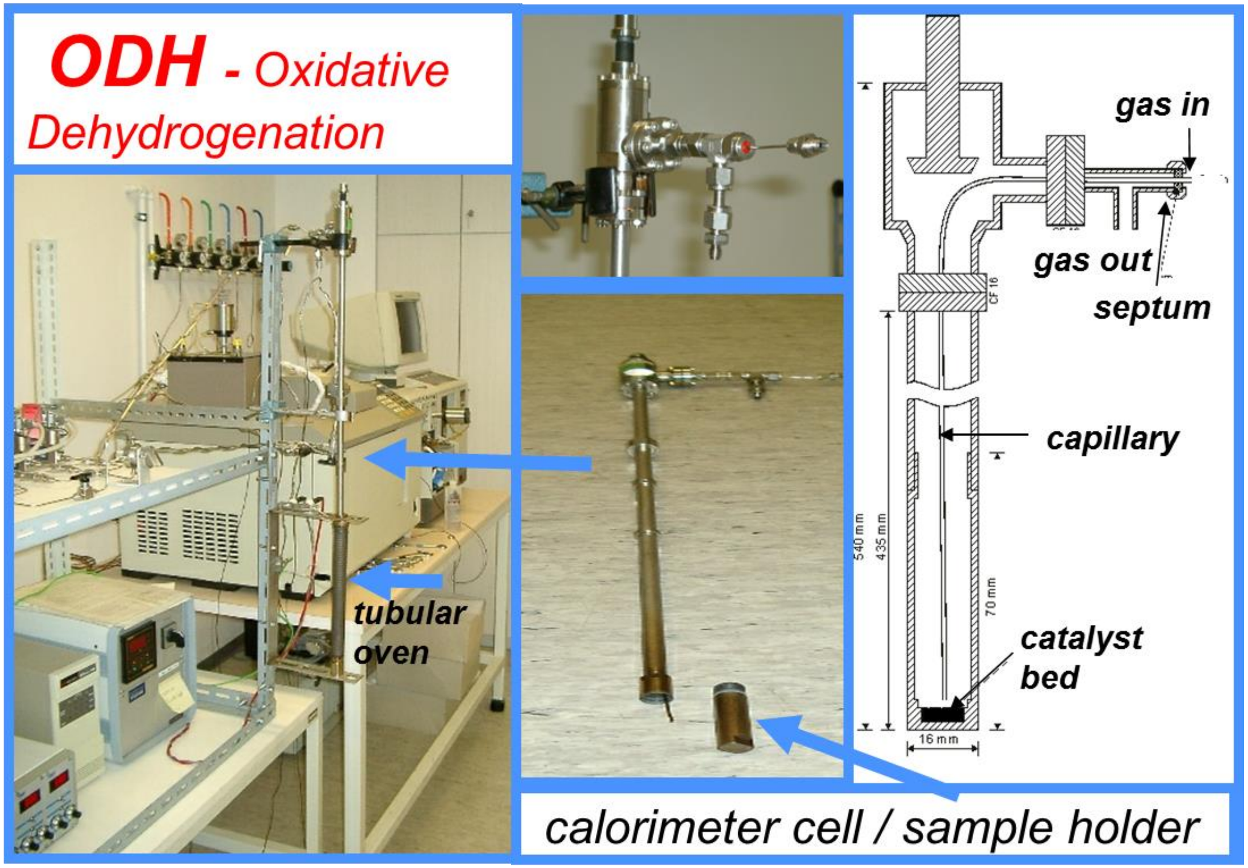
[1] P. Kube, B. Frank, S. Wrabetz, J. Kröhnert, M. Hävecker, J. Valasco-Vélez, J. Noack, R. Schlögl, A. Trunschke, ChemCatChem 9 (2017) 1-14.

[2] a) D. C. Tranca, N. Hansen,J.A.Swisher, B. Smit, F. J. Keil, J. Phys. Chem. C 2012, 116,23408 –23417; b) E.J.Maginn, A. T. Bell, D. N. Theodorou, J. Phys. Chem. 1995, 99,2057 –2079.

[3] K. Chen, A. T. Bell, E. Iglesia, J. Phys. Chem. B 2000, 104, 1292–1299

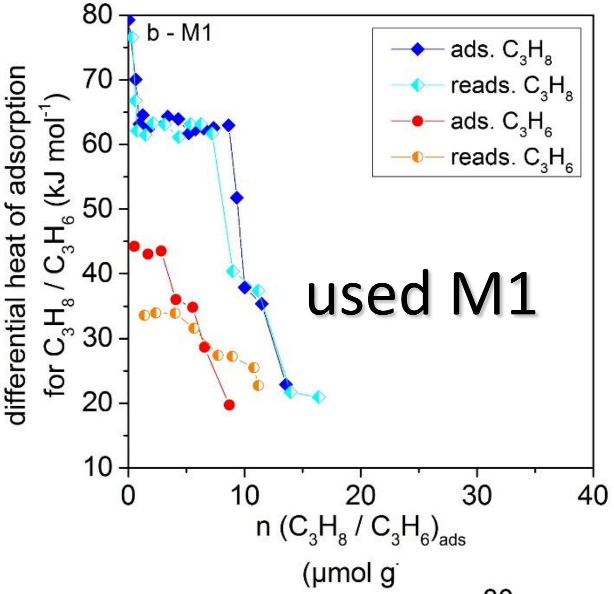
Creation of an active catalyst surface

- Feed of 10% hydrocarbon (C_3H_8 or C_2H_6) and 5% oxygen in helium with a total flow rate of 20 $mLmin^{-1}$.
- $T_{reaction}$ = 400°C for 6V/SBA-15, 360°C for P/oCNT and 350°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.

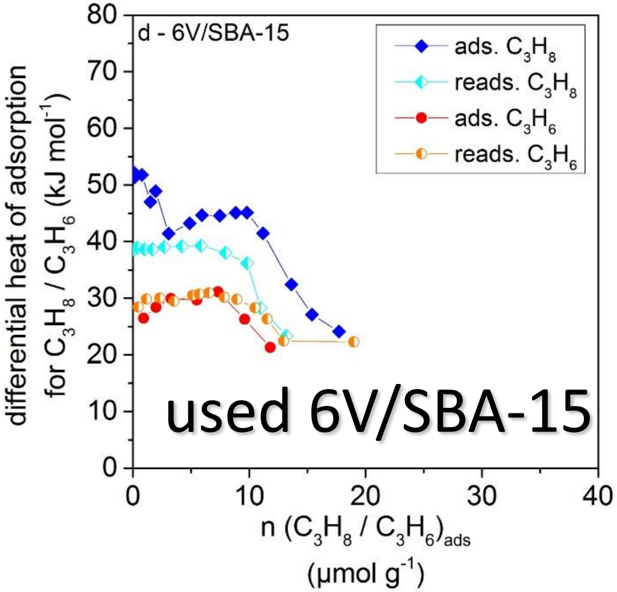


B. Frank, S. Wrabetz, O.V. Khavryuchenko, R. Blume, A. Trunschke, R. Schlögl, ChemPhysChem 12 (2011) 2709

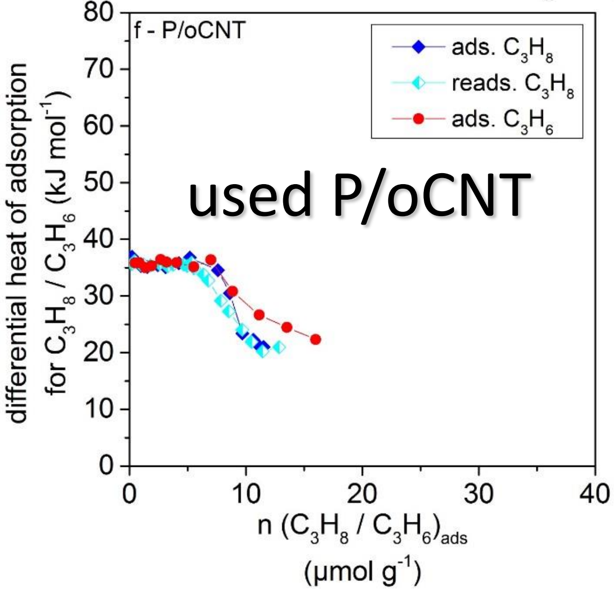
Adsorption Experiments
C_3H_8 & C_3H_6 Adsorption at 40°C



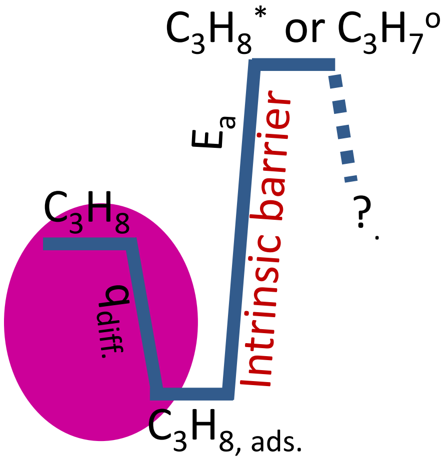
used M1



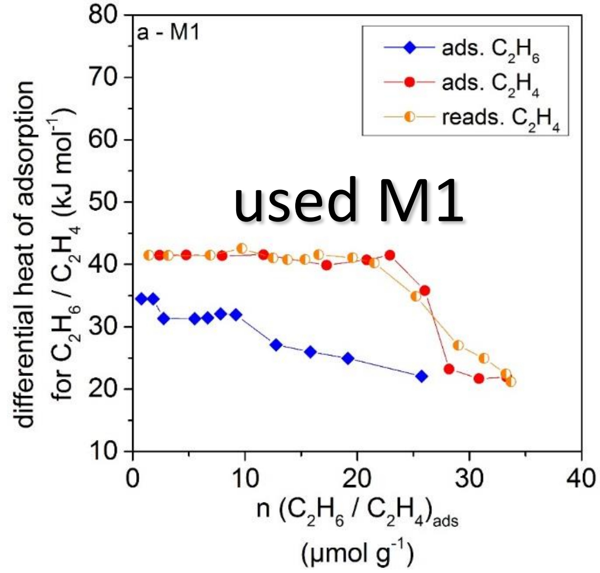
used 6V/SBA-15



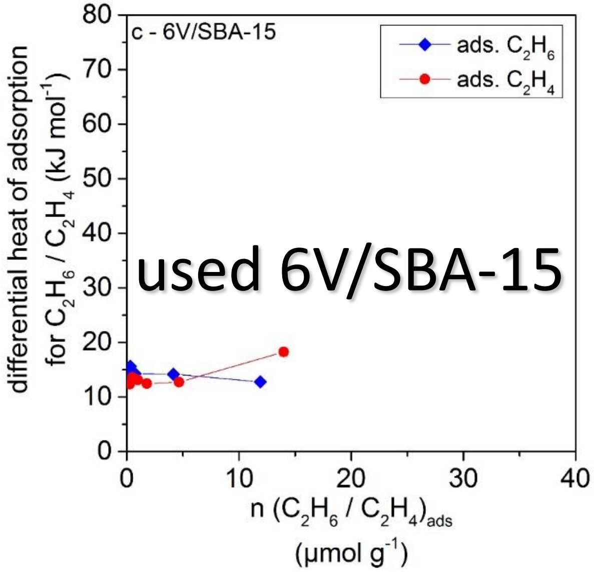
used P/oCNT



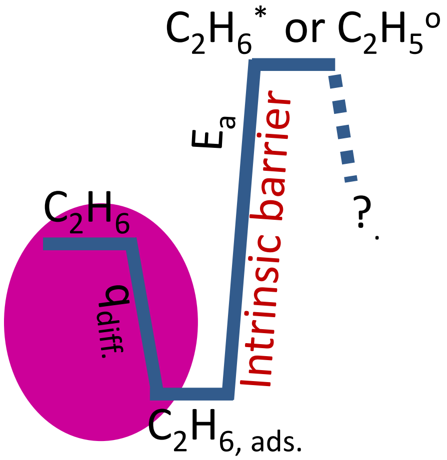
Adsorption Experiments
C_2H_6 & C_2H_4 Adsorption at 40°C

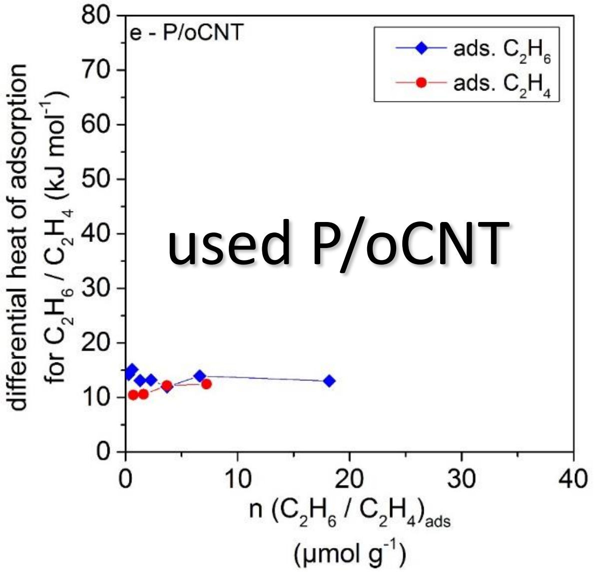


used M1



used 6V/SBA-15





used P/oCNT

Data Discussion

	M1	6V/SBA-15	P/oCNT
S_{BET} m^2g^{-1}	10.6	355	229
$V_{surf.}$; $O_{surf.}$	30	1113	1063
Γ_V atoms nm^{-2}	1.7	1.9	2.8
Γ_{C3H8} molecules nm^{-2}	0.44 (63 kJ/mol)	0.0014 (52 kJ/mol) 0.0114 (44 kJ/mol)	0.013 (36 kJ/mol)
$V_{surf.}/C_3H_6$ ads.	~4	~150	
$r_{C3H8,consumtion,0}$ $mmolg^{-1}h^{-1}$	5.3 ±0.2	0.45 ±0.006	0.21 ±0.004
$r_{C2H6,consumtion,0}$ $mmolg^{-1}h^{-1}$	5.4 ±0.2	0.055 ±0.001	0.03 ±0.001
q_{diff} (C_3H_8)	79 / 63 rev. ads.	52 / 44 irrev. ads.	36 rev. ads.
q_{diff} (C_3H_6)	44 irrev. ads.	30 rev. ads.	36 rev. ads.
q_{diff} (C_2H_6)	34 rev. ads.	14 *	14 *
q_{diff} (C_2H_4)	41 rev. ads.	14 *	14 *
$E_{a, propane}$	80 ±3	110 ±2	103 ±7
$E_{a, ethane}$	90 ±2	121±2	110 ±7
intrinsic barrier for **propane** activation	143 (63 kJ/mol)	162 154	139
intrinsic barrier for **ethane** activation	124		

q_{diff} - Differential heat of adsorption of hydrocarbons (kJ mol^{-1})

$V_{surf.}$, $O_{surf.}$: Surface concentration of V (M1 and 6V/SBA-15) and O (P/oCNT) atoms (µmol g^{-1})

Γ_{C3H8} - Density of adsorbed propane (molecules nm^{-2})

Γ_V - Surface density of V or O (atoms nm^{-2})

E_a: propane/ethane consumption,0 (kJ/mol); initial rate

* Differential heat near the condensation enthalpy of reaction molecules at 40°C

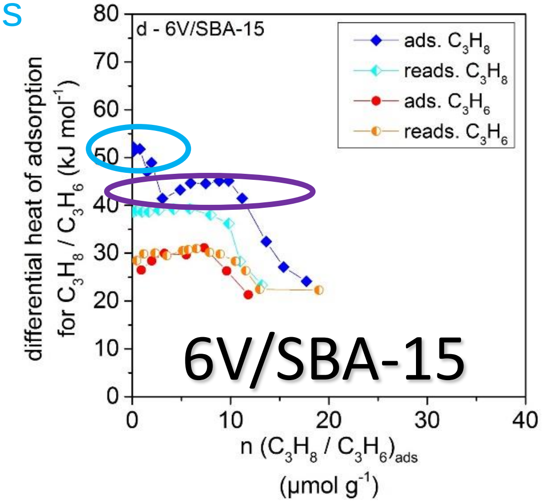
intrinsic barrier= E_a+q_{diff} (kJ mol^{-1})

6V/SBA-15:

- Γ_{C3H8} = 0.0014 molecules nm^{-2}
- intrinsic barrier for C_3H_8 activation = 162 kJ/mol
- DFT calculations by Rozanska [2] = 160 kJ/mol due to monomeric species

→ **~0.1%** of all V atoms.

~ 1%



- intrinsic barrier for C_3H_8 activation = 154 kJ/mol
- DFT calculations by Rozanska [2] = 148 kJ/mol due to silica-supported vanadium oxide dimers

→ ~ **0.6%** of all V atoms

---

1 Hävecker, M.; Wrabetz, S.; Kröhnert, J.; Csepei, L.-I.; Naumann d'Alnoncourt, R.; Kolen'ko, Y. V.; Girgsdies, F.; Schlögl, R.; Trunschke, A. *Journal of Catalysis* 2012, 285, 48.

2 X. Rozanska, R. Fortrie, J. Sauer, *J. Am. Chem. Soc.* 2014, 136, 7751 –776.

3 P. Concepcjìn, P. Botella, J. M. L. Nieto, *Appl. Catal. A* 2004, 278, 45–56; f) R. Coast, M. Pikus, P. N. Henriksen, G. A. Nitowski, *J. Phys. Chem.* 1996, 100, 15011–15014.

Conclusion

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

V_xO_y	***Microcalorimetry*** Intrinsic barrier for C_3H_8 activation *kJ/mol*	***Density functional theorie DFT*** [1] Energy barriers *kJ/mol*	***Microcalorimetry*** % of the total amount of $V_{surf.}$
Monomer (a)	162	160	0.1
Dimer (b)	154	148	0.6
trimer		143	
tetramer	143	139	

~ 1%

ODH of propane over M1 phase: tetramers of vanadium oxide species have been postulated to be the required ensemble size [2]

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

[1] X. Rozanska, R. Fortrie, J. Sauer, J. Am. Chem. Soc. 2014, 136, 7751 –776.

[2] *R. Schlögl, Top. Catal. 2011, 54, 627–638.*

Conclusion

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V_xO_y	*Microcalorimetry* Intrinsic barrier for C_3H_8 activation *kJ/mol*	*Density functional theorie DFT* [1] Energy barriers *kJ/mol*	*I*
Monomer (a)	162	160	
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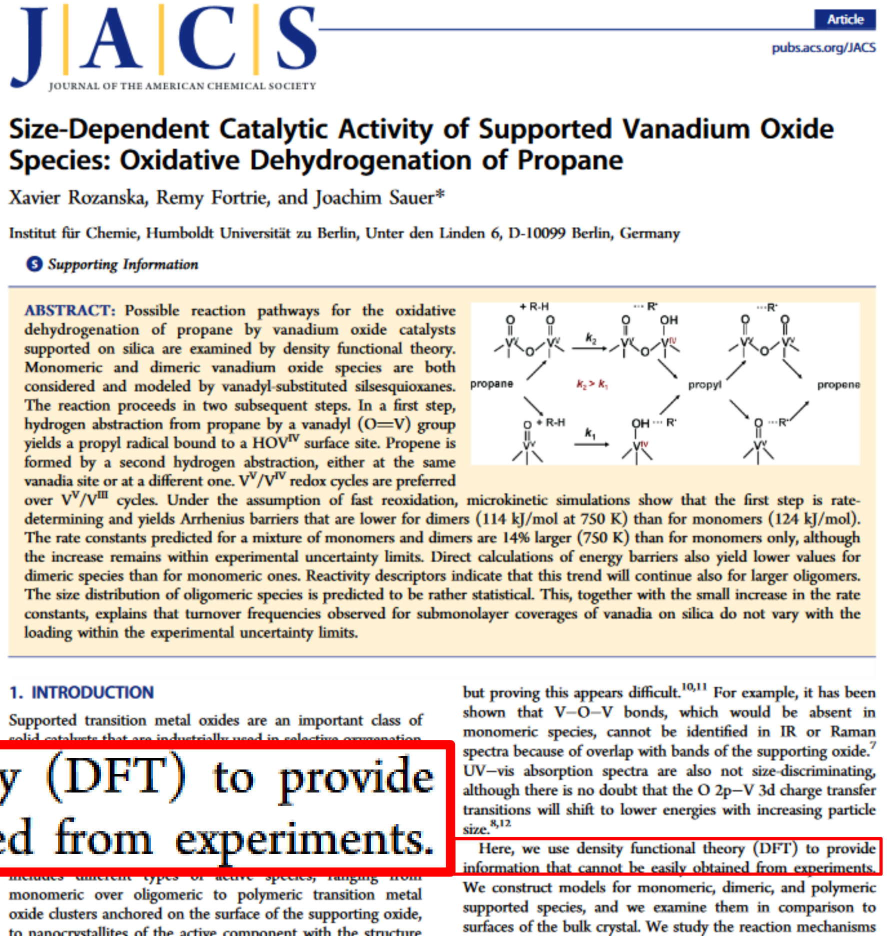

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Size-Dependent Catalytic Activity of Supported Vanadium Oxide Species: Oxidative Dehydrogenation of Propane

Xavier Rozanska, Remy Fortrie, and Joachim Sauer*

Institut für Chemie, Humboldt Universität zu Berlin, Unter den Linden 6, D-10099 Berlin, Germany

Supporting Information

ABSTRACT: Possible reaction pathways for the oxidative dehydrogenation of propane by vanadium oxide catalysts supported on silica are examined by density functional theory. Monomeric and dimeric vanadium oxide species are both considered and modeled by vanadyl-substituted silsesquioxanes. The reaction proceeds in two subsequent steps. In a first step, hydrogen abstraction from propane by a vanadyl (O=V) group yields a propyl radical bound to a HOV^{IV} surface site. Propene is formed by a second hydrogen abstraction, either at the same vanadia site or at a different one. V^V/V^{IV} redox cycles are preferred over V^V/V^{III} cycles. Under the assumption of fast reoxidation, microkinetic simulations show that the first step is rate-determining and yields Arrhenius barriers that are lower for dimers (114 kJ/mol at 750 K) than for monomers (124 kJ/mol). The rate constants predicted for a mixture of monomers and dimers are 14% larger (750 K) than for monomers only, although the increase remains within experimental uncertainty limits. Direct calculations of energy barriers also yield lower values for dimeric species than for monomeric ones. Reactivity descriptors indicate that this trend will continue also for larger oligomers. The size distribution of oligomeric species is predicted to be rather statistical. This, together with the small increase in the rate constants, explains that turnover frequencies observed for submonolayer coverages of vanadia on silica do not vary with the loading within the experimental uncertainty limits.

1. INTRODUCTION

Supported transition metal oxides are an important class of solid catalysts that are industrially used in selective oxygenation

includes different types of active species, ranging from monomeric over oligomeric to polymeric transition metal oxide clusters anchored on the surface of the supporting oxide, to nanocrystallites of the active component with the structure

but proving this appears difficult.[10,11] For example, it has been shown that V–O–V bonds, which would be absent in monomeric species, cannot be identified in IR or Raman spectra because of overlap with bands of the supporting oxide.[7] UV–vis absorption spectra are also not size-discriminating, although there is no doubt that the O 2p–V 3d charge transfer transitions will shift to lower energies with increasing particle size.[8,12]

Here, we use density functional theory (DFT) to provide information that cannot be easily obtained from experiments. We construct models for monomeric, dimeric, and polymeric supported species, and we examine them in comparison to surfaces of the bulk crystal. We study the reaction mechanisms

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

[1] X. Rozanska, R. Fortrie, J. Sauer, J. Am. Chem. Soc. 2014, 136, 7751 –776.

[2] *R. Schlögl, Top. Catal. 2011, 54, 627–638.*

Limitations of method:

Propane ads. on vanadium-phosphorus-oxide / VPO
at $T_{reaction}$ = 100 - 400°C

vanadium-phosphorus-oxide - VPO

Natural gas as raw material

Methane
Ethane
Propane
Butane

$\xrightarrow{+\ O_2 \quad \mathrm{VPO}}$

OCM
Oxidative Dehydrogenation
Selective Catalytic Oxidation

Olefines, Oxygenates

Ethane, Ethylene
Ethylene,Acetic acid
Propylene,Acrylic acid
Butylenes, Butadiene,
Maleic anhydride

Intention: Determination of kinetic data: N_o, K and ΔH_{ads} of alkanes on VPO at $T_{reaction}$

Adsorption Microcalorimetry :

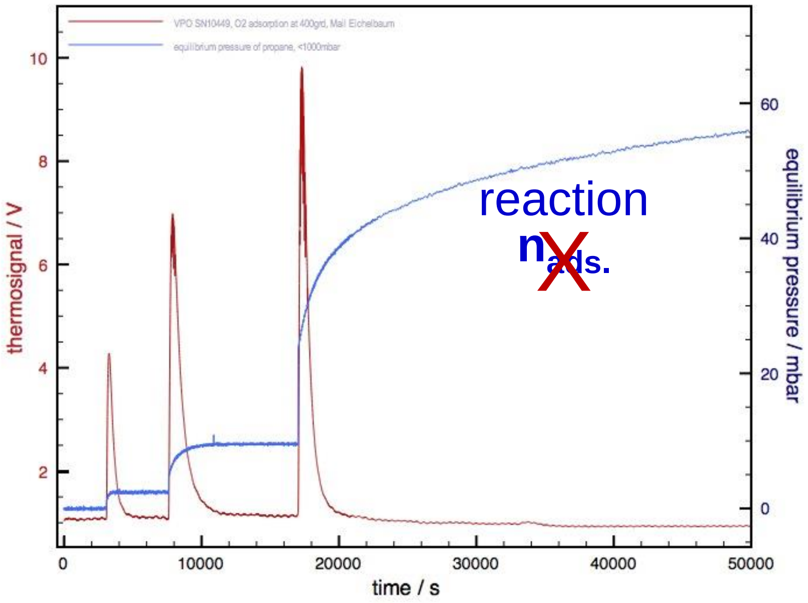
★ propane, ethane and n-butane as probe molecule
★ $T_{adsorption}$ = 400, 300, 200,100 and 40°C
★ selected catalyst: VPO #10449

vanadium-phosphorus-oxide - VPO

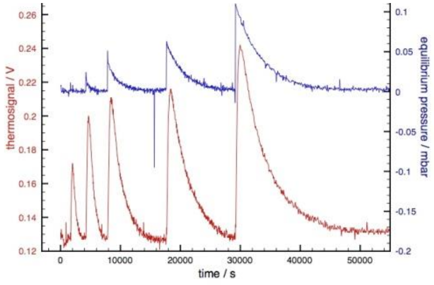
The temporal evolution of the thermo signal during propane ads. at 400°C

Catalyst was oxidized at 400°C for 2h

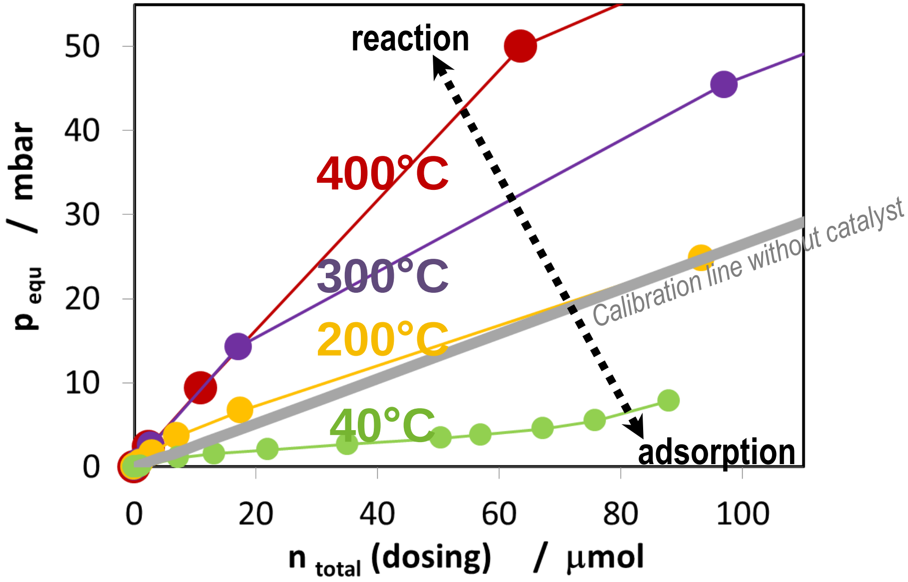
Integral heat / pressure

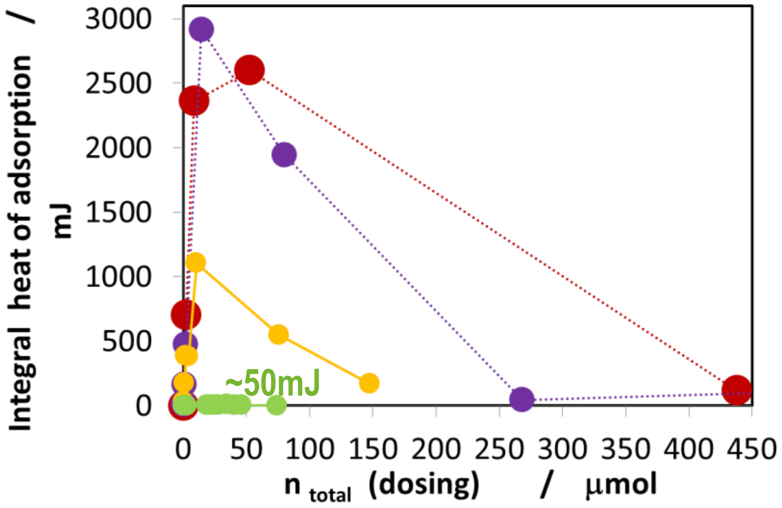


Classical pressure profile



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

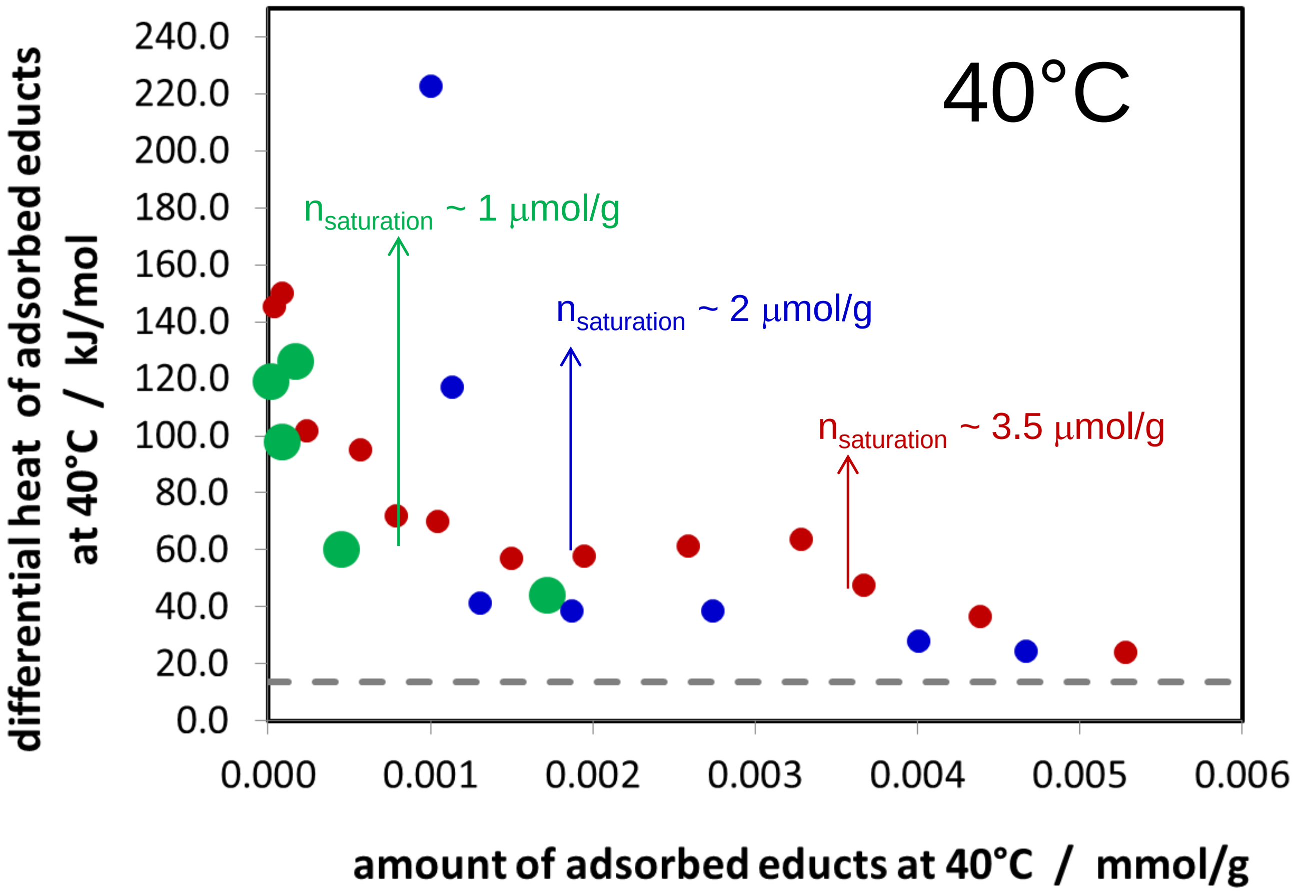




vanadium-phosphorus-oxide - VPO

Differential heat of propane / ethane / n-butane

Catalyst was oxidized at 400°C for 2h



Validation

in situ DSC and Microcalorimetry

C_2H_4 adsorption at 40°C on Ag catalyst ethylene epoxidation

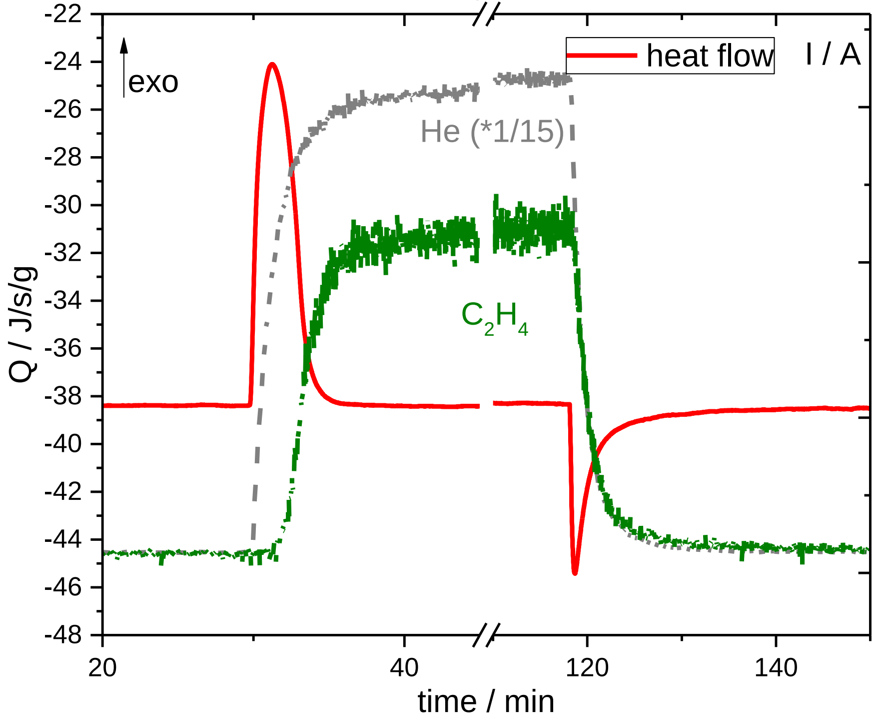
Case study: Validation, C_2H_4 adsorption on Ag catalyst

5%Ag/SiO2, Max Lamoth

In-situ DSC

30°C, total flow 30mlm, Ptotal 1,15bar

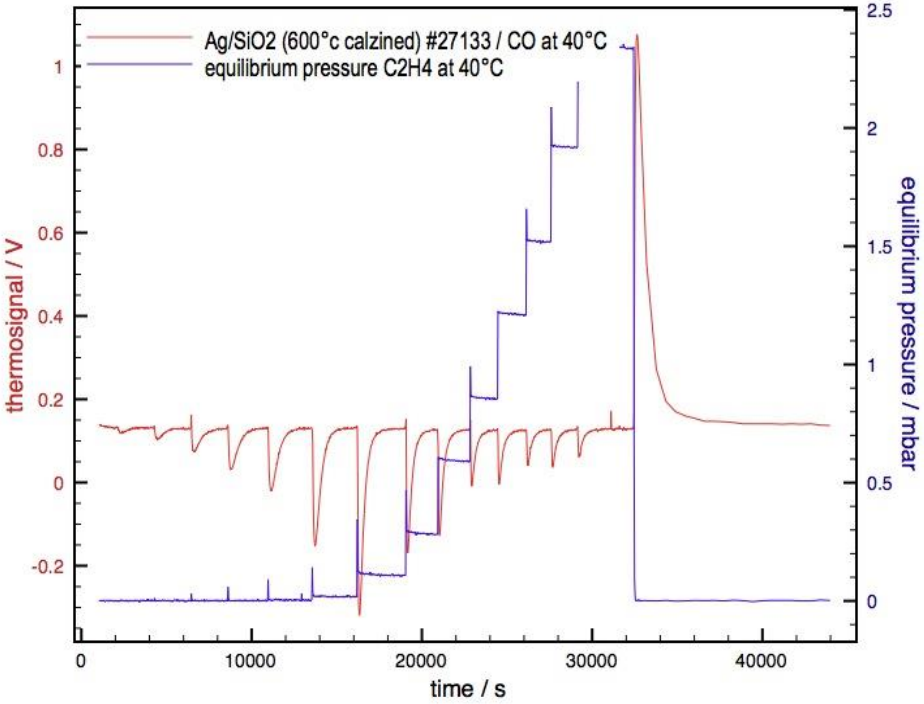
12 hours SynAir 300°C



Microcalo

40°C, Prange 0-3mbar

3 hours SynAir 300°C



ΔH_{ads}=-94kJ/mol(C_2H_4)

N(C_2H_4)=26µmol/g(cat)

reversible

ΔH_{ads}=-87-33kJ/mol(C_2H_4)

N(C_2H_4)=33µmol/g(cat)

reversible

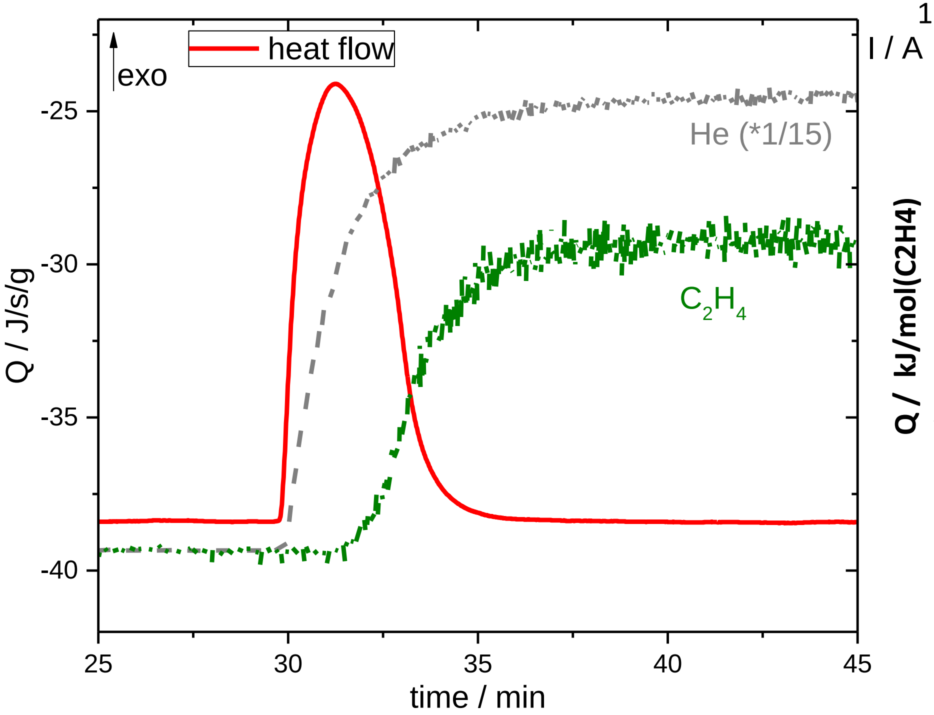
Case study: Validation, C_2H_4 adsorption on Ag catalyst

5%Ag/SiO2, Max Lamoth

In-situ DSC

30°C, total flow 30mlm, P_{total} 1.15bar, P_{C2H4}0.6mbar

12 hours SynAir 300°C



ΔH_{ads}=-94kJ/mol(C_2H_4)

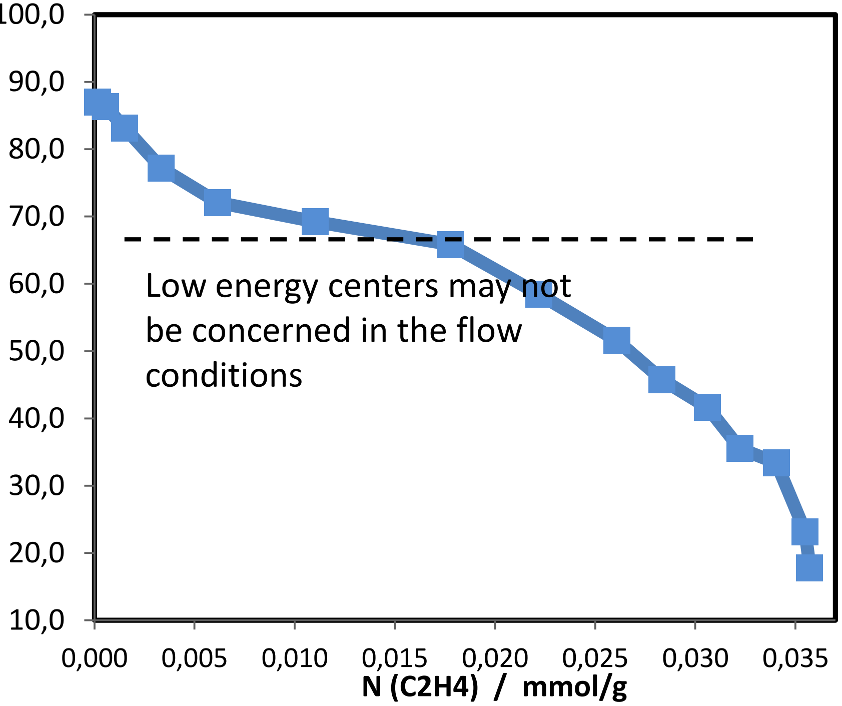
N(C_2H_4)=26µmol/g(cat)

reversibile

Microcalo

40°C, Prange 0-3mbar

3 hours SynAir 300°C



Low energy centers may not be concerned in the flow conditions

ΔH_{ads}=-87-33kJ/mol(C_2H_4)

N(C_2H_4)=33µmol/g(cat)

reversibile

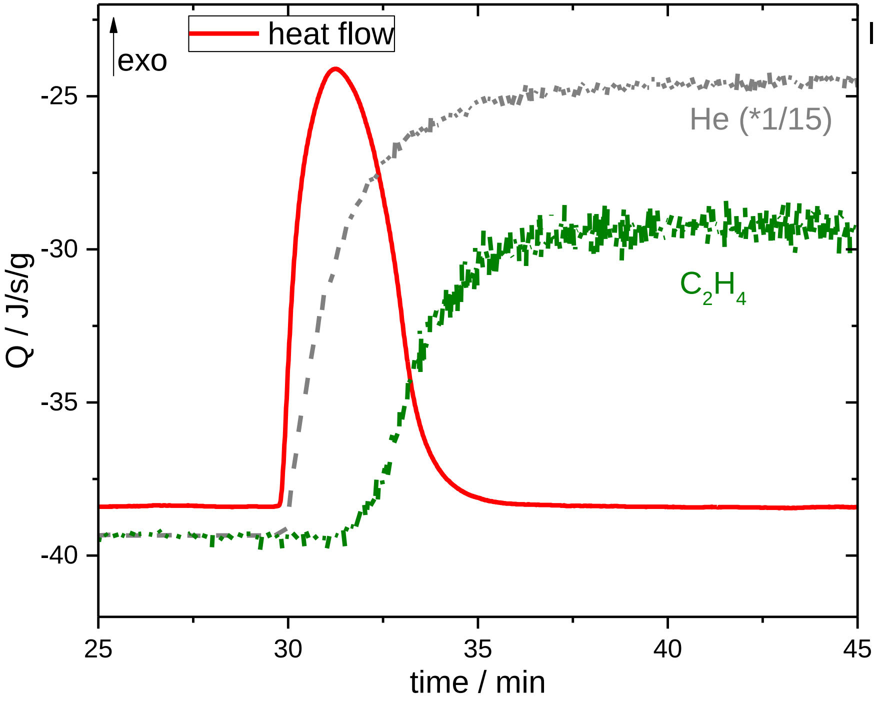
Case study: Validation, C_2H_4 adsorption on Ag catalyst

5%Ag/SiO2, Max Lamoth

In-situ DSC

30°C, total flow 30mlm, P_{total} 1.15bar, P_{C2H4}0.6mbar

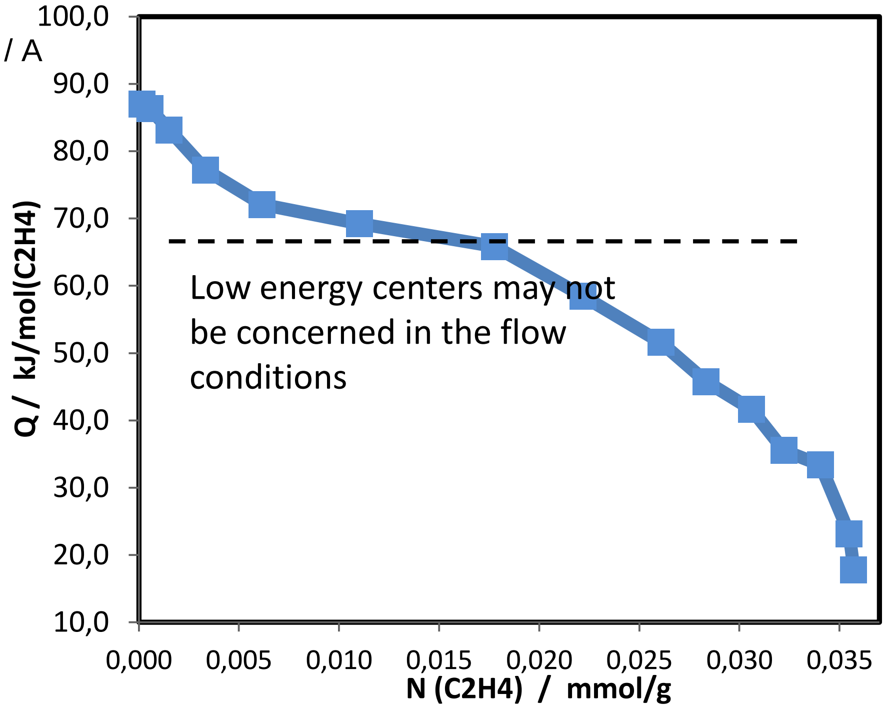
12 hours SynAir 300°C



Microcalo

40°C, Prange 0-3mbar

3 hours SynAir 300°C



Low energy centers may not be concerned in the flow conditions

Desorption and readsorption are occurring simultaneously with diffusion

In UHV systems diffusion takes part in a very limited extent, while readsorption can be avoided using sufficiently high pumping speed

FINAL

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 inmersion, 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 thechniques

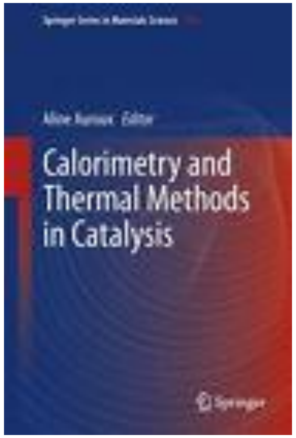
Determination of kinetic data: N_{ads}, K_{ads}, ΔH_{ads} , $SSA_{m2/g}$

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



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Thank you for your attention

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