Adsorption phenomena in oxidation catalysis studied by microcalorimetry

S. Wrabetz, R. Arrigo, B. Frank, D. Teschner,

A. Trunschke and R. Schlögl

Fritz-Haber-Institute of the Max Planck Society

Department of Inorganic Chemistry, 14195 Berlin, Germany,

wrabetz@fhi-berlin.mpg.de

7th World Congress on Oxidation Catalysis – June 9 - 12, 2013

Introduction

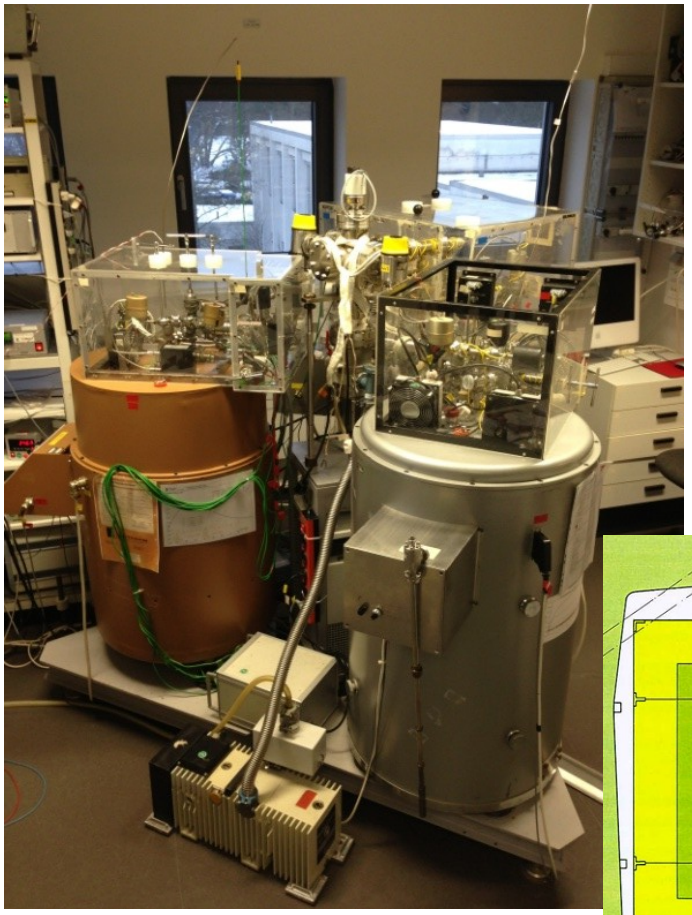
- adsorption phenomena play an important role in oxidation catalysis
- adsorption steps, surface reaction processes, and desorption steps
- The knowledge about e.g. heat of adsorption of reactant on the surface can contribute to a better understanding of the complex microkinetics.
- since perhaps only a minor fraction of all surface atoms form active centers

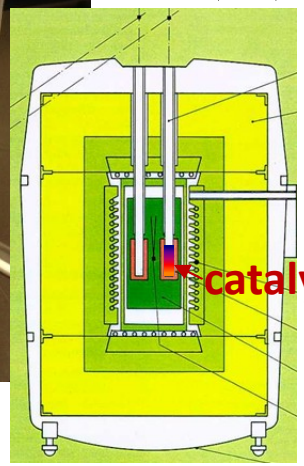
Adsorption Isothermal Microcalorimetry

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

Equipment

Micro-calorimeters

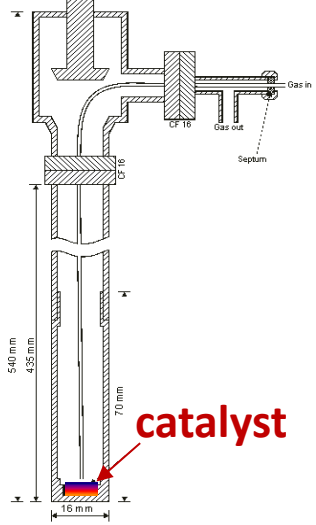




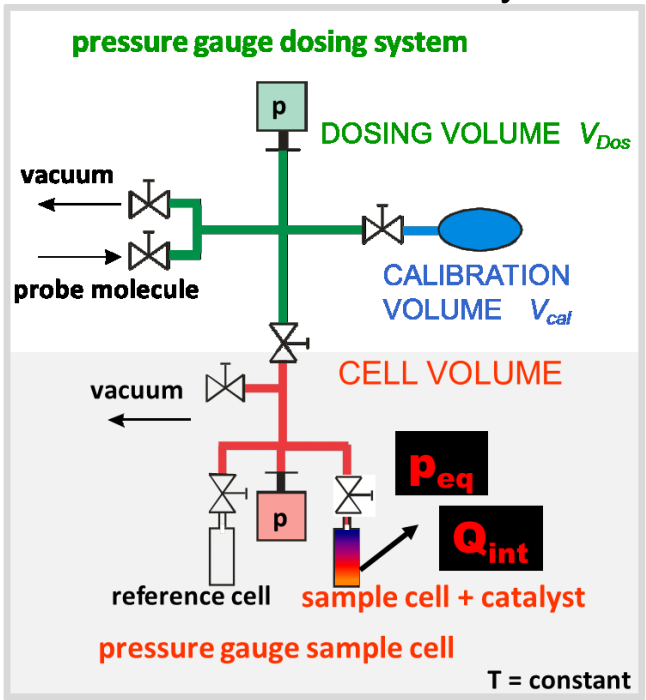
HT1000 (rt-1000 C) and **MS 70** (rt-100 C) Tian-Calvet calorimeter of SETARAM combined with a custom-designed high vacuum and gas dosing apparatus.

Karge, H.G. etal., J. Phys. Chem. 98, 1994, 8053.

Sample Cell



Volumetric-Barometric System



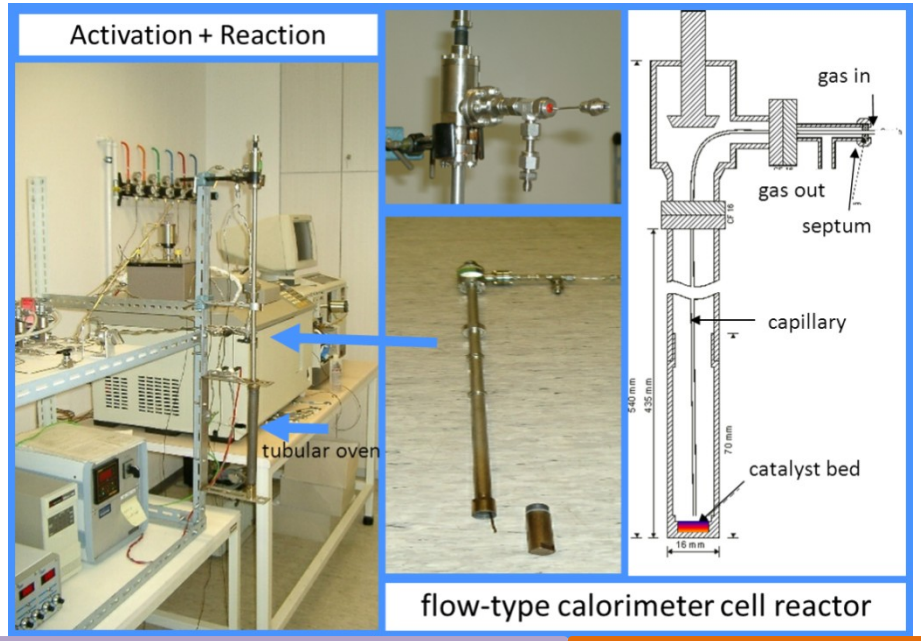
$$\Sigma\ n_{ads}\ vs\ p_{eq}\ ,\ mmol\,*g^{-1}\ \ mmol*m^{-2}$$

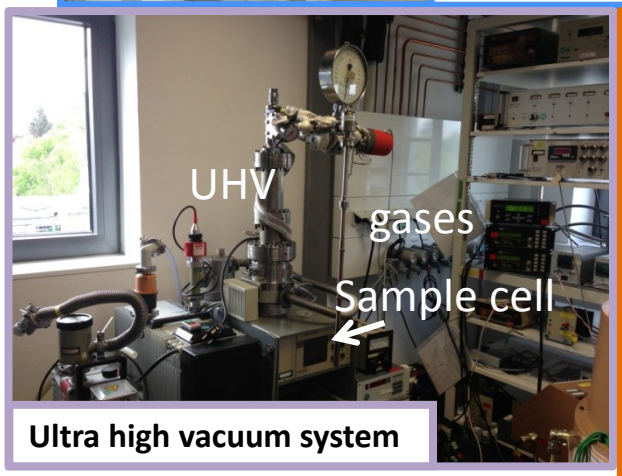
$$q_{diff} = \frac{Q_{int}}{n_{ads}} = \Delta\ H_{ads}\ ,\ kJ/mol$$

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

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

Experimental procedure





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

Transfer
of the sample cell into the calorimeter and degassing/equilibration at $T_{ads.}$

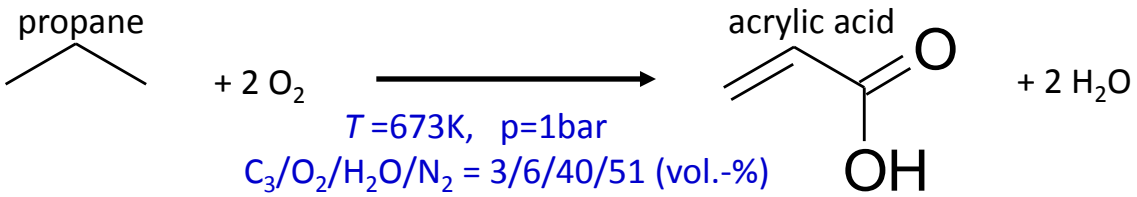
Adsorptive microcalorimetric experiment:
Stepwise adsorption, desorption and re-adsorption of the selected probe molecule at the selected temperature.

Selected Applications

Adsorption microcalorimetry is broadly employed in several projects of our department.

1. Selective oxidation of propane to acrylic acid over pure-phase MoVTeNb oxide catalyst - M1 catalyst.
2. Oxidative dehydrogenation over oxygen functionalized carbon nanotube - oCNT
3. Oxidation of HCl to Cl_2 over bare and supported CeO_2
4. Oxidation of alcohol over vanadium supported Al_2O_3

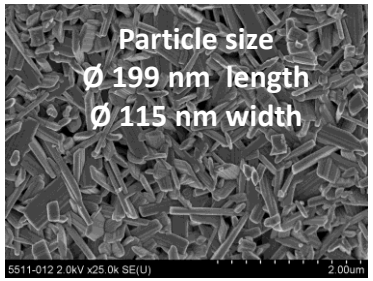
Selective oxidation of propane to acrylic acid [1,2]

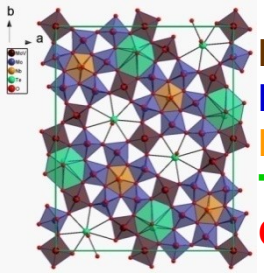


T =673K, p=1bar

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

Catalyst: **Highly crystalline MoVTeNb oxide catalyst**





MoV
Mo
Nb
Te
O

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

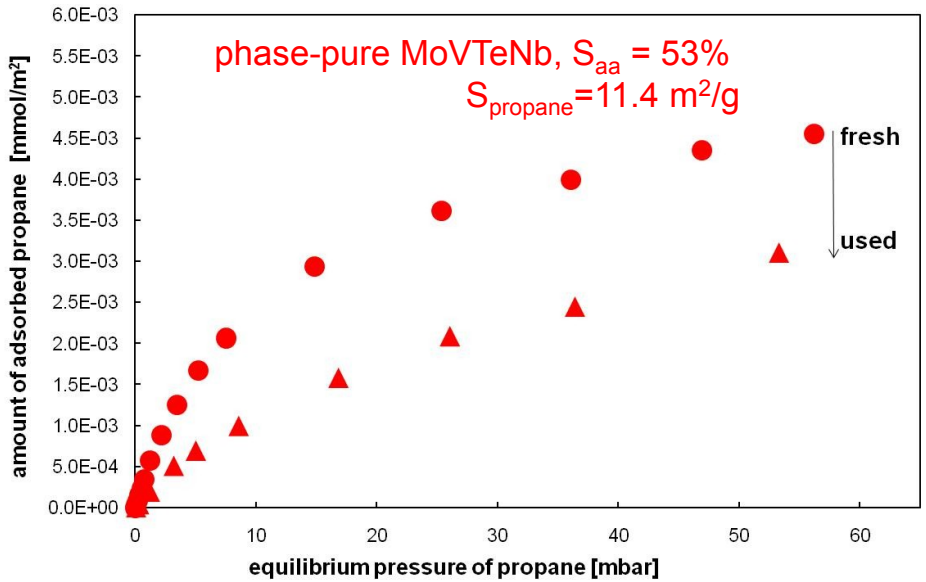
Adsorption Microcalorimetry :

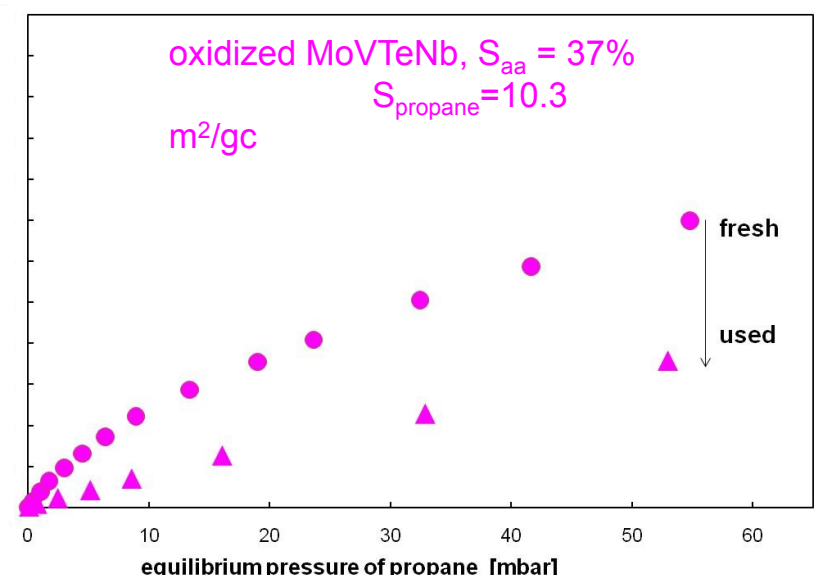
- ★ propane as probe molecule
- ★ $T_{adsorption}$=313K < 673 K=$T_{reaction}$
- ★ selected catalysts: different selective catalysts

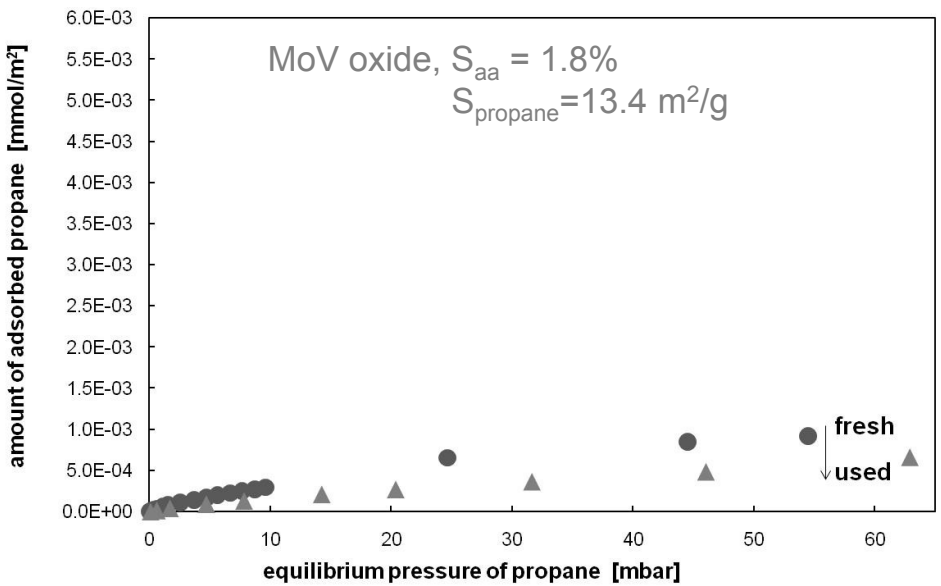
	pure-phase MoVTeNb	**S_{aa} = 53%**
modified	**MoVTeNb by an oxidizing agent**	**S_{aa} = 37%**
	MoV oxide	**S_{aa} = 1.8 %**

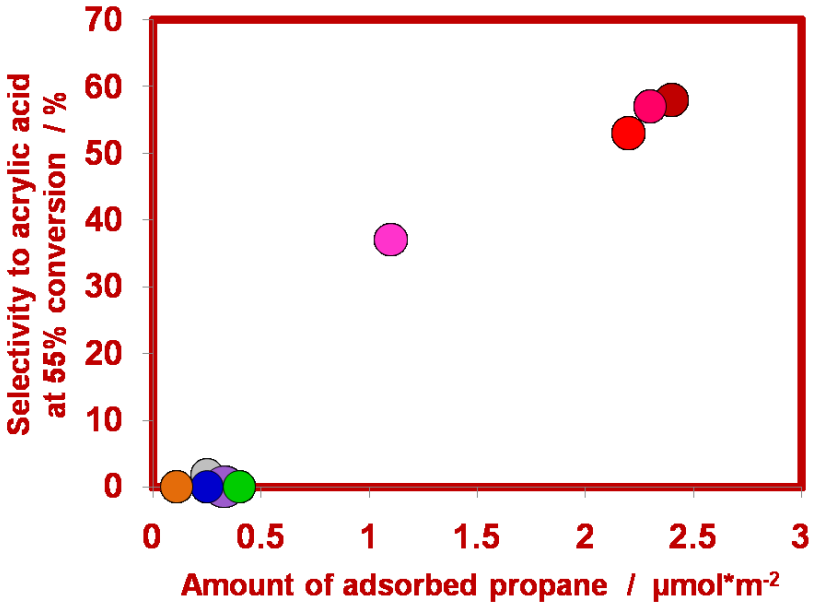
[1] Botella, P., et al., The preparation, characterization, and catalytic behavior of MoVTeNbO catalysts prepared by hydrothermal synthesis. Journal of Catalysis, 2002. 209(2): p. 445-455.
[2] Ueda, W., et al., Structural organization of catalytic functions in Mo-based oxides for propane selective oxidation. Catalysis Today, 2004. 96(4): p. 235-240.

Propane adsorption isotherms of different selective catalysts

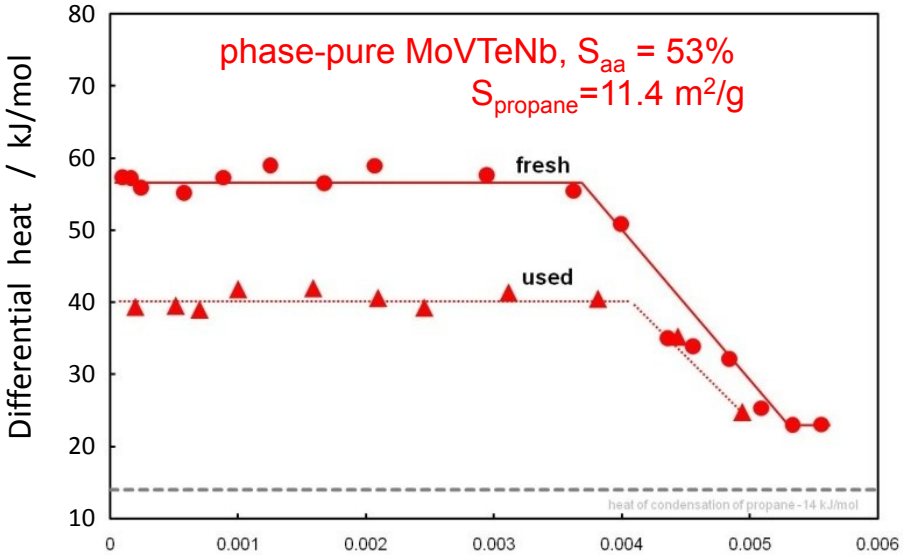


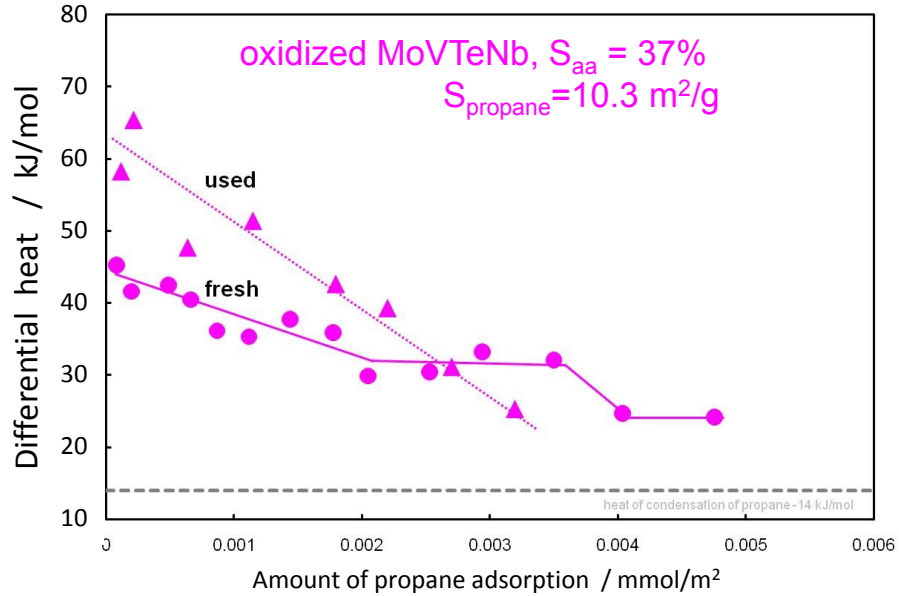


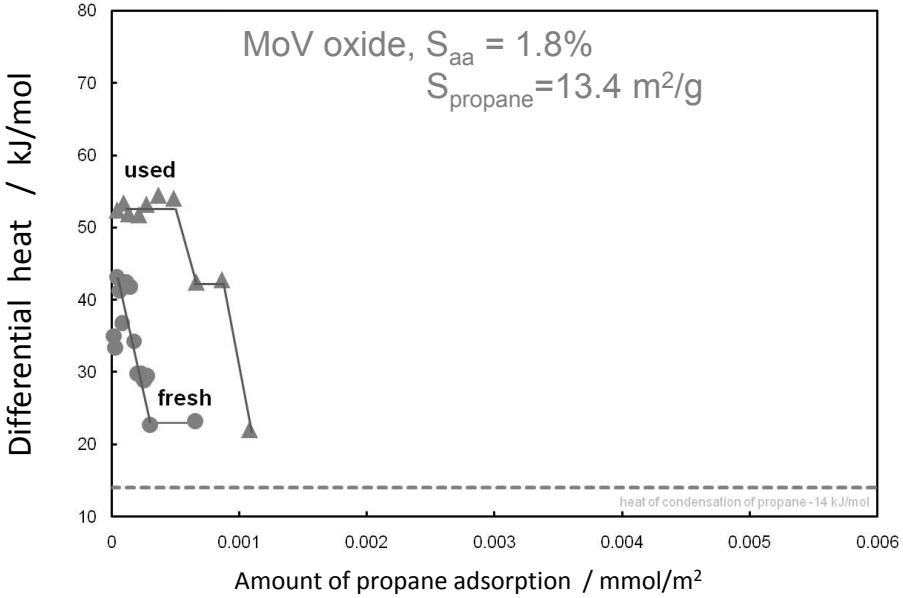




Differential heats of adsorbed propane of different selective catalysts







- 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.

Selected Applications

Adsorption microcalorimetry is broadly employed in several projects of our department.

1. Selective oxidation of propane to acrylic acid over pure-phase MoVTeNb oxide catalyst - M1 catalyst.

2. Oxidative dehydrogenation over oxygen functionalized carbon nanotube - oCNT

3. Oxidation of HCl to Cl_2 over bare and supported CeO_2

4. Oxidation of alcohol over vanadium supported Al_2O_3

Oxidative dehydrogenation of propane over carbon materials

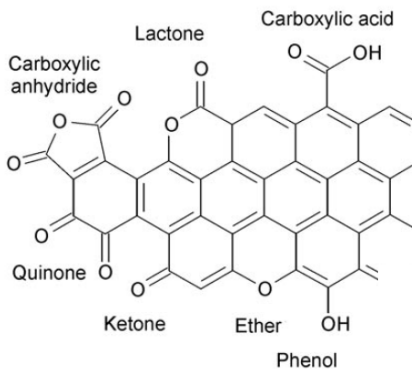
Intention: **To establish a mechanistic model for carbon-catalyzed ODH. Ads. properties (reversibility, heat of ads., number of ads. sites) are important input for kinetic modeling.**

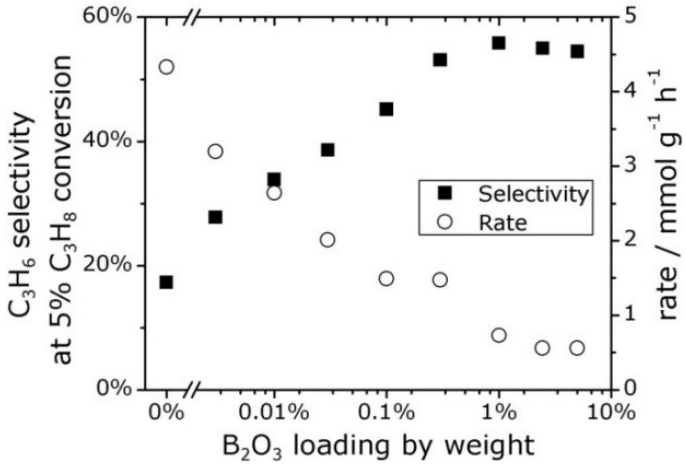
propane ⟶ propylene

400 C, $C_3H_8/O_2/He$ = 10/5/85, 50 ml min^{-1}

Catalyst: **oCNT** **5wt% B_2O_3 -oCNT**

to reach a sufficient self-oxidation stability





strong improvement of the alkene selectivity by surface modification using oxides of boron

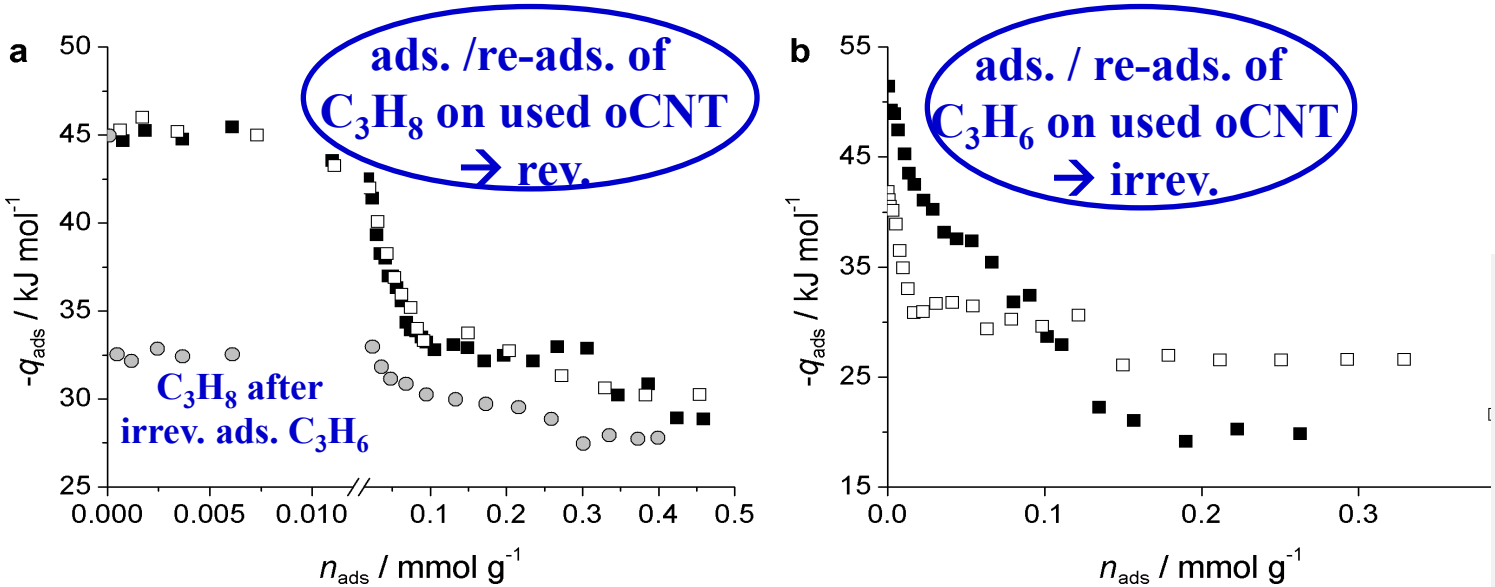
Adsorption ★ propane & propylene as probe molecule

Microcalorimetry : ★ $T_{adsorption}$=313K < 673K=$T_{reaction}$

★ selected catalysts: used oCNT used B_2O_3-oCNT

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

Oxidative dehydrogenation of propane over carbon materials



Graphite:
(free of oxygen)
33 – 22 kJ/mol
for propane and propylene ads.

Oxidative dehydrogenation of propane over carbon materials

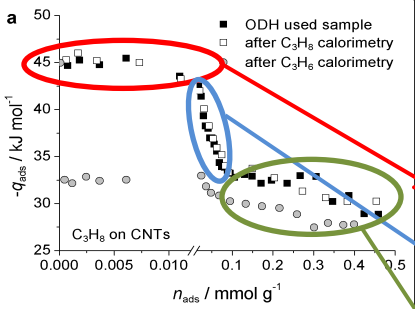
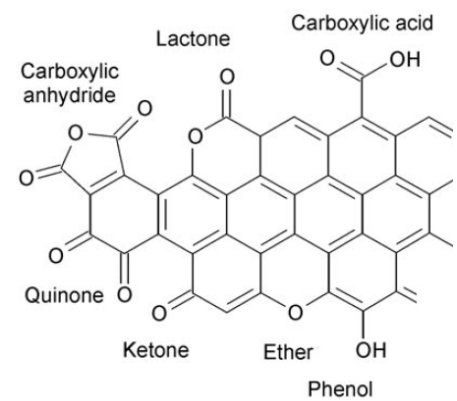


Table 1. Quantitative evaluation of calorimetric measurements of propane and propylene adsorption on CNT and B_2O_3-CNT catalysts (Figure 1).

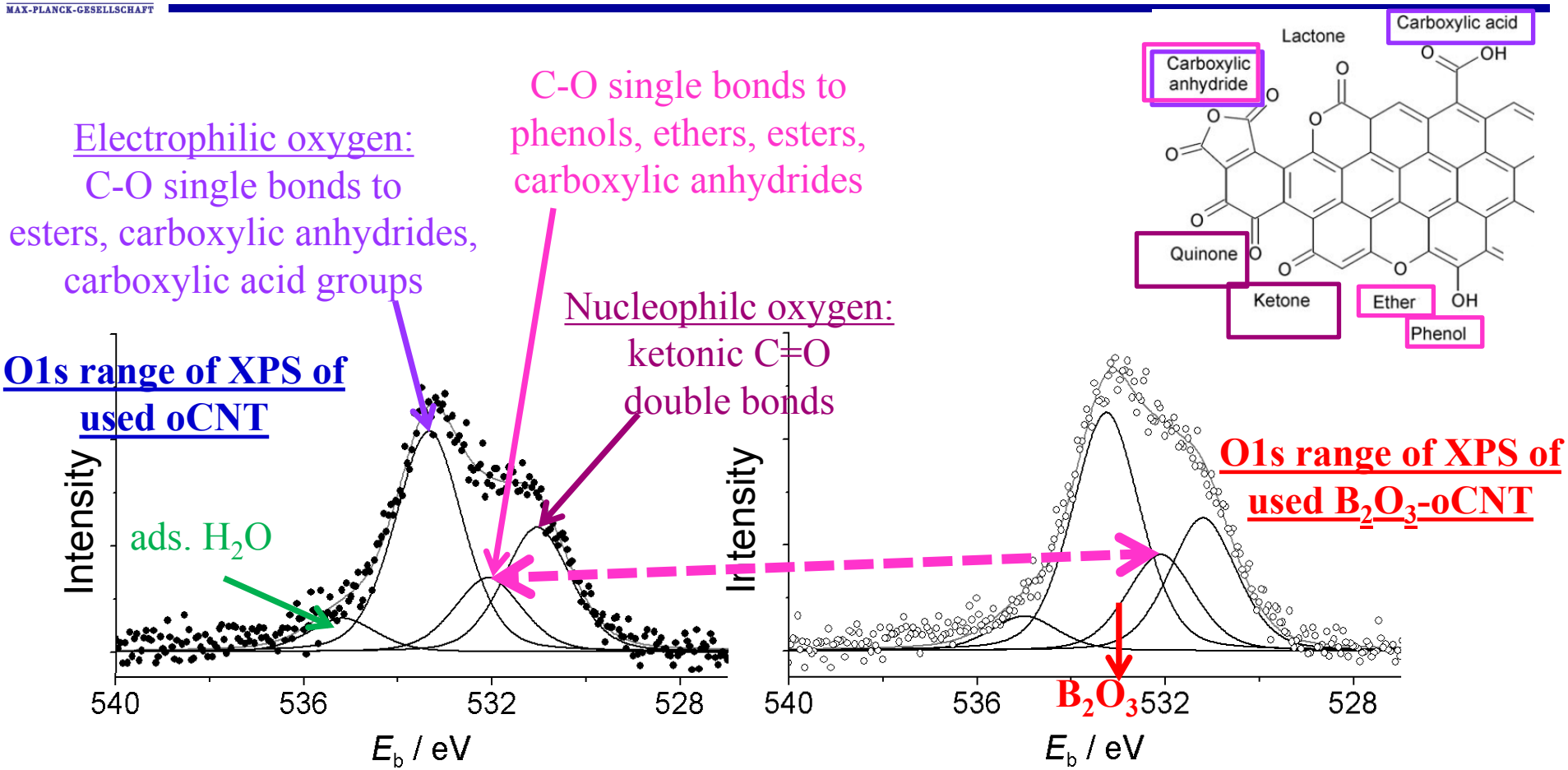
	Sample Adsorbent	CNTs C_3H_8	 C_3H_6	B_2O_3–CNTs C_3H_8	 C_3H_6
High-Energy Plateau	$-q_{ini}$ (kJ mol^{-1})	45	51	40	45
	n_{ads} (μmol m^{-2})	0–0.015	–	0–0.016	–
	$-q_{ads}$ (kJ mol^{-1})	45 ± 0.5	–	39 ± 1	–
Steady-Decay Range	n_{ads} (μmol m^{-2})	0.015–0.18	0–0.27	0.016–0.24	0–0.32
	$-q_{ads}$ (kJ mol^{-1})	45–33	51–20	39–30	45–27
Low-Energy Plateau	n_{ads} (μmol m^{-2})[a]	–	–	–	–
	q_{ads} (kJ mol^{-1})[b]	33 ± 0.5	20 ± 1	28 ± 2	26 ± 1

[a] Total number could not be determined, [b] Maximum differential adsorption heat.



- High energy sites can be assigned to oxygen surface groups, low energy sites to carbon surface (0001)
- 3-5% of the surface is capable of strong interaction with C_3 hydrocarbons *(high-energy adsorption sites)*
- Irreversibility of propylene adsorption due to surface reaction with ketones and anhydrides
- The weaker interaction of propane/propylene with the used B_2O_3-oCNT surface is apparently favorable for the catalytic selectivity.

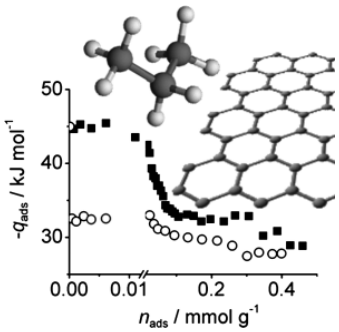
Oxidative dehydrogenation of propane over carbon materials



- The near surface oxygen concentration of 4.3-4.7% on used oCNT and B_2O_3-oCNT *(XPS)* correlates to the 3-5% of the high-energy adsorption sites *(Calorimetriy)*.

Oxidative dehydrogenation of propane over carbon materials

Combination of Microcalorimetry[1] , XPS and TPD [2] results allows for a quantitative description of the carbon surface under reaction conditions.



Type	Differential heat kJ/mol	Ads. surface site
A	45 homogeneous high energy sites	**ketone and quinone groups** sites react rev. with C_3H_8 sites react irrev. with C_3H_6
B	35 - <45 heterogeneous composition	**carboxylic anhydrides, phenol, ether** sites react rev. with C_3H_8 sites react irrev. with C_3H_6
C	30 homogeneous low energy sites	**lactone/ester, carboxylic acid** sites react rev. with C_3H_8 & C_3H_6
D	20 - < 25	**basal plane of graphitic carbon** (free of oxygen) sites react rev. with C_3H_8 & C_3H_6

Indications for a higher selective surface:

- more medium energy adsorption sites, such as phenol
- weaker interaction of propane/propylene with the oxygen surface sites

[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. Blume, R. Schlögl, D.S. Su, Angew. Chemie 121 (2009) 7046-6917.
B. Frank, M. Morassutto, R. Schomäcker, R. Schlögl, D.S. Su, ChemCatChem, 2 (2010) 644-648.

Selected Applications

Adsorption microcalorimetry is broadly employed in several projects of our department.

1. Selective oxidation of propane to acrylic acid over pure-phase MoVTeNb oxide catalyst - M1 catalyst.

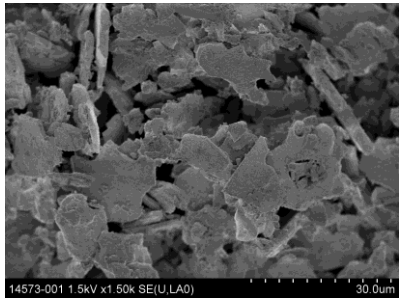
2. Oxidative dehydrogenation over oxygen functionalized carbon nanotube - oCNT

3. Oxidation of HCl to Cl_2 over bare and supported CeO_2

4. Oxidation of alcohol over vanadium supported Al_2O_3

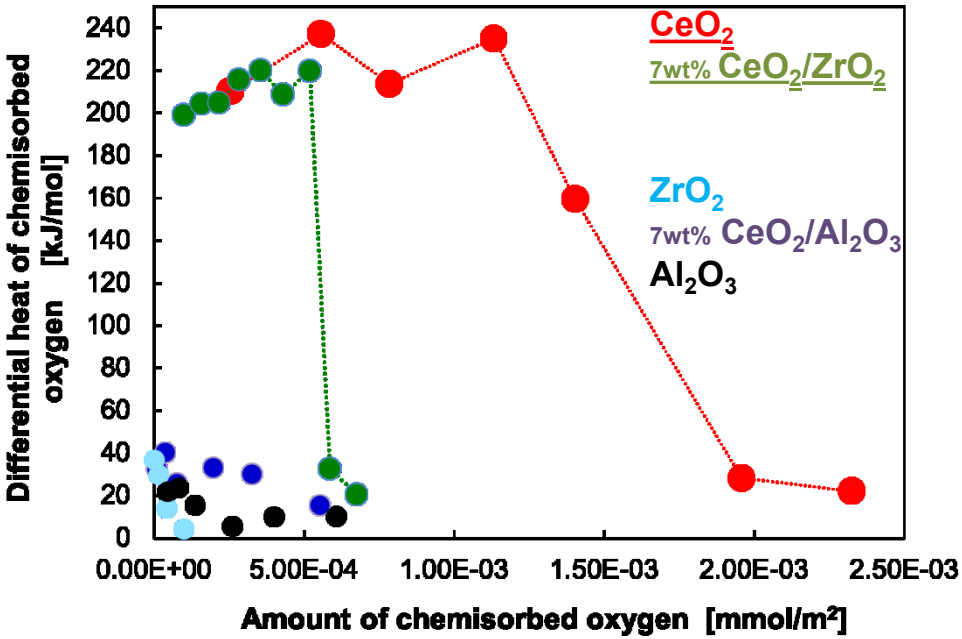
DEACON reaction

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



Heat of adsorption of O_2 at 200°C

H_2 reduced catalysts at 200°C



- **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.

- **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.

Selected Applications

Adsorption microcalorimetry is broadly employed in several projects of our department.

1. Selective oxidation of propane to acrylic acid over pure-phase MoVTeNb oxide catalyst - M1 catalyst.

2. Oxidative dehydrogenation over oxygen functionalized carbon nanotube - oCNT

3. Oxidation of HCl to Cl_2 over bare and supported CeO_2

4. Oxidation of alcohol over vanadium supported Al_2O_3

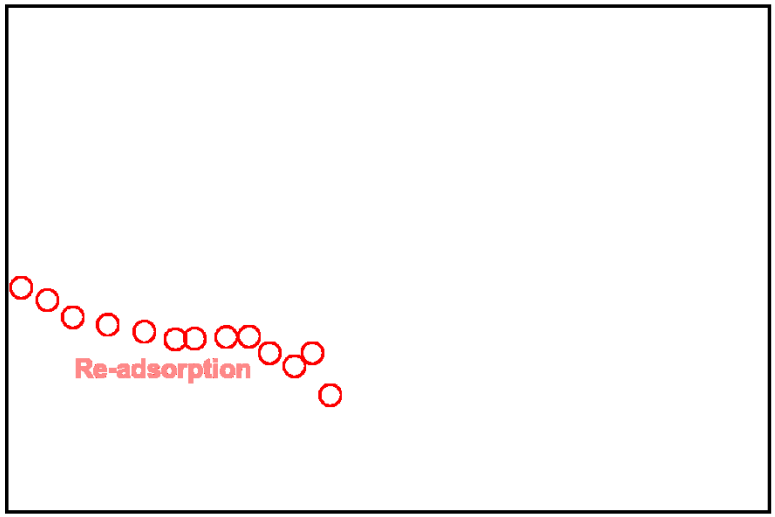
Oxidation of Alcohol

$$C_2H_5OH + \frac{1}{2}O_2 \longrightarrow \frac{1}{2}H_4O + \frac{1}{2}H_2O \quad \Delta_R H = -78{,}5\ \mathrm{kJ/mol}$$

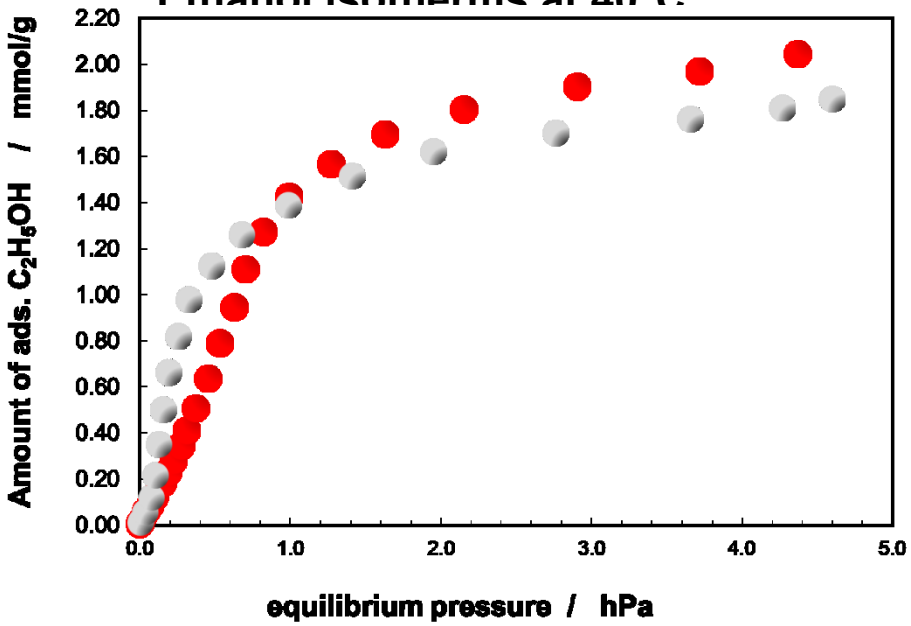
Catalyst: $V_xO_y / \gamma\text{-}Al_2O_3$
$T_{reaction}$ = 140 - 200 °C

Intention: Determination of kinetic data: N_o, K 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



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

N_o	=	2.077	$mmol*g^{-1}$
K_o	=	1.99×10^{-15}	hPa^{-1}
[redacted]$_{ads.}$	=	90 [redacted]0	$kJ*mol^{-1}$

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.

Summary

- 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.

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

Thank you for your attention

http://www.fhi-berlin.mpg.de
Dept. of Inorganic Chemistry, Director: Prof. R. Schlögl

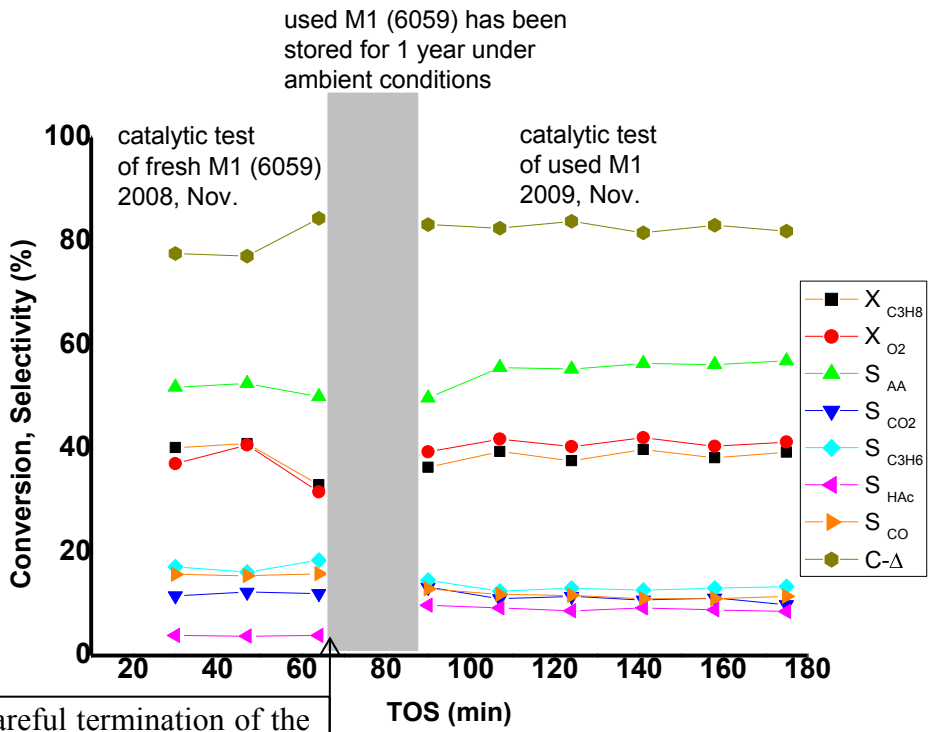
Supporting Material

Obtained physical quantities
&
evaluation criteria of the calorimetric results

Active catalyst surface stable under ambient conditions ?

CATALYTIC TEST (fresh/used catalyst)

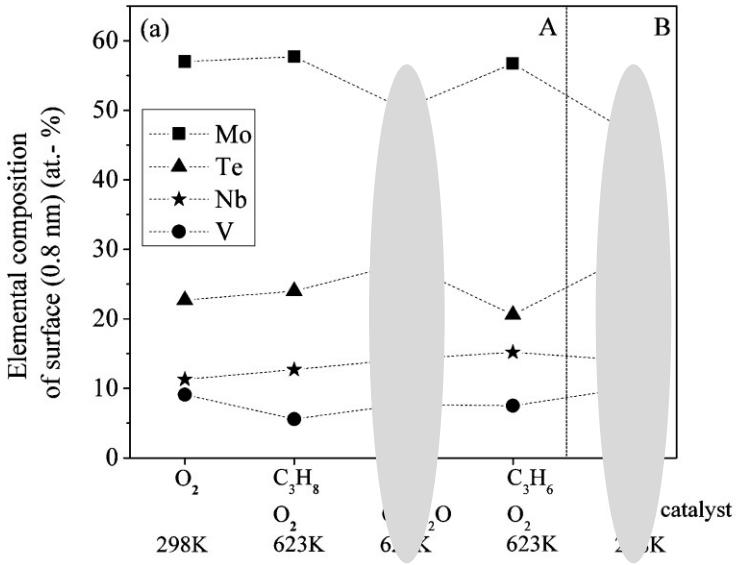
propane oxidation data obtained from fresh and used MoVTeNb catalyst



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

SURFACE STUDY (fresh/used catalyst)

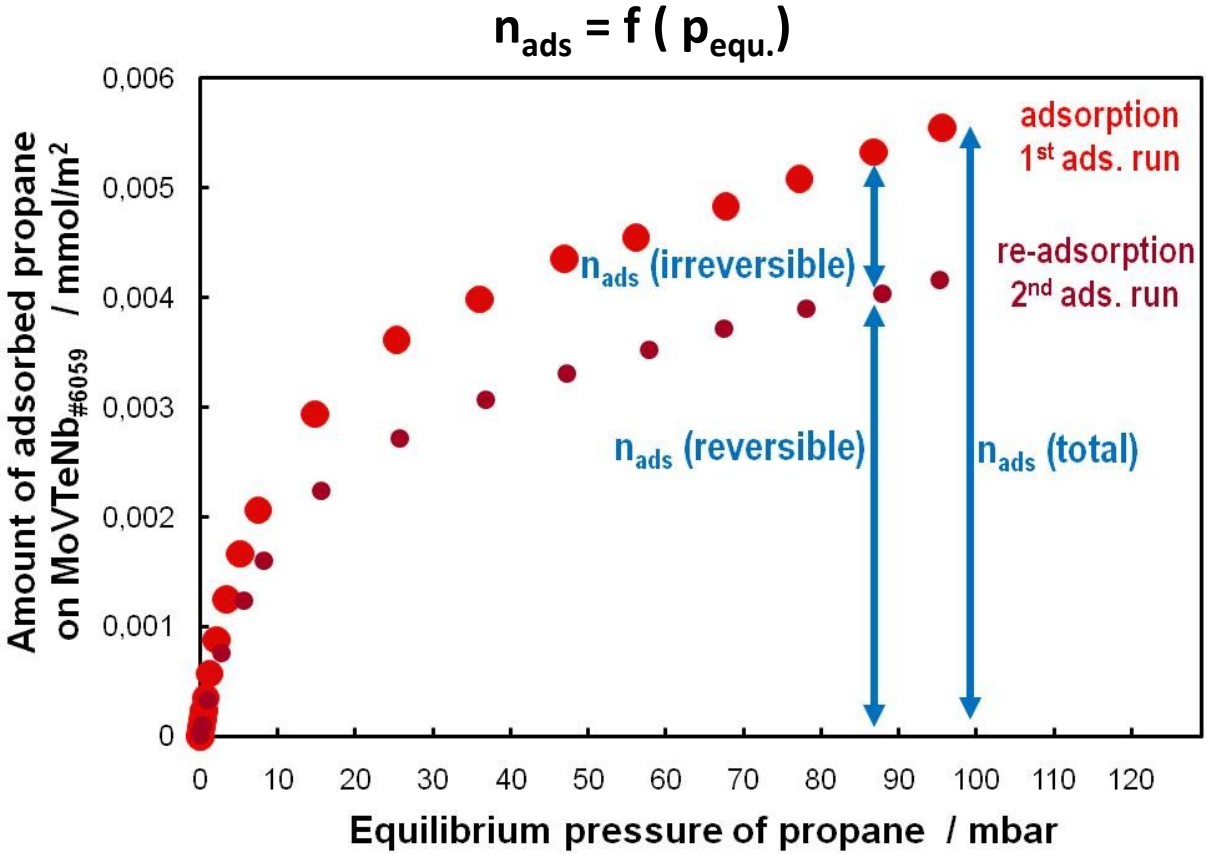
in situ XPS: surface element composition during and after PO over MoVTeNb catalyst



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**

obtained results
Adsorption Isotherm



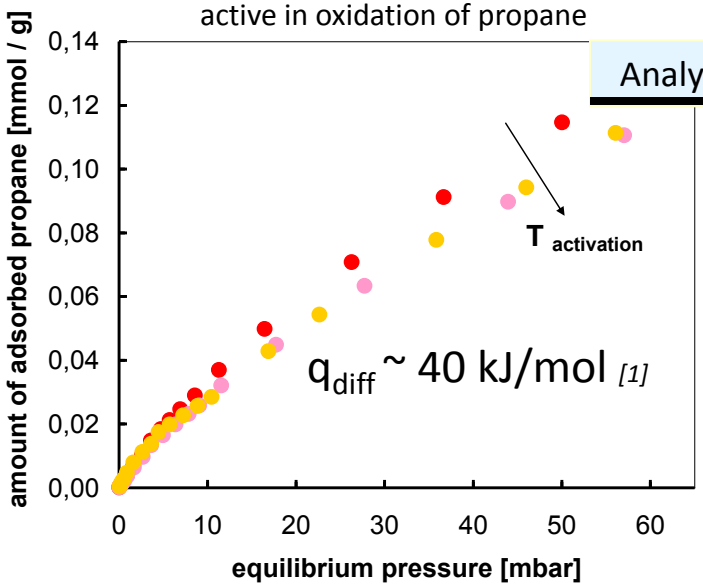
n_{ads} (total) : overall adsorbed amount under an equilibrium pressure of 95 mbar

n_{ads} (irrev.) : chemisorbed amount

Analysis of the adsorption isotherm
-Specific surface area-

Adsorption Isotherm

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



Analysis →

higher order Langmuir model,

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

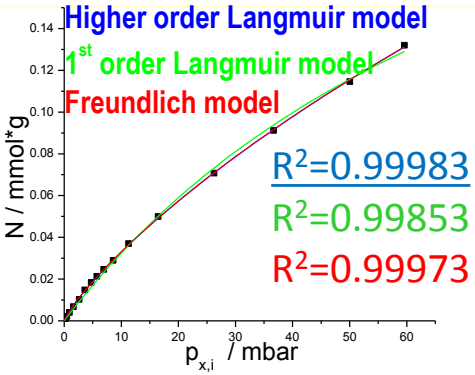
The enthalpy of adsorption $\Delta_a H$ (q_{diff}) per site is constant at increasing Θ

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

Freundlich model

$$N_{ads} = \frac{A\,p^{\frac{1}{n}}}{1+A\,p^{\frac{1}{n}}} \quad ; R^2$$

The enthalpy of adsorption $\Delta_a H$ (q_{diff}) per site decreases at increasing Θ



Specific surface area $_{propane}$ = N $_{mono}$ * S * cross-section area $_{propane,T}$ * Avogadro constant

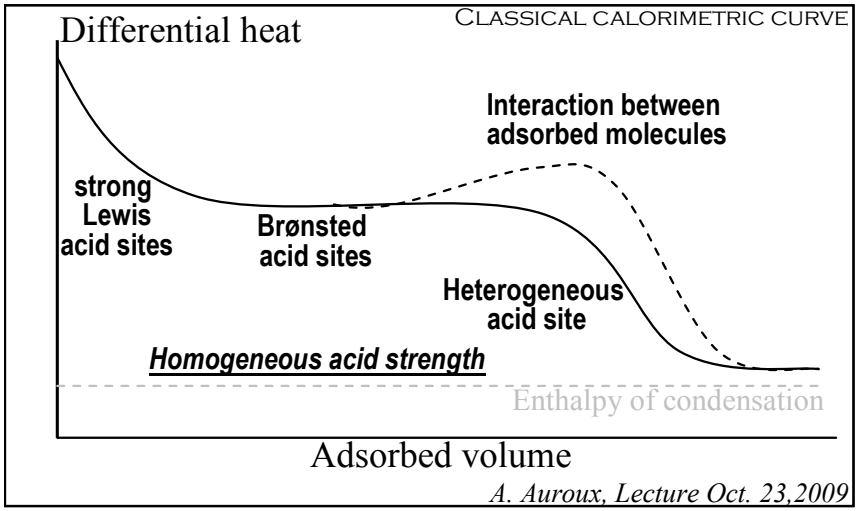
n = 1 non-dissociative ads.
n > 1 dissociative ads. ; activated ads.

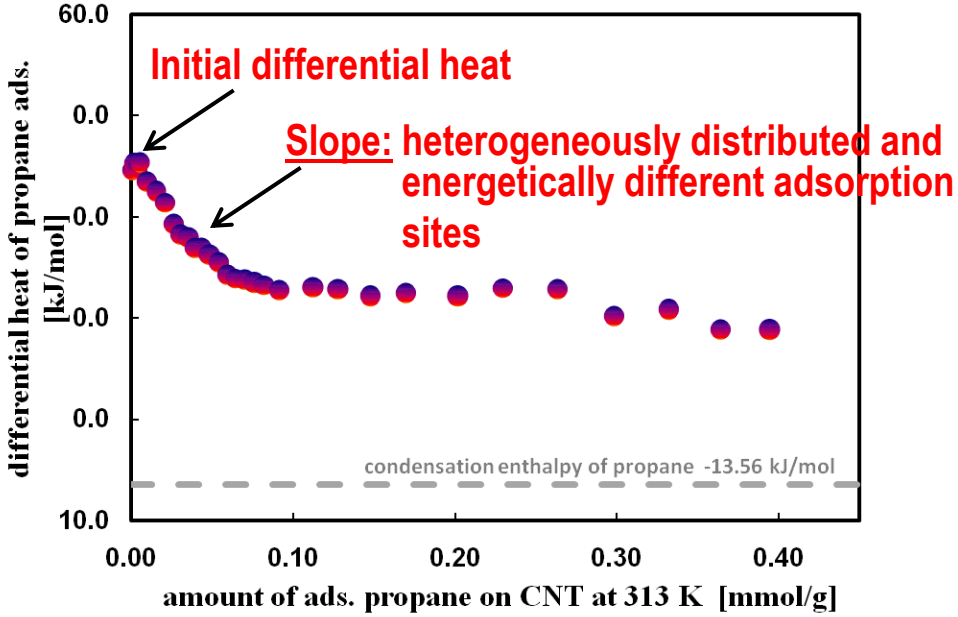
10%V/SBA15 dehydration temperature	N_{mono} µmol *g^{-1}	n	R^2	$S_{propane}$ m^2*g^{-1}	BET S_{N2} m^2*g^{-1}
	higher order Langmuir				
373 K	0.9 (2)	**1.20 (2)**	0.99983	**226 (10)**	**329 (4)**
573 K	1.3 (4)	**1.22 (2)**	0.99982	304 (10)	
673 K	1.2 (3)	**1.22 (2)**	0.99905	290 (10)	

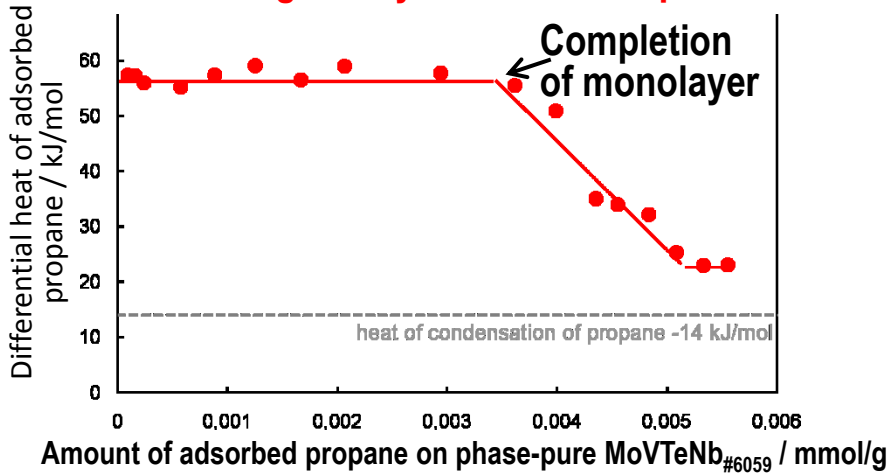
[1] Dinse, A.; Wrabetz, S. et.al., J.Mol.Catal. A 307 (2009)43.

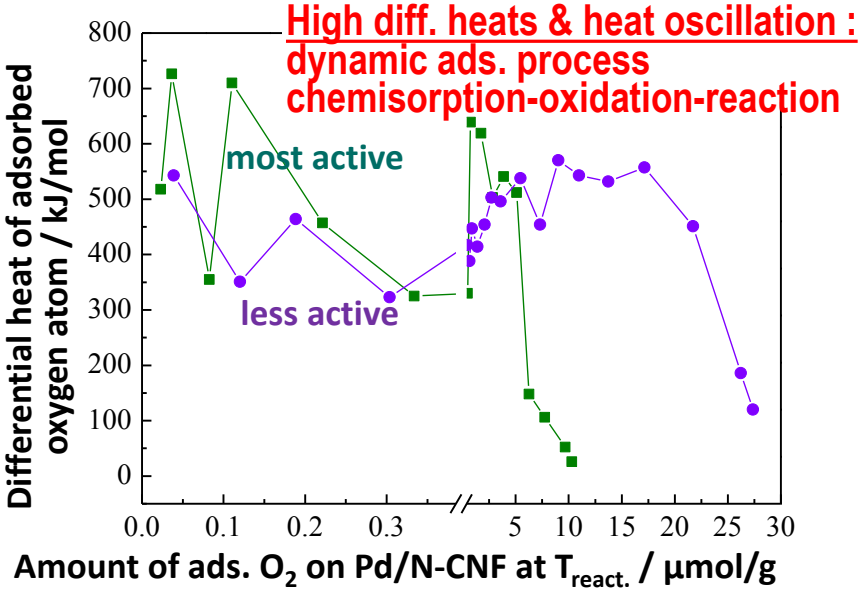
obtained results
Differential heat versus the n_{ads}

Classical Calorimetric Curve





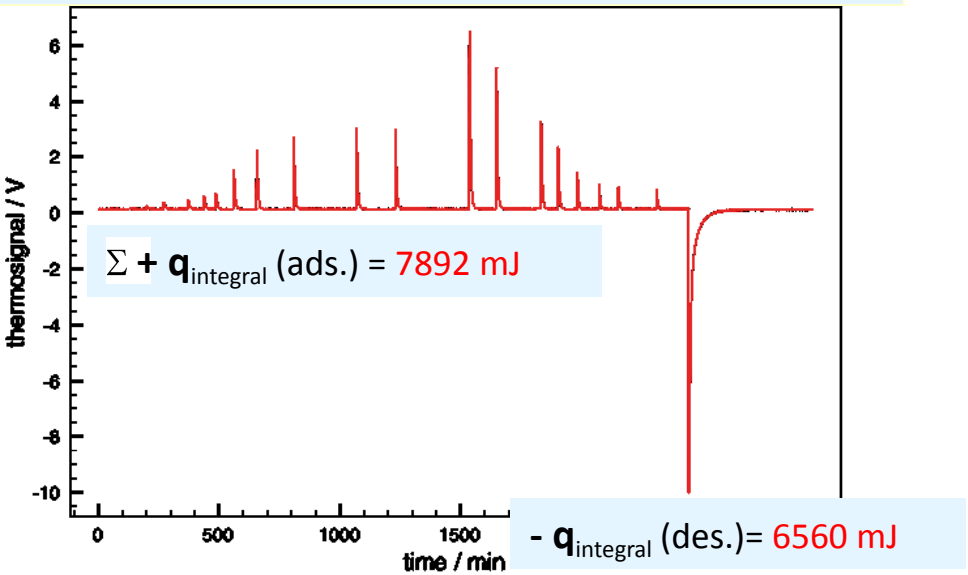




Evaluation criteria of the calorimetric experiment

Integral heat signal of adsorption and desorption

stepwise adsorption of propane on MoVTeNb oxide at 313K



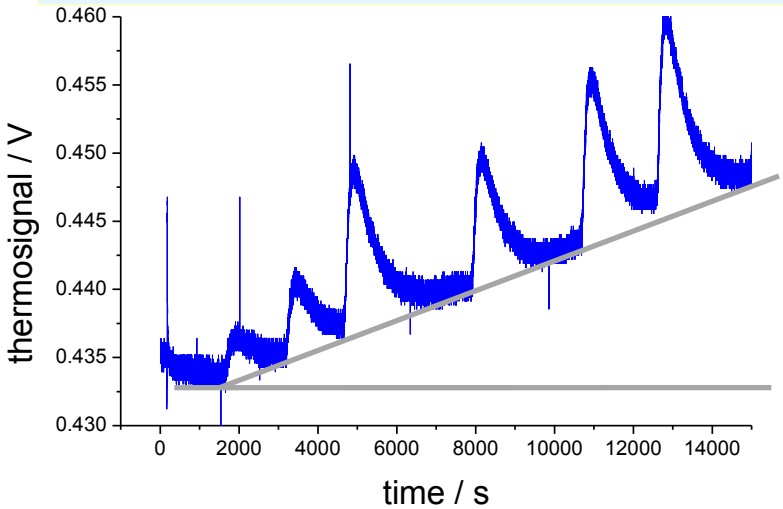
Σq_{int} (ads.) > q_{int} (des.) → partially irreversible ads.; activated ads. process

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 313 K



Background deviates from the base-line

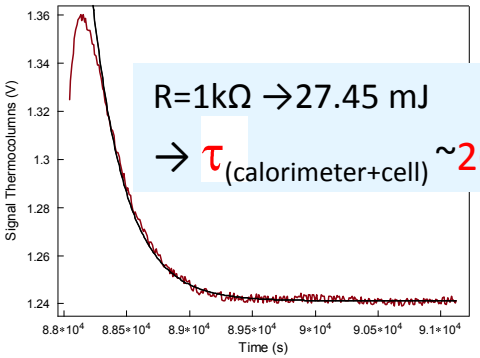
→ Adsorption process is accompanied by secondary processes

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

Evaluation criteria of the calorimetric experiment

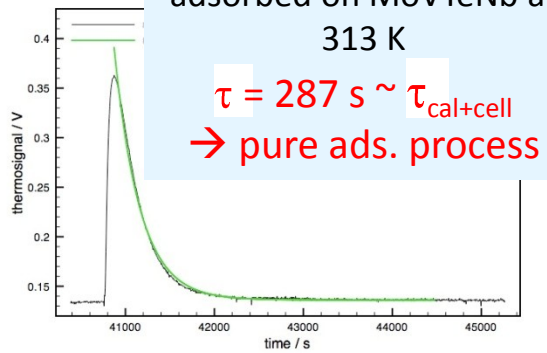
Determination of the time constant τ of the integral heat signal

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



R=1kΩ →27.45 mJ

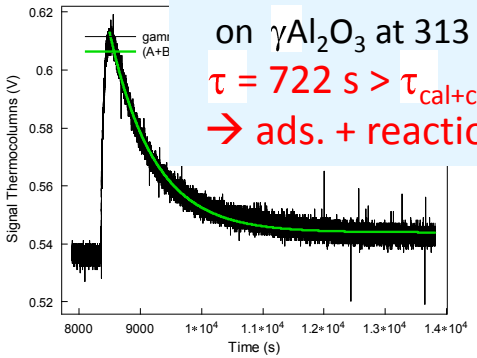
→ $\tau_{(calorimeter+cell)}$ ~265 s



5.9 µmol/g propylene adsorbed on MoVTeNb at 313 K

τ = 287 s ~ $\tau_{cal+cell}$

→ pure ads. process



4.8 µmol/g methanol adsorbed on γAl_2O_3 at 313 K

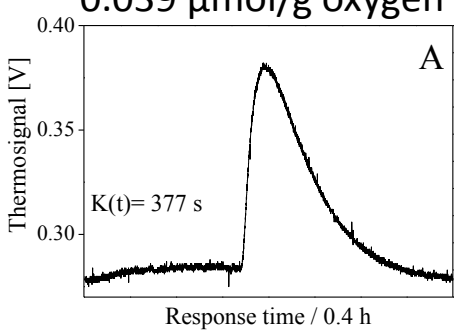
τ = 722 s > $\tau_{cal+cell}$

→ ads. + reaction

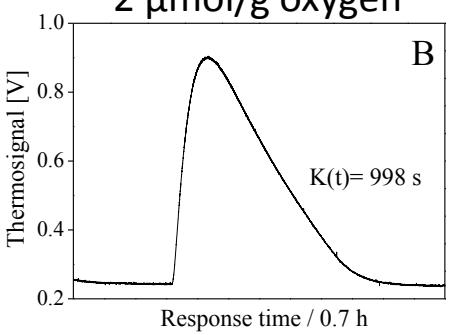
Shape of the integral heat signal

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

0.039 µmol/g oxygen



2 µmol/g oxygen



14 µmol/g oxygen