Propane activation over vanadia clusters on different catalysts

S. Wrabetz, P. Kube, S. Carey, A. Trunschke and R. Schlögl

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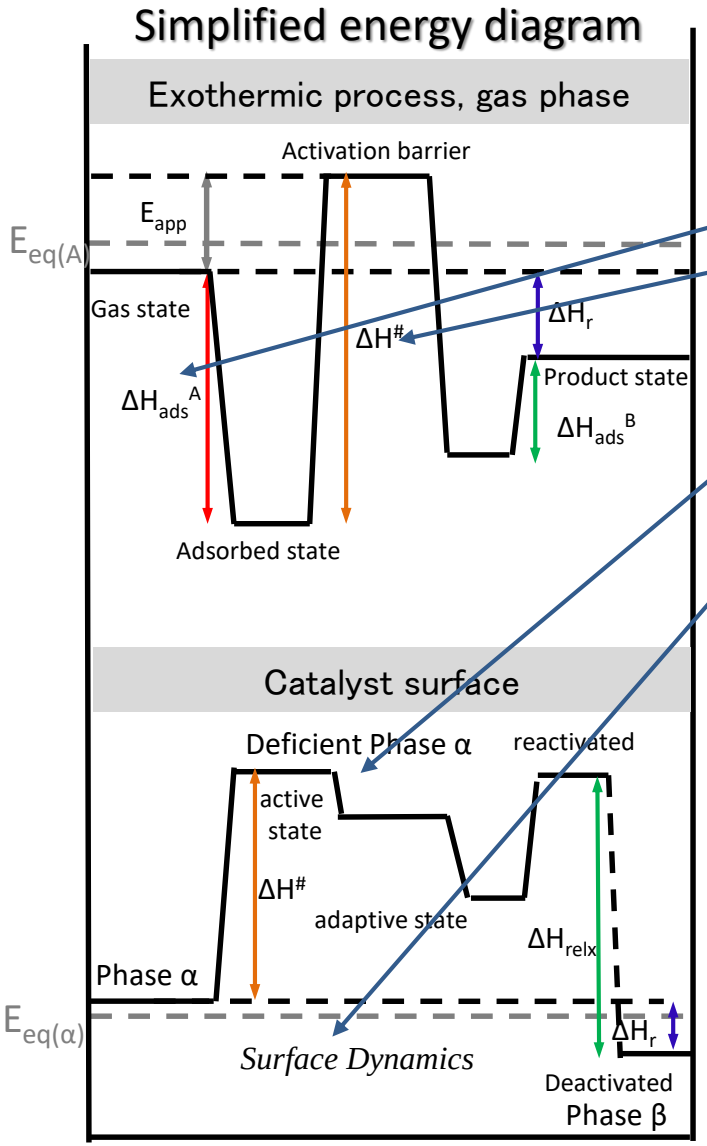
AACHEN · GERMANY · 18 – 23 AUGUST

Date: 21.08.2019 , Time: 11:30
Topic: Catalysis for Base Chemicals

Introduction



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

- For a detailed understanding of the mechanism of propane oxidation[1] , we need knowledge about the
  - ACTIVATION of the reacting molecules
  - energy BARRIERS
  - catalytic RELEVANT surface SITES
  - Surface DYNAMICS

that requires

Quantitative data and information about the catalyst surface during reaction

- Correlation of surface and kinetic data
  → STRUCTURE-REACTIVITY relationship
- Experiment meets Theory

Microcalorimetry beyond adsorption
Catalytic Test
DFT

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.*
A. Trunschke, J. Noack, S. Trojanov, F. Girgsdies, T. Lunkenbein, V. Pfeifer, M. Hävecker, P. Kube, C. Sprung, F. Rosowski, R. Schlögl, ACS Catalysis, 2017, 7, 3061−3071.
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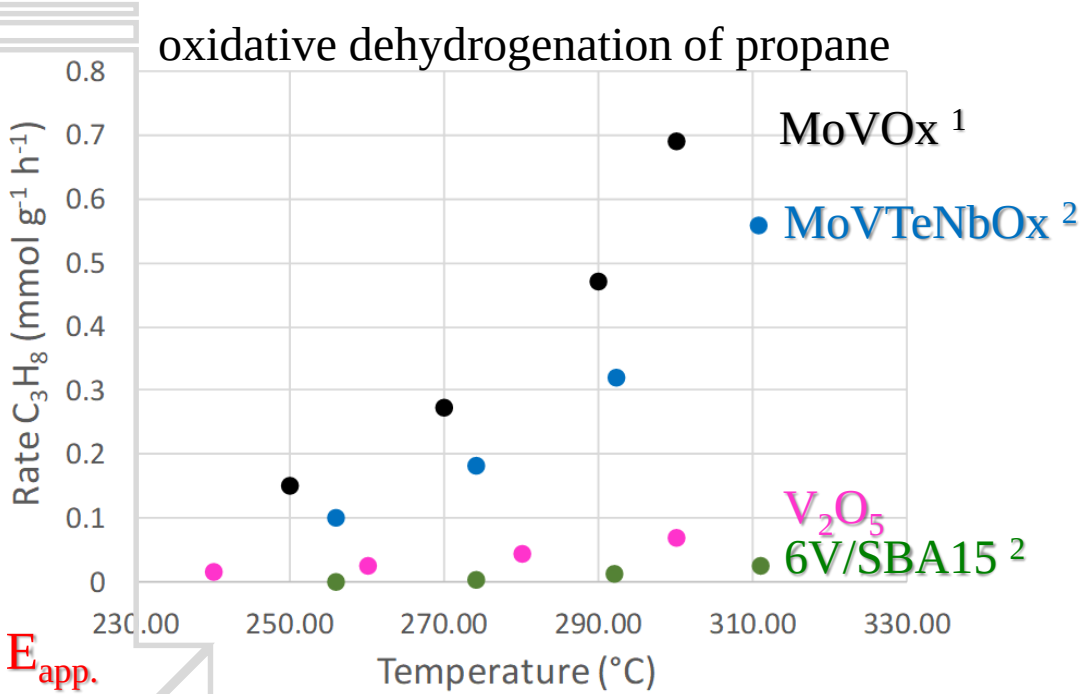
Propane activation over vanadia clusters on different catalysts

oxidative dehydrogenation of propane



V-containing model catalysts
with
structurally similar functional groups
V-OH V=O V-O-V
and
substantial structural diversity

$E_{app.}$
r_{C3H8}

Microcalorimetry $\Delta H_{ads.}$
C_3H_8 at 40° $N_{ads.}$

- **ACTIVATION of educt**
- **C_3H_8 induced response of the surface "DYNAMICS"**
- **Enthalpy of formation of the transition state "ACTIVATION BARRIER** [2]
  Note: $\Delta H_{ads.} \neq T_{ads.}$ [3]*; ads. in quasi-equilibrium* [4]*; intermediates occur in pseudo-steady-state*
- **Structure Reactivity Relationship**

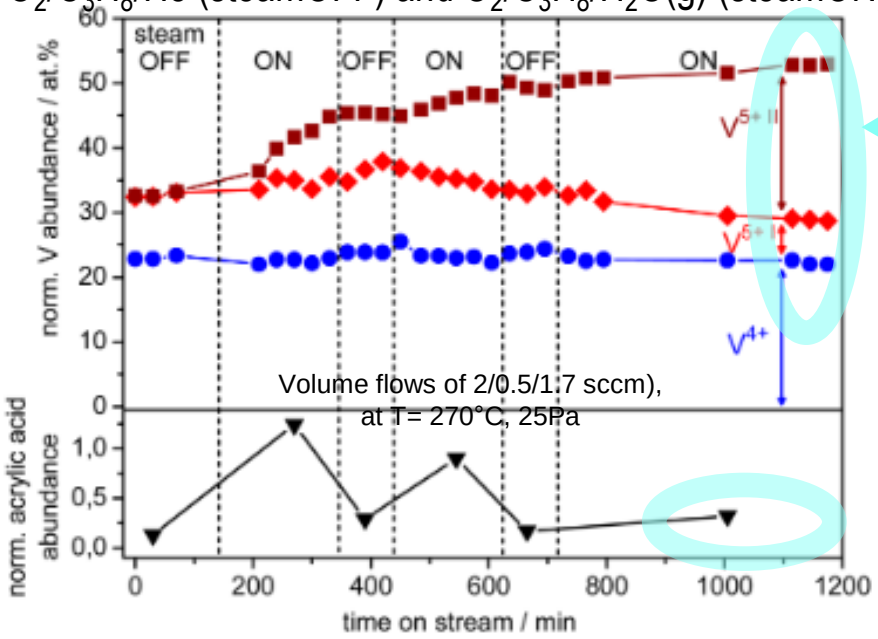
1 Naumann D'Alnoncourt, R.; Csepei, L. I.; Hävecker, M.; Girgsdies, F.; Schuster, M. E.; Schlögl, R.; Trunschke, A. J. of Catalysis 2014, 311, 369.
2 P. Kube, B. Frank, S. Wrabetz, J. Kröhnert, M. Hävecker, J. Valasco-Vélez, J. Noack, R. Schlögl, A. Trunschke, ChemCatChem 9 (2017) 1-14.
3 a) D. C. Tranca, 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.
4 K. Chen, A. T. Bell, E. Iglesia, J. Phys. Chem. B 2000, 104, 1292–1299

DYNAMICS of the MoV oxide surface

in situ XPS [1]

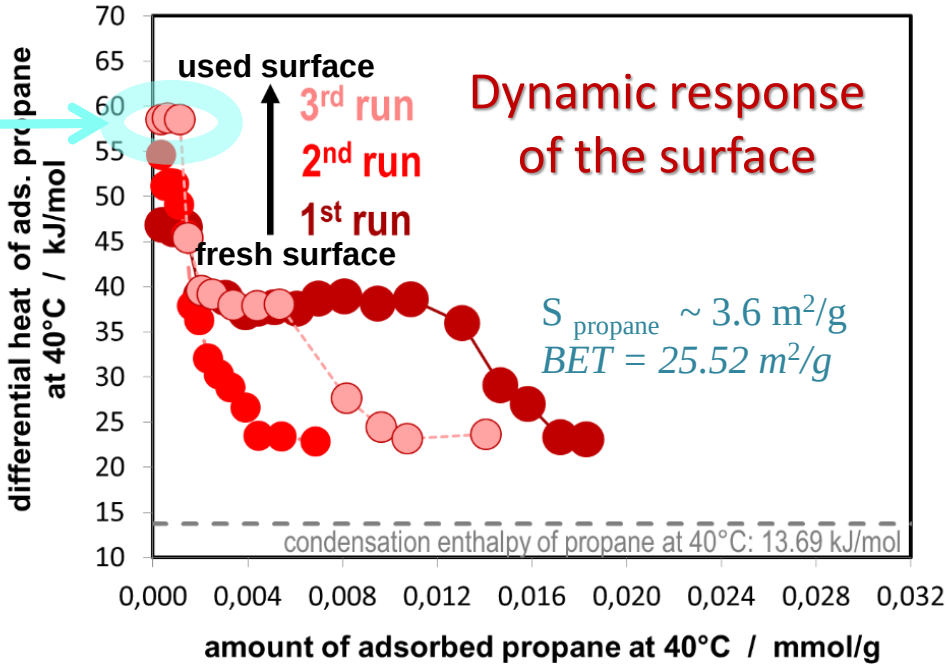
ODH of propane

$O_2/C_3H_8/He$ (steamOFF) and $O_2/C_3H_8/H_2O(g)$ (steamON)



Calorimetry

Differential heat of PROPANE ads. at 40°C



The newly generated very strong C_3H_8 adsorption sites might be related to the segregated of V^{5+} and reflects a decrease in selectivity to acrylic acid.

1 A. Trunschke, J. Noack, S. Trojanov, F. Girgsdies, T. Lunkenbein, V. Pfeifer, M. Hävecker, P. Kube, C. Sprung, F. Rosowski, R. Schlögl, ACS Catalysis, 2017, 7, 3061−3071.

DYNAMICS of the complex MoVTeNb oxide surface

in situ XPS [1]

ODH of propane

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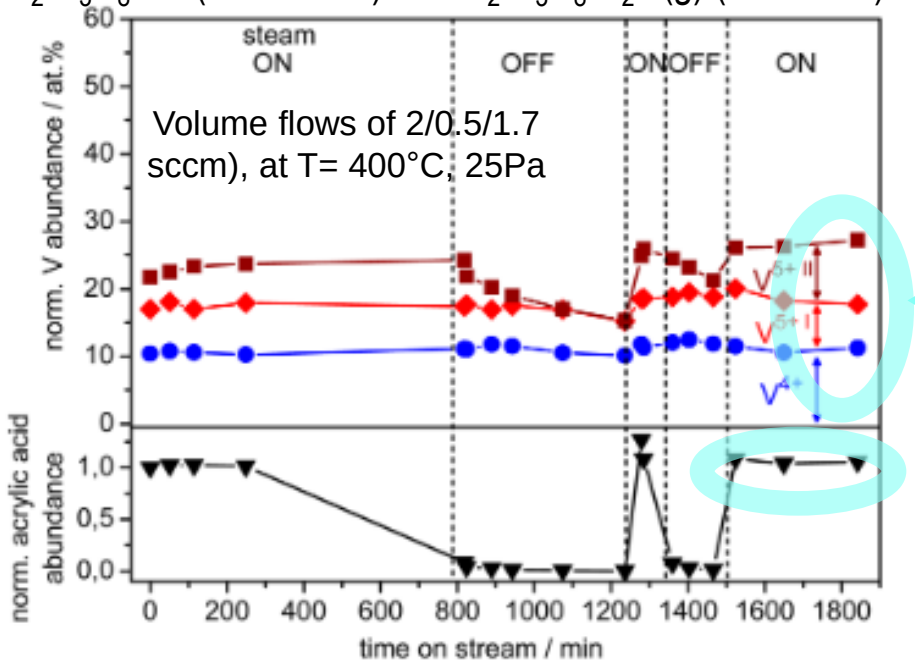

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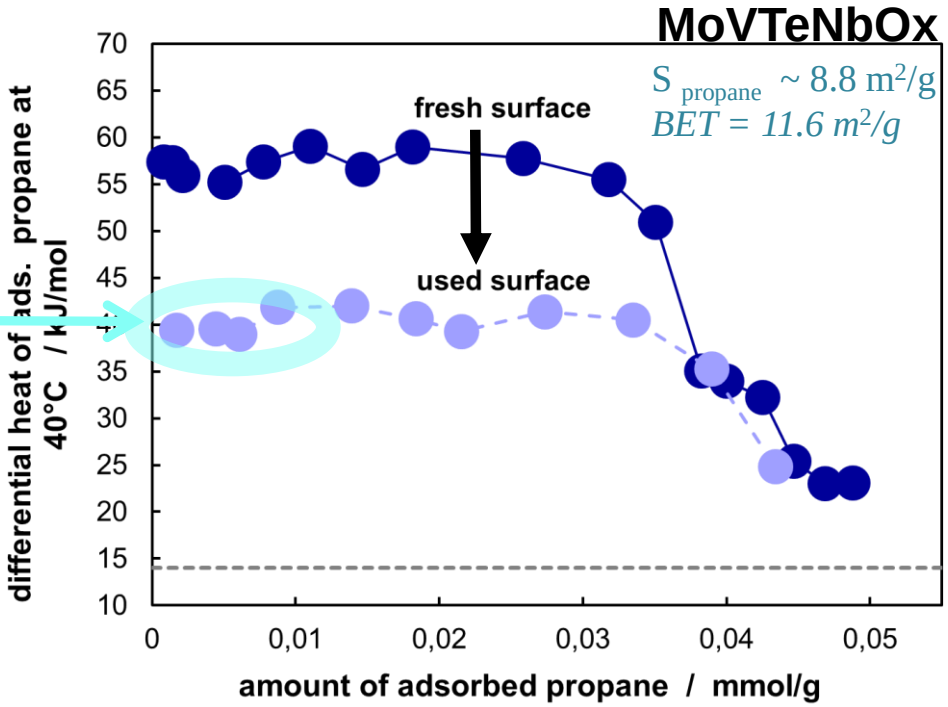
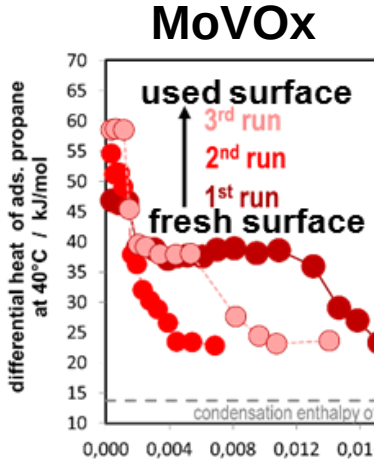


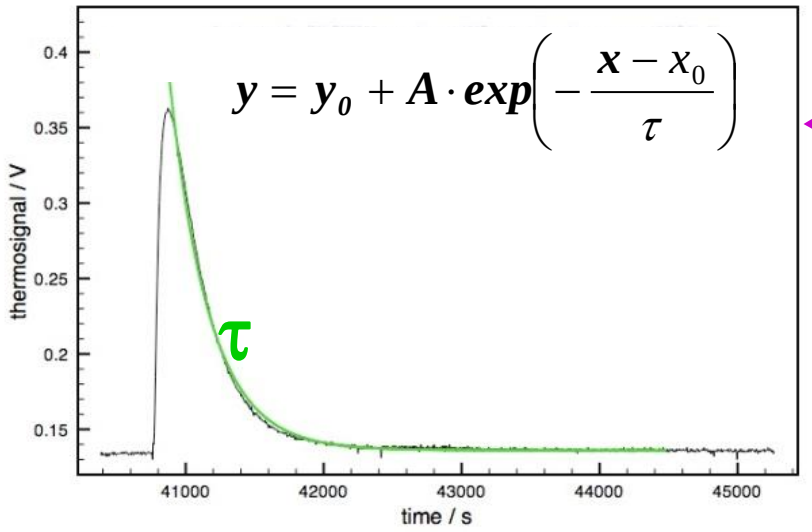


- **Dynamic nature of the surface during reaction.**
- **Very strong interaction of propane with the used surface explains the decrease in selectivity caused by V^{5+}-segregation already at r.t. .**

1 *A. Trunschke, J. Noack, S. Trojanov, F. Girgsdies, T. Lunkenbein, V. Pfeifer, M. Hävecker, P. Kube, C. Sprung, F. Rosowski, R. Schlögl, ACS Catalysis, 2017, 7, 3061−3071.*

Activation of C_3H_8

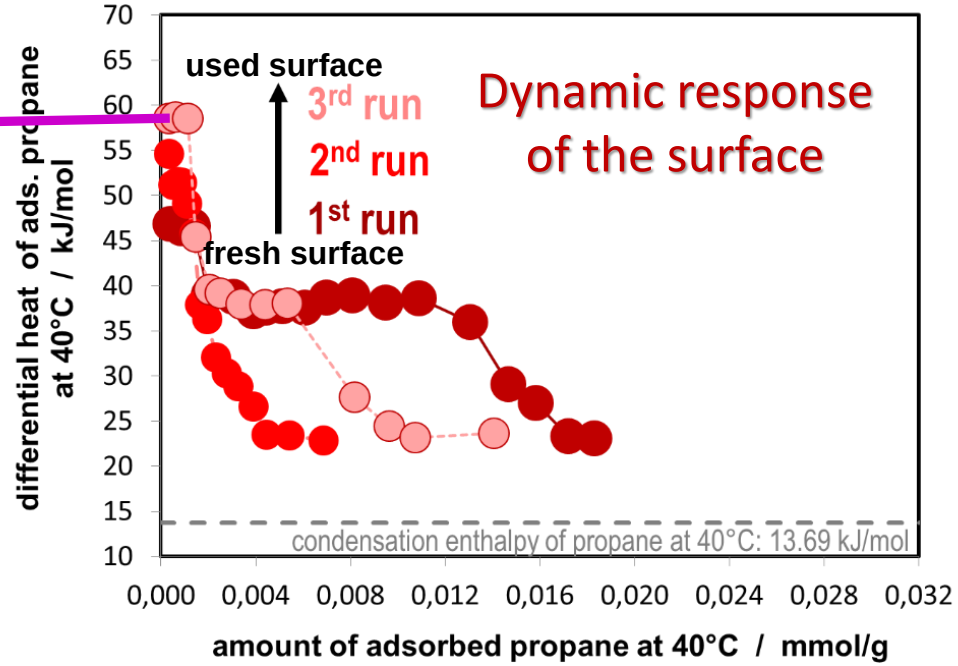
Corresponding integral heat signal



run	$H_{diff,\ inital}$ kJ/mol	n_{mono} µmol/g	time constant τ s τ_0~ 265s
1	47	15	434
2	55	2	371
3	59	8	352

Calorimetry

Differential heat of PROPANE ads. on MoV oxide at 40°C



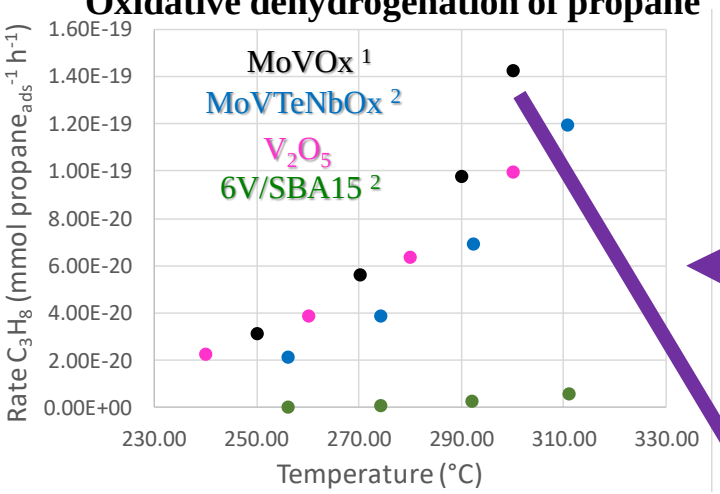
$\tau > \tau_0$ indicates :

Propane is activated already at 40°C and consequently traces of H_2O might be formed during the experiment

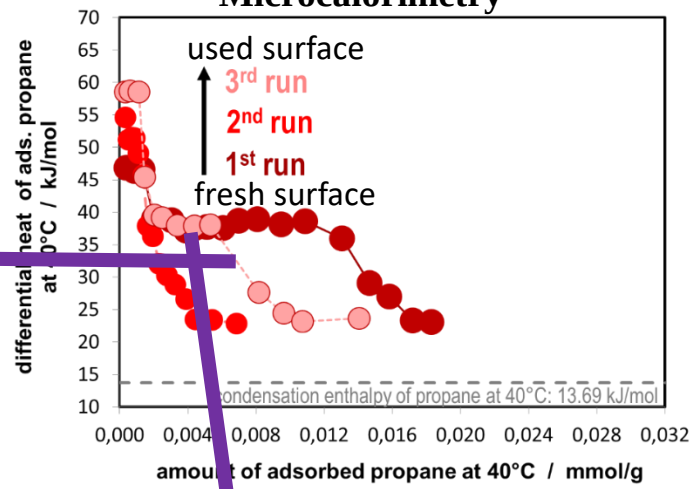
Activation Barrier & Catalytic Activity

MoV oxide V_2O_5 MoVTeNb oxide 6V/SBA15

Oxidative dehydrogenation of propane



Microcalorimetry



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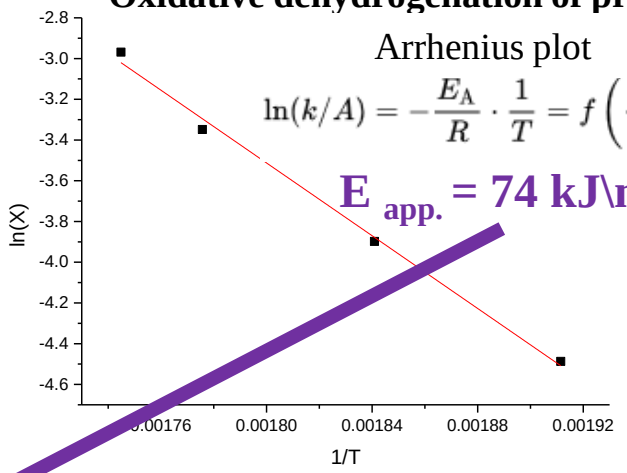

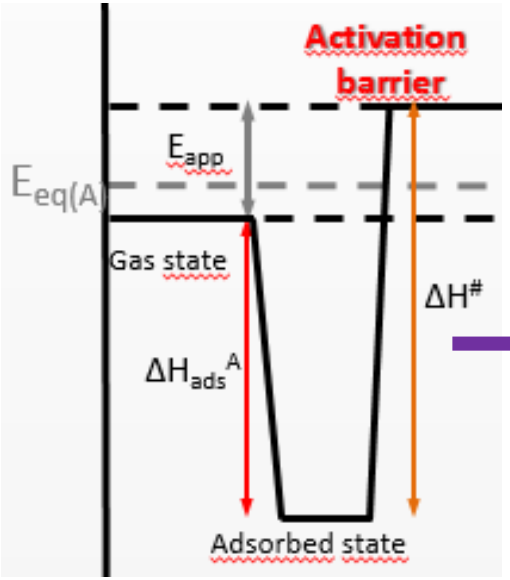

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2 P. Kube, B. Frank, S. Wrabetz, J. Kröhnert, M. Hävecker, J. Valasco-Vélez, J. Noack, R. Schlögl, A. Trunschke, ChemCatChem 9 (2017) 1-14.

Activation Barrier & Catalytic Activity

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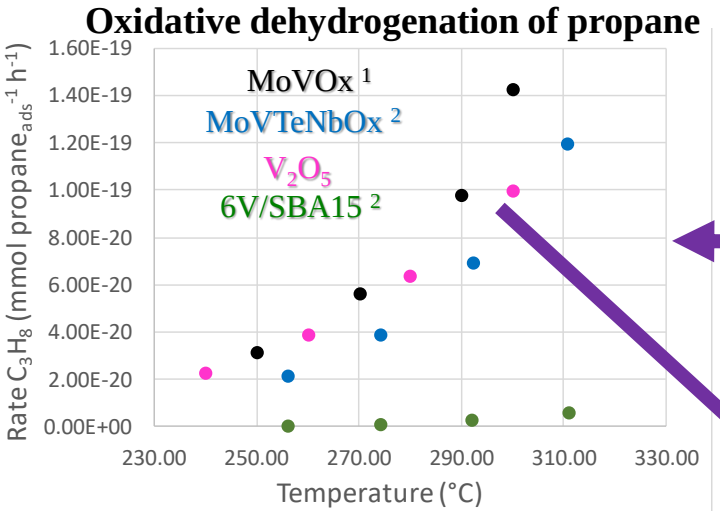

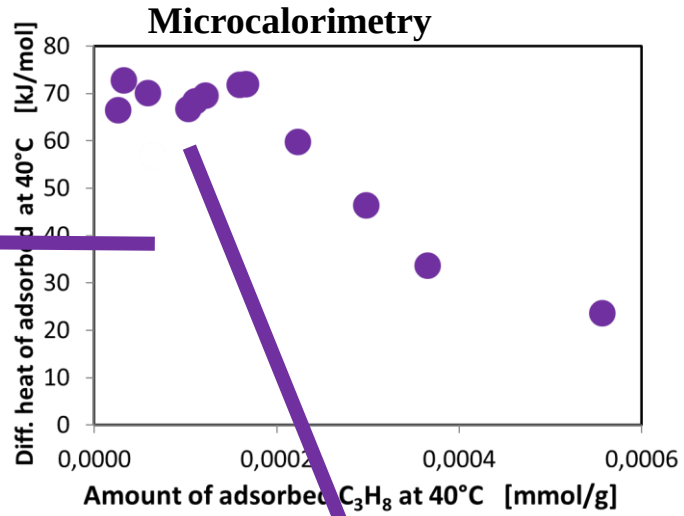

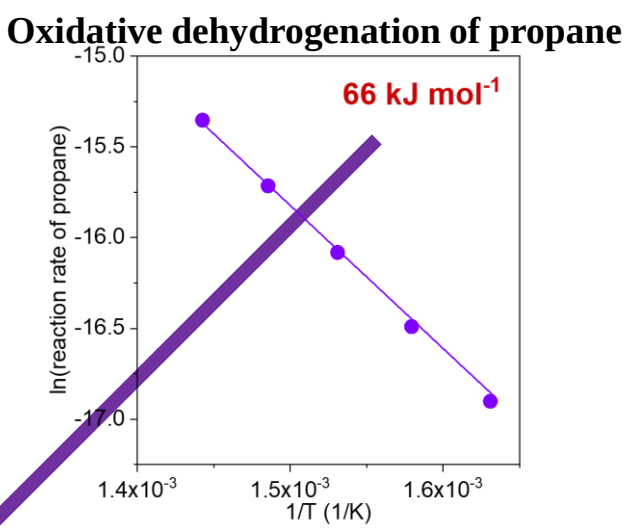

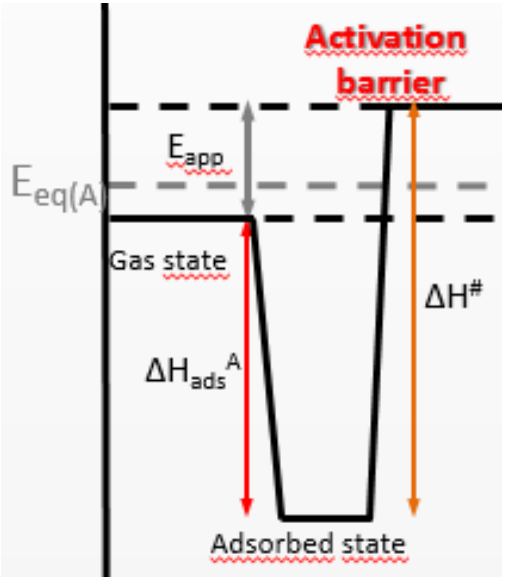

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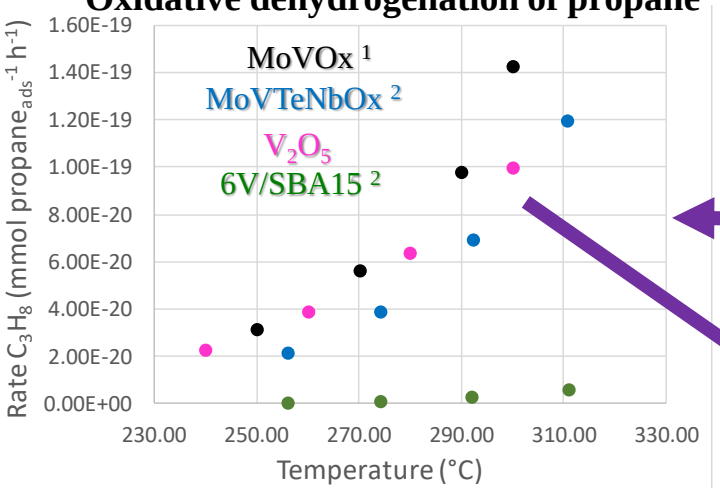
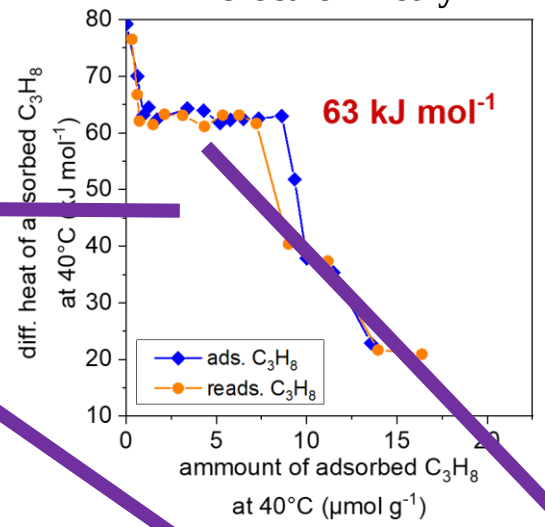


Microcalorimetry



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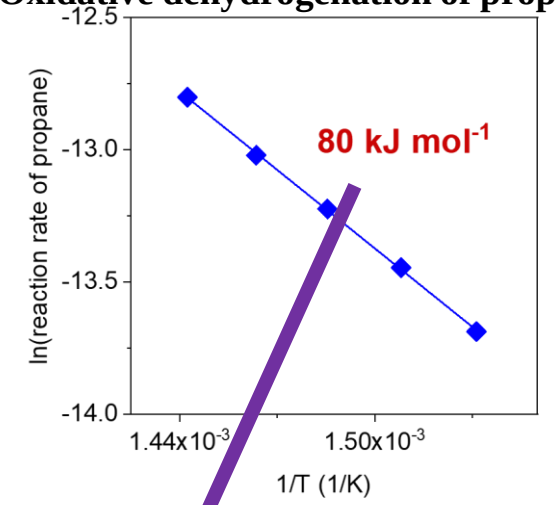

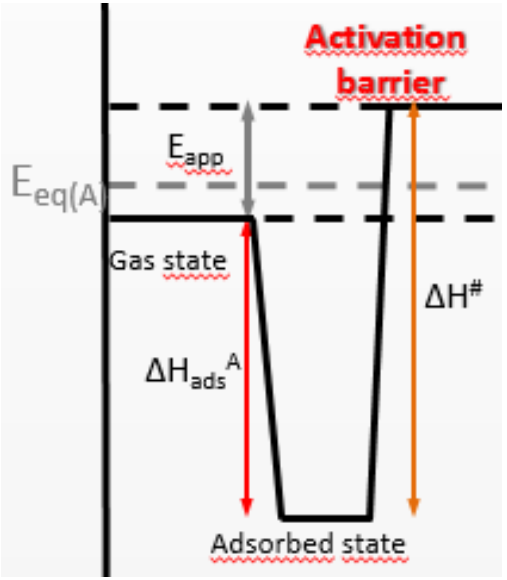

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Activation Barrier & Catalytic Activity

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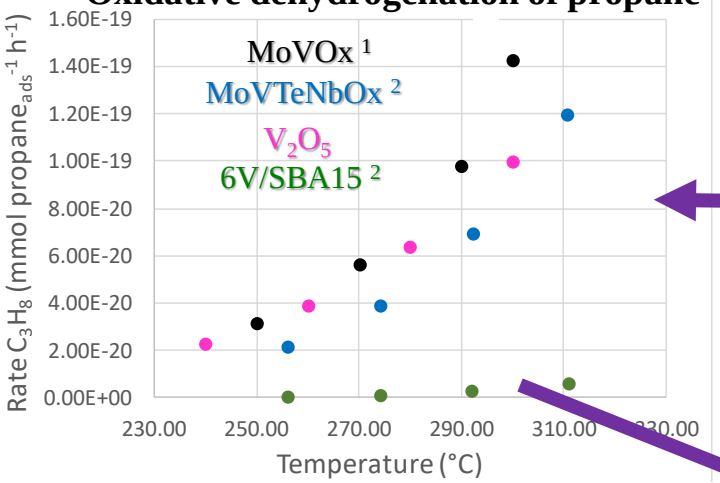

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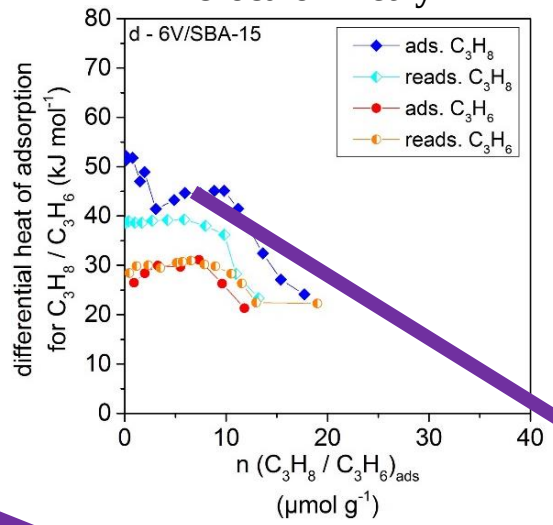

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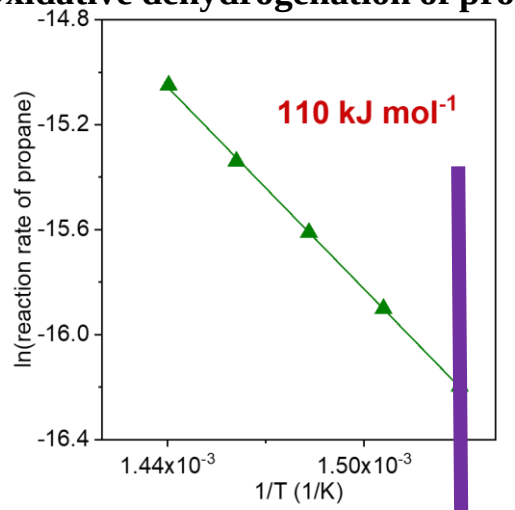

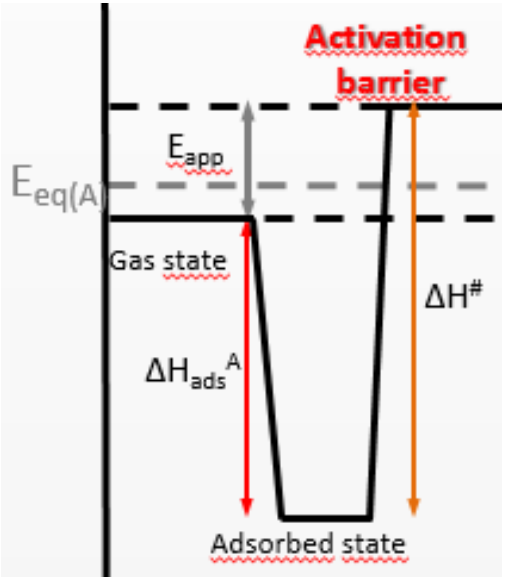

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Activation Barrier & Catalytic Activity

Experiment meets Theory

JACS — JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

DFT: direct calculation of the ENERGY BARRIERS of the first hydrogen abstraction from propane by a vanadyl (O=V) group yields a propyl radical bound to a HVO^{IV} surface sites.

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

Xavier Rozanska, Remy Fortrie, and Joachim Sauer*

J. Am. Chem. Soc. 2014, 136, 7751-7761.

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Energy barrier DFT [3]	132 kJ/mol octamer	139 tetramer	143 kJ/mol trimer	148 / 160 di-/ monomer

The cluster size of the active surface vanadium oxide ensembles decreases with increasing the energy barrier.

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.

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3 X. Rozanska, R. Fortrie, J. Sauer, J. Am. Chem. Soc. 2014, 136, 7751-7761.

Summary

A structure reactivity relationship can be retrieved by a combination of kinetic measurements, the determination of the heat of adsorption and DFT calculations.

Higher rates of propane oxidation are correlated with **lower barriers for propane activation** and seem to be linked with **larger vanadium oxide cluster size.**

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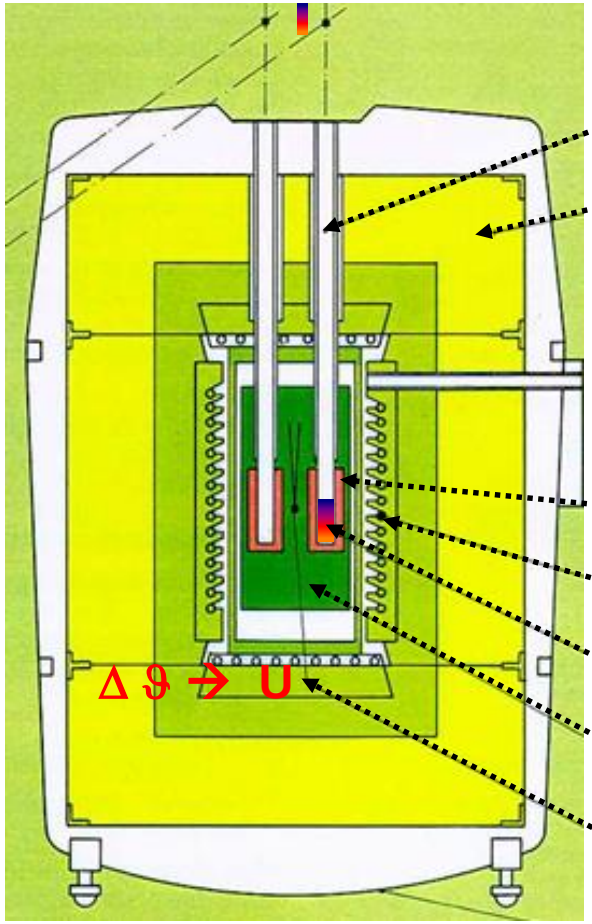
	cluster size of the active surface vanadium oxide			

Thank you for your attention !

Equipment

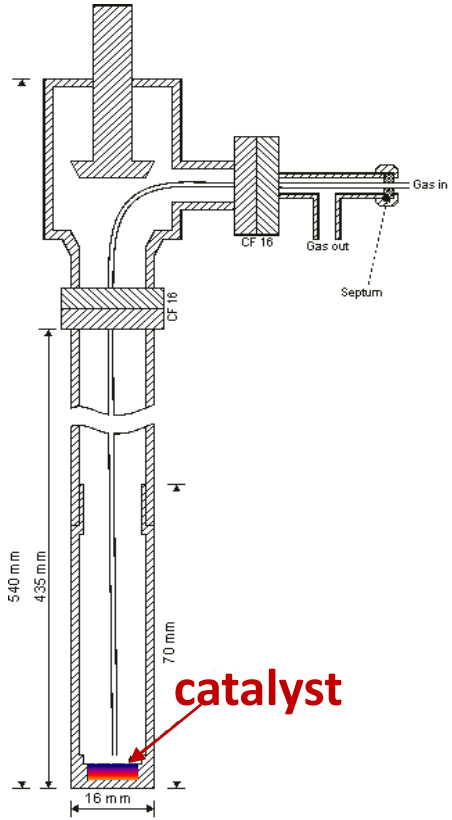
Microcalorimeter



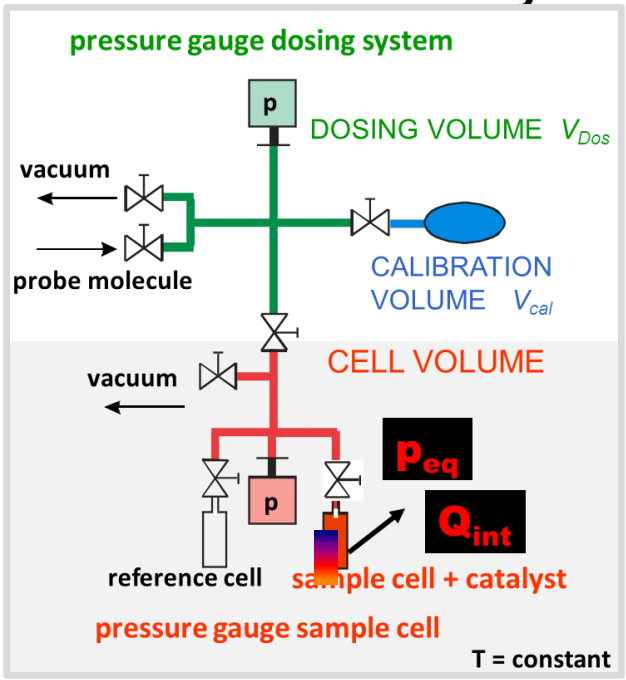
Tian-Calvet calorimeters from SETARAM (77K-1000°C) combined with a custom-designed high vacuum and gas dosing apparatus.

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

Sample Cell



Volumetric-Barometric System



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

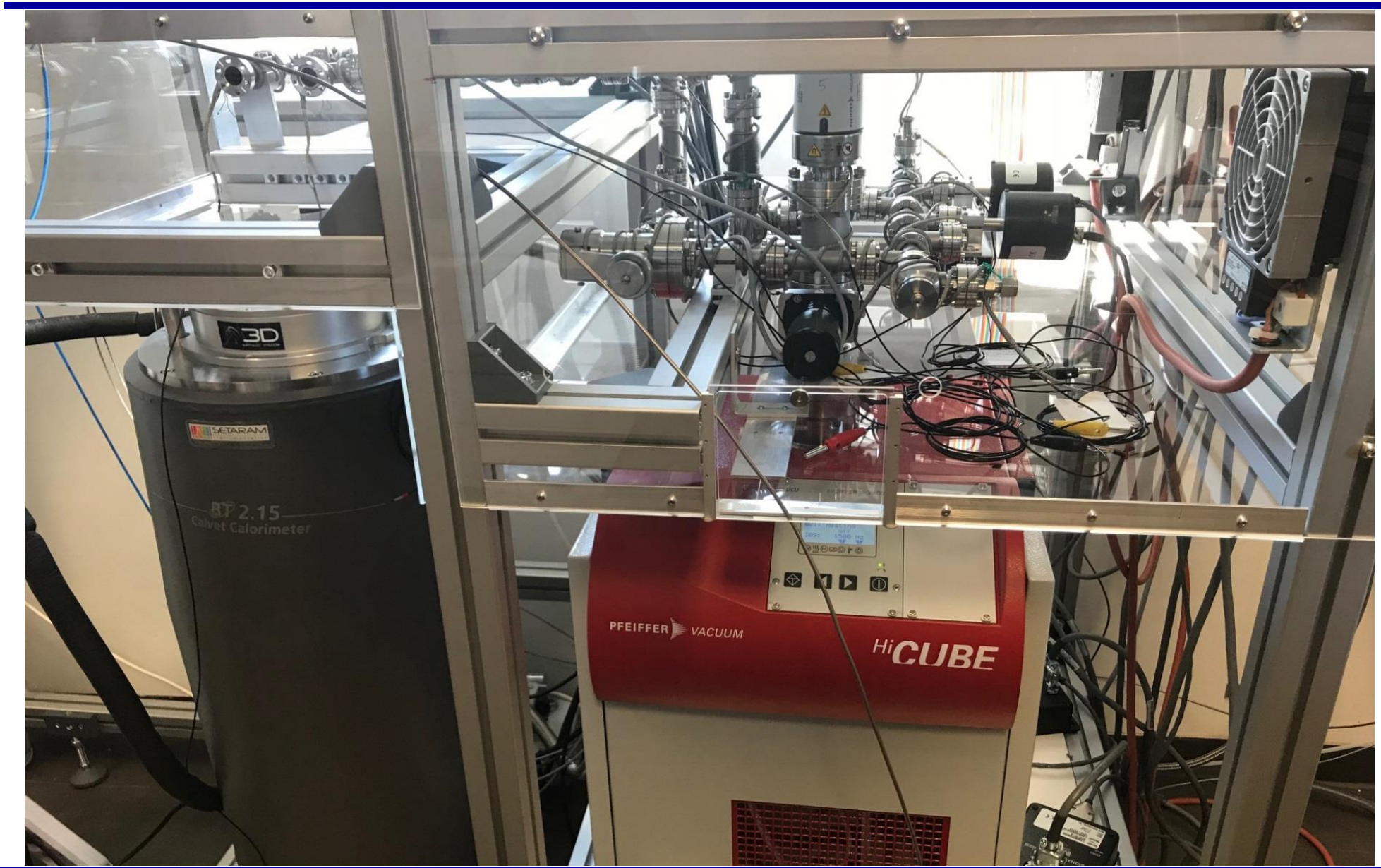
$$q_{diff} = \frac{Q_{int}}{n_{ads}} = \Delta H_{ads} \quad , \quad kJ/mol$$

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

$$K = K_o\ exp\ \frac{\Delta H_{ads}}{RT} \quad , \quad hPa^{-1}$$

$$specific\ surface\ area \quad , \quad m^2*g^{-1}$$

Equipment


3D
SETARAM
BT 2.15
Calvet Calorimeter
PFEIFFER VACUUM
HiCUBE