

Active Sites Characterization using Adsorption Microcalorimetry under Reaction Conditions

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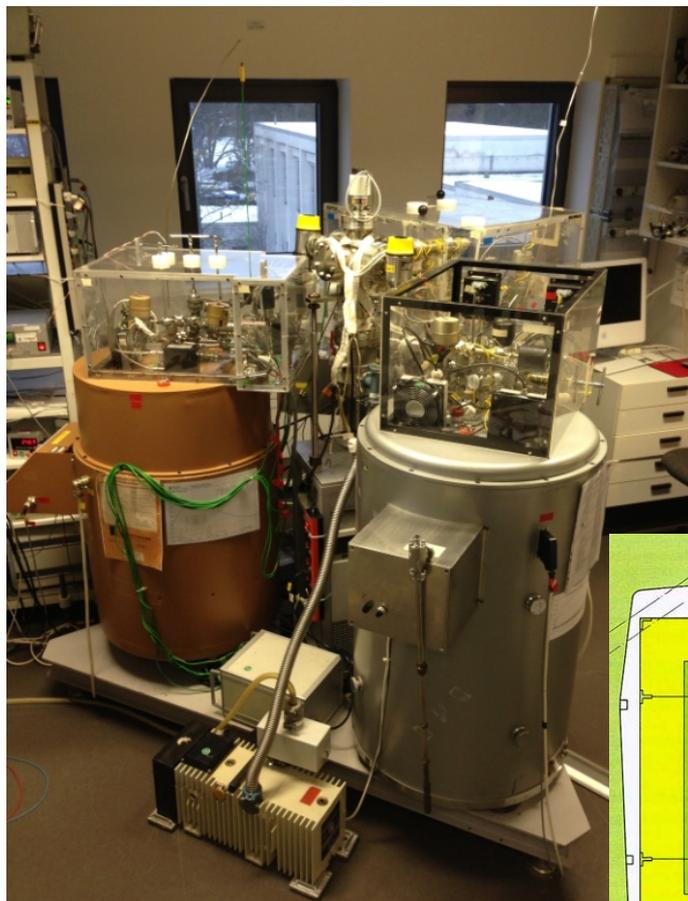
**TAC 2015: 50th Anniversary Conference
of the RSC Thermal Methods Group**
*Churchill College, Cambridge,
30th March to 1st April 2015.*

- 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 - to get a better understanding of the complex microkinetics
- since perhaps only a **minor fraction** of all surface atoms **form active centers**

Adsorption Isothermal Microcalorimetry

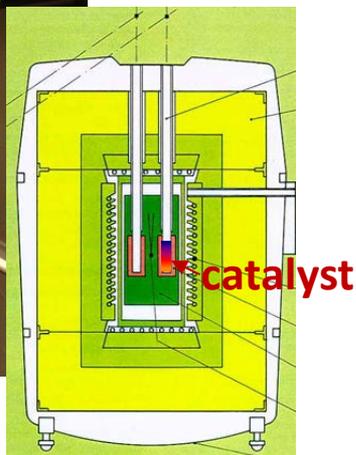
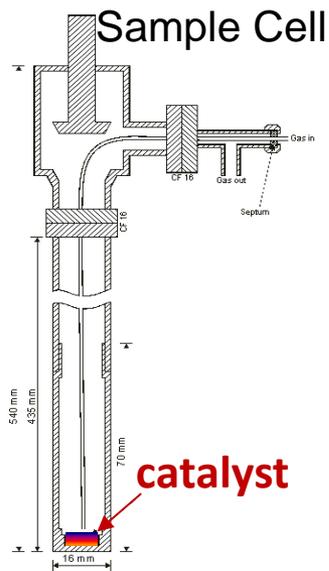
- **direct method to determine number, strength and energy distribution of the adsorption sites**
- key to the effective use of adsorptive microcalorimetry is the **careful choice of probe molecules and the adsorption temperature** to study
- use of probe molecules such as **educt, intermediate, product** or molecules closely related to the reactants is an elegant method to study the surface sites relevant for catalytic reaction

Micro-calorimeters

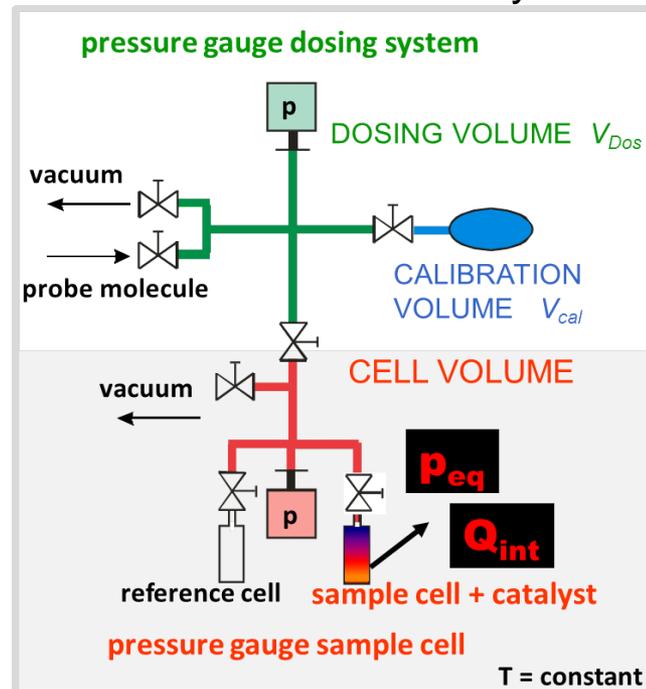


HT1000 (rt-1000°C) and **MS 70** (rt-100°C) Tian-Calvet calorimeter of SETARAM combined with a custom-designed high vacuum and gas dosing apparatus.

Karge, H.G. et al., J. Phys. Chem. 98, 1994, 8053.



Volumetric-Barometric System



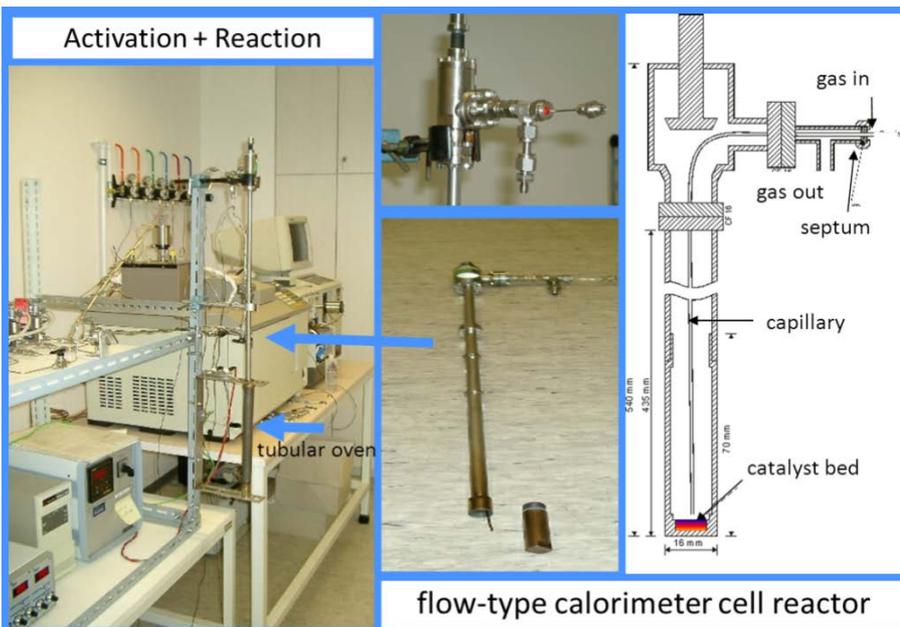
$$\Sigma n_{ads} \text{ vs } p_{eq} \quad , \quad \begin{matrix} \text{mmol} * \text{g}^{-1} \\ \text{mmol} * \text{m}^{-2} \end{matrix}$$

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

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

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

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



Activation:

UHV (10^{-8} hPa), gases (H_2 , O_2 ),
rt - $600^\circ C$

Reaction:

Calorimeter cell can be used as a flow-type reactor.

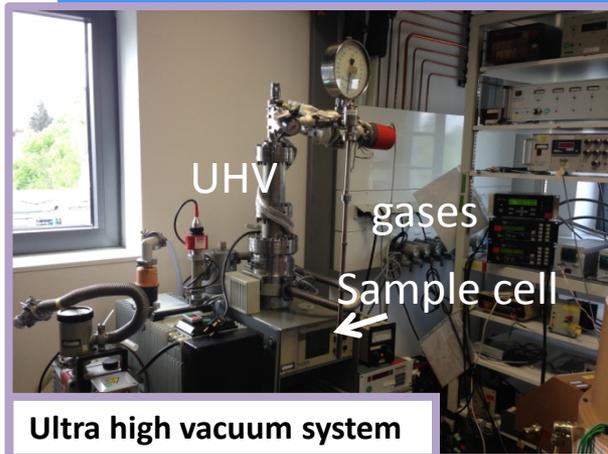
Catalyst is used in the selected reaction until steady-state performance, rt - $600^\circ C$

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.



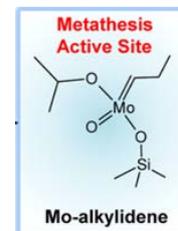
Ultra high vacuum system



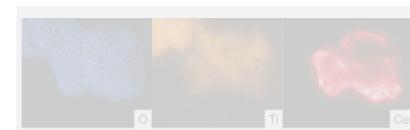
Microcalorimeter + volumetric system

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

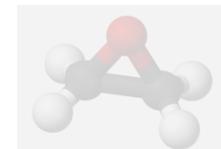
1. Propylene Metathesis over MoO_x/SBA-15

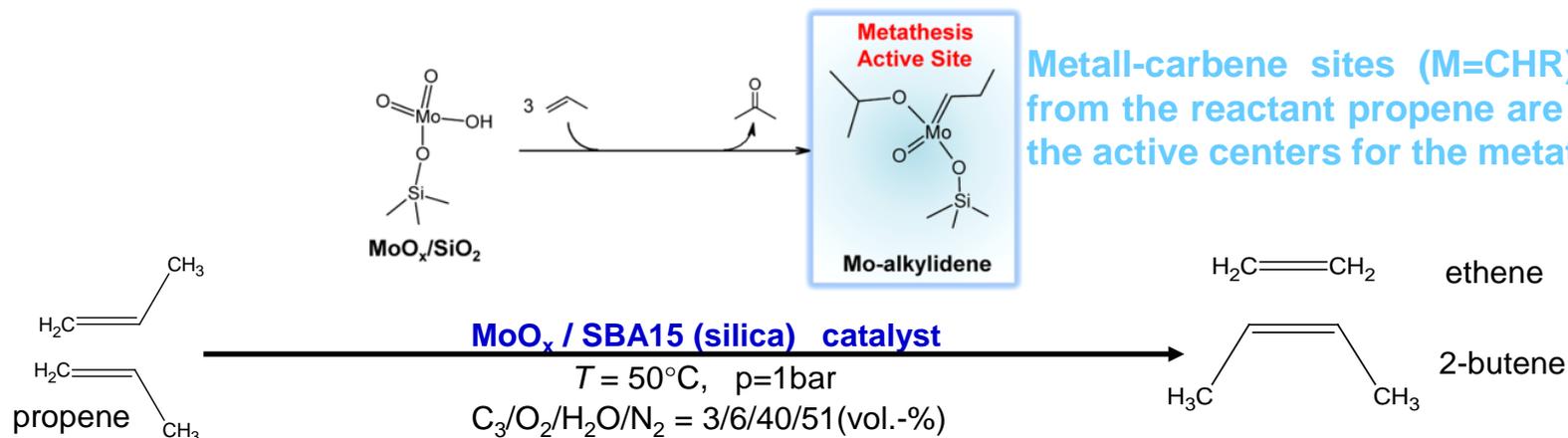


2. 1-hexyne adsorption at $T_{\text{react.}}$ on supported ceria, being unexpectedly active in the three-phase semi-hydrogenation of 1-hexyne.



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





Intention: Studying of the catalytically active surface sites - quantification

Adsorption



propylene as probe molecule

Microcalorimetry :



$T_{\text{adsorption}} = 50^\circ\text{C} = T_{\text{reaction}}$



selected catalysts: different activity

13 % MoO_x/SBA15

Metathesis rate = 3.0 μmol/m²*h

10 % MoO_x/SBA15

Metathesis rate = 13.0 μmol/m²*h

5 % MoO_x/SBA15

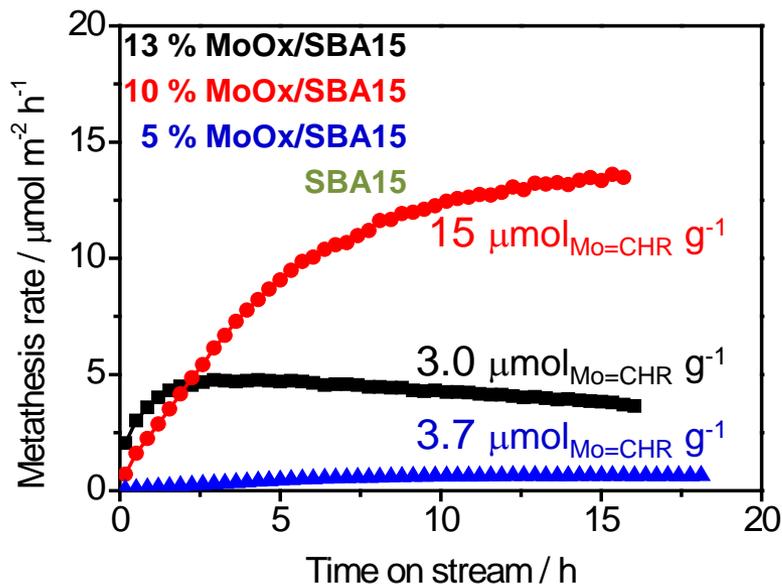
Metathesis rate = 1.5 μmol/m²*h

SBA15

Metathesis rate = 0.0 μmol/m²*h

Propene Metathesis Activity

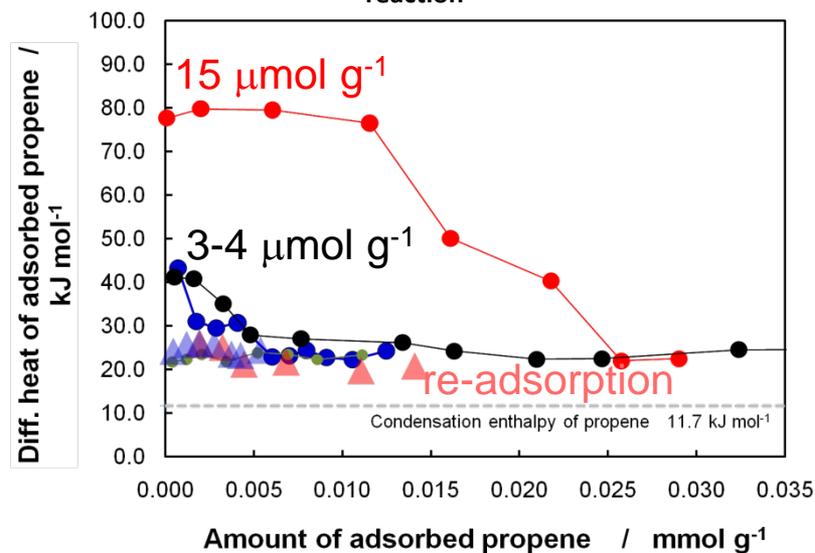
T = 50 °C



Microcalorimetry

Differential heat of propene adsorbed on MoOx/SBA15

T_{reaction} = 50 °C

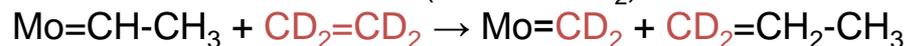


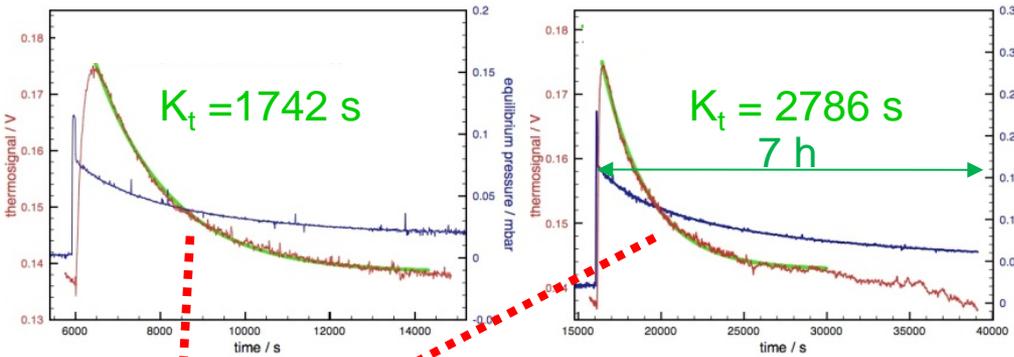
➤ Activity strongly depends on the Mo loading

➤ Correlation between amount & strength of C₃H₆ adsorption sites and catalytic activity.

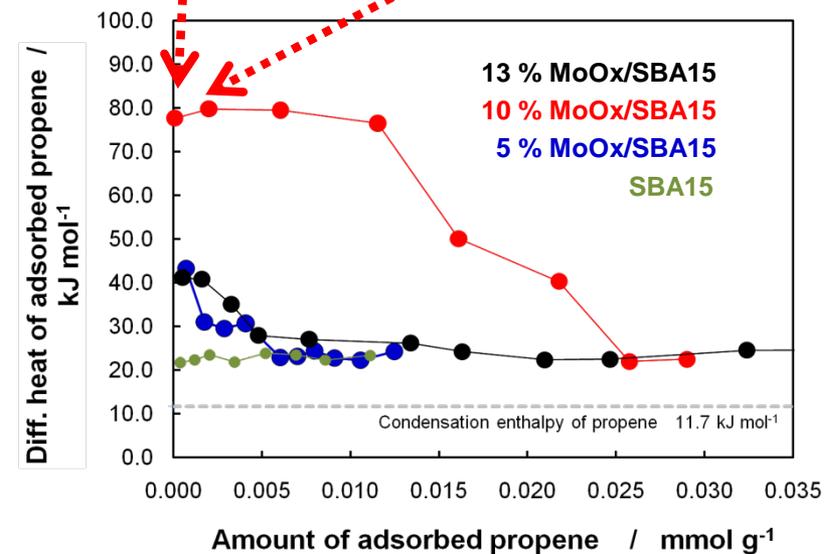
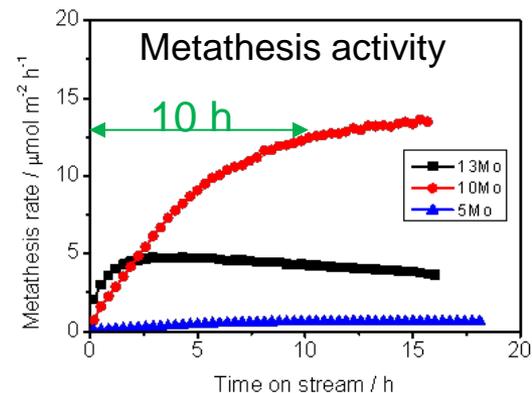
Post-reaction carbene titration

Active site counting was performed after metathesis using post-reaction ethene-*d*₄ (CD₂=CD₂) metathesis to titrate the formed metal-carbene (Mo=CH-CH₂) sites.

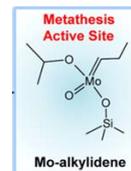
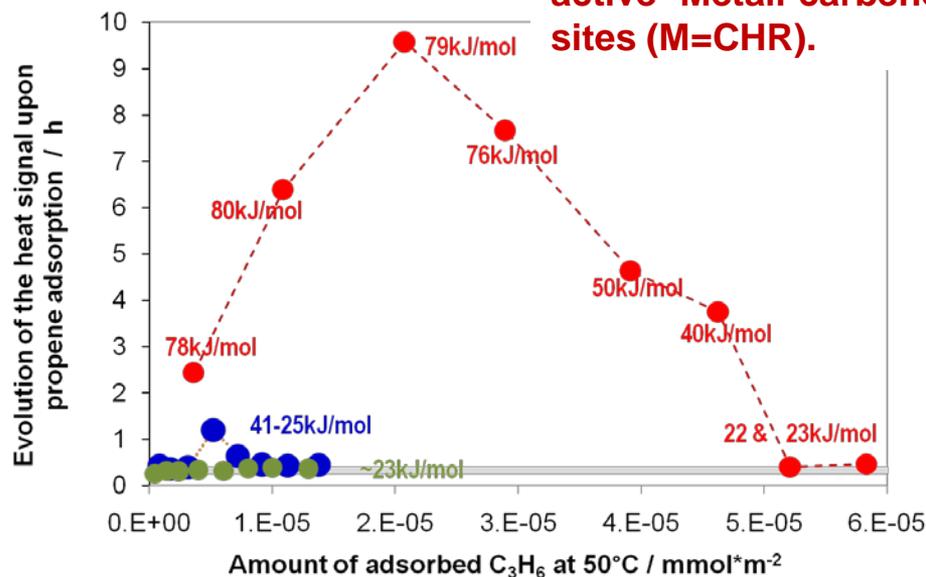




A long decay time and fine structure in the exothermic signal indicate reactive adsorption.



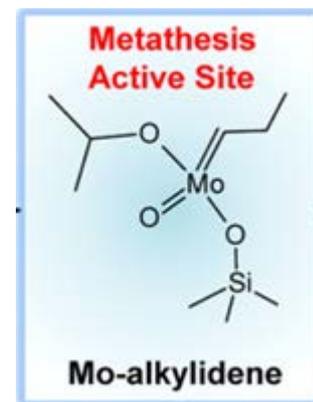
Generation of the active Metall-carbene sites ($\text{M}=\text{CHR}$).



- The active catalyst is characterized by:
- higher amount of ads. sites for propylene
 - strong and irreversible adsorption of propylene on MoO_x sites
 - energetically homogeneously distributed active sites

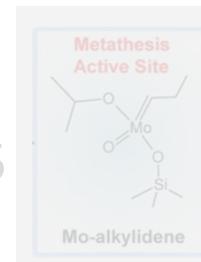
- Catalytic activity is directly correlated with the strength of the propylene interaction with the active surface site.

- ca. 1% of Mo atoms formed active sites

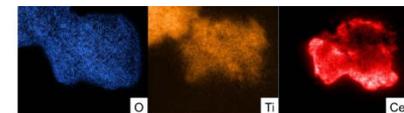


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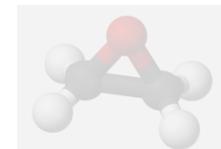
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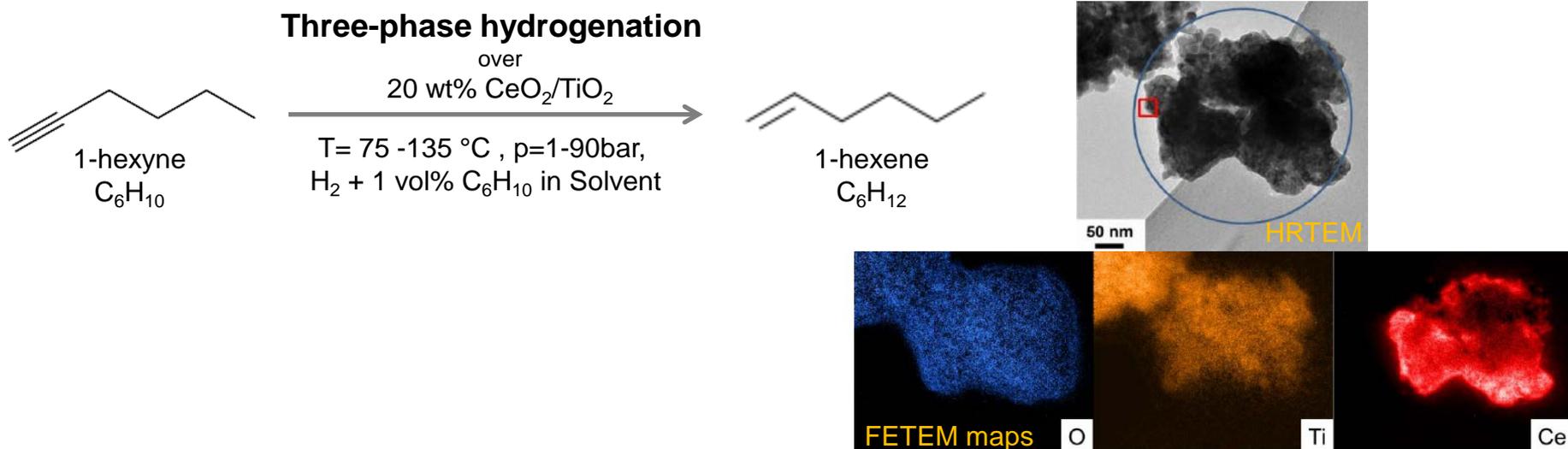
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3. Silver as a catalyst for the ethylene epoxidation - Ag-O system in catalysis



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



Intention: Does calorimetry offers the possibility to distinguish between catalysts of similar characteristic properties (IR , XRD , TEM , XPS , BET), but different catalytic activity?

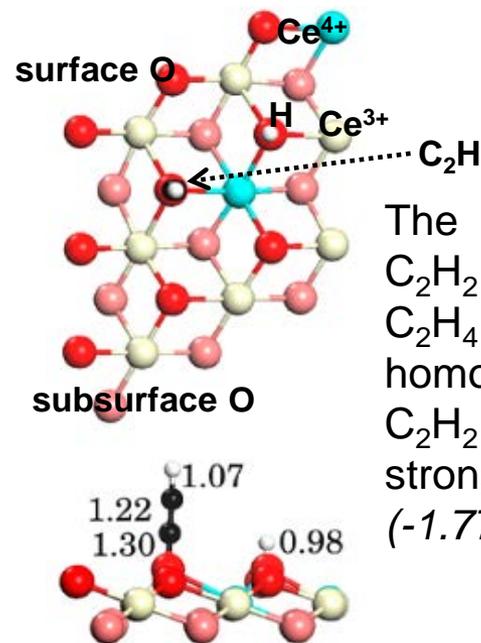
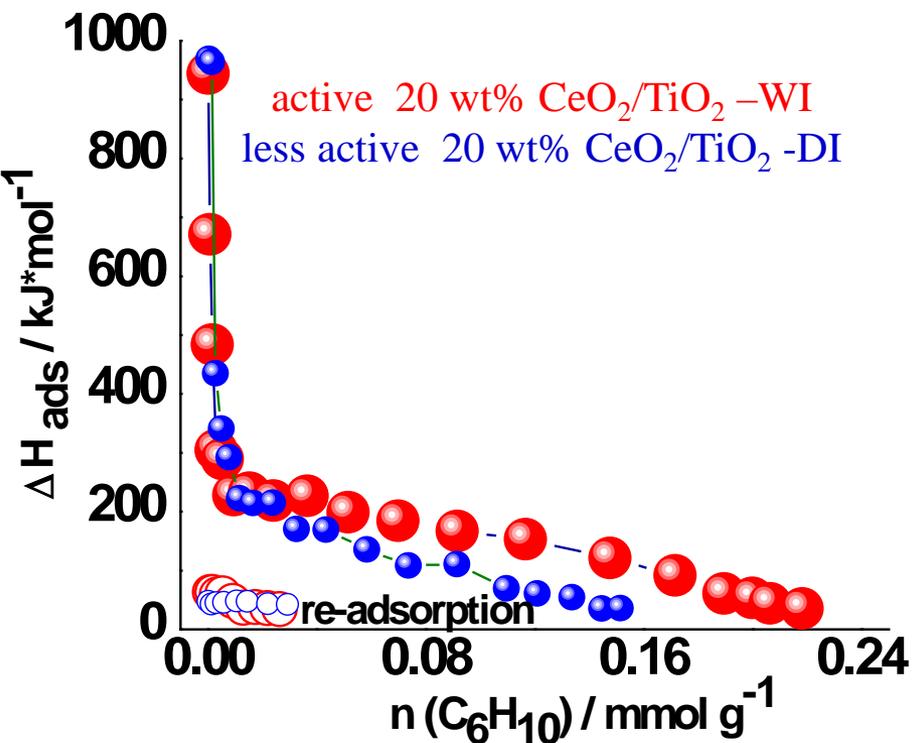
Adsorption
Microcalorimetry :

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

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

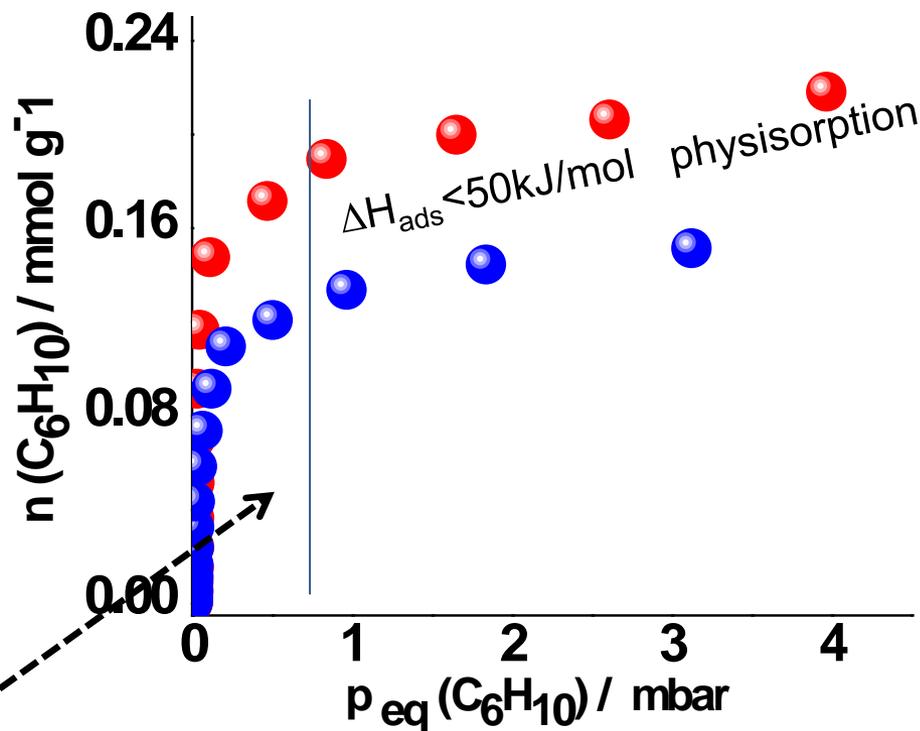
- $\Delta H_{\text{ads.}, \text{initial stage}}$: $\leq 200 - 900 \text{ kJ/mol}$ $10 \mu\text{mol/g}$ \rightarrow very strong irreversible ads.
 \rightarrow multiple dehydrogenation steps [1]
formation of stable surface intermediates [2]
- $\Delta H_{\text{ads.}, \text{plateau}}$: $\sim 200 \text{ kJ/mol}$ $60 \mu\text{mol/g}$ \rightarrow dissociative homolytic adsorption of C_6H_{10}
 \rightarrow 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 $T_{\text{react.}} = 80^\circ\text{C}$ on supported ceria

Adsorption Isotherm



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

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

less active 20 wt% $\text{CeO}_2/\text{TiO}_2$ -DI \rightarrow 130 $\mu\text{mol/g}$ reacted 1-hexyne molecules

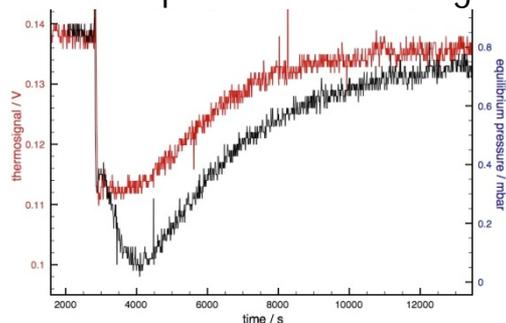
1-hexyne adsorption at $T_{\text{react.}} = 80^\circ\text{C}$ on supported ceria

Corresponding integral heats

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

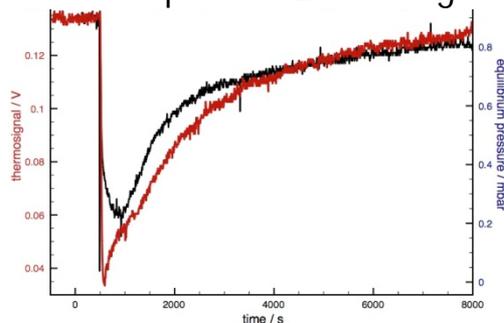
1st ads. step = 0.0023 mmol/g

1st ads. step = 0.00039 mmol/g



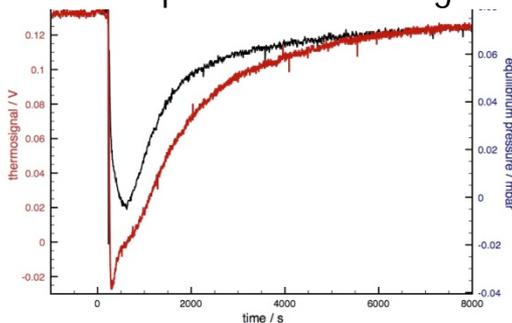
4th ads. step = 0.0031 mmol/g

3rd ads. step = 0.0029 mmol/g



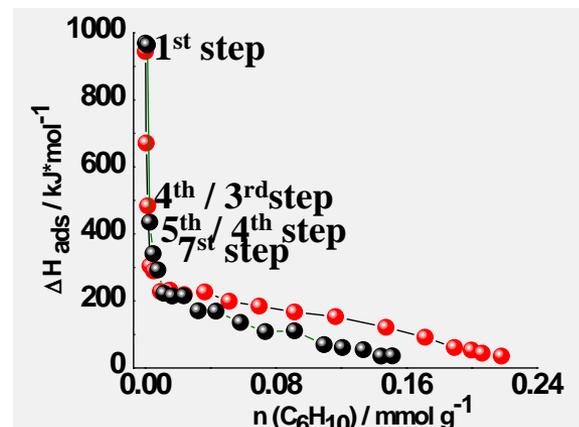
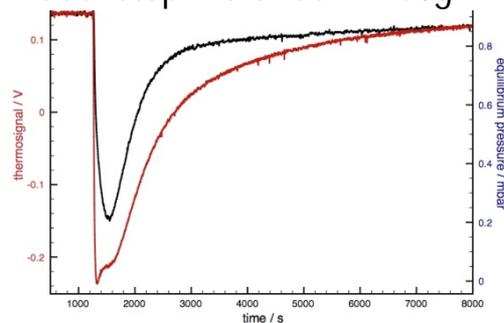
5th ads. step = 0.0053 mmol/g

4th ads. step = 0.0050 mmol/g



7th ads. step = 0.0153 mmol/g

7th ads. step = 0.0166 mmol/g



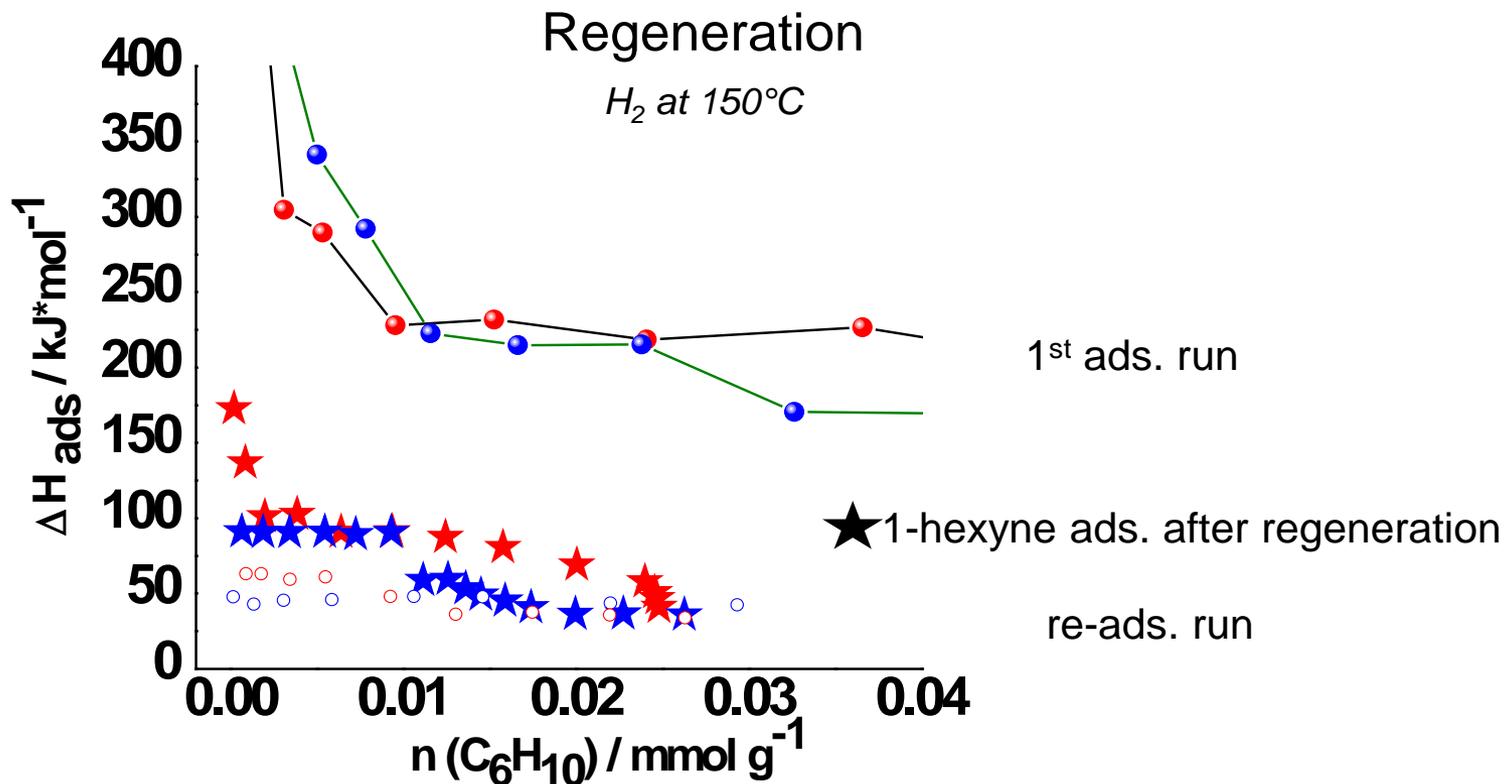
The adsorption signature is composed of two main contributions:

- physisorption / *fast-signal*
- reaction / *delayed signal*

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

In the **less active sample** the physisorbed molecule undergoes much faster side reactions or strong chemisorption.

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

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:

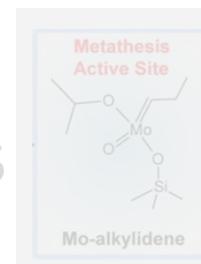
- 1) unspecific adsorption (physisorption $<50\text{kJ/mol}$)
- 2) time-consuming secondary process is due to single or multiple dehydrogenation steps and potentially oligomerization. ^[10] ($>50 - 900\text{ kJ/mol}$)

The most active catalyst is characterize by:

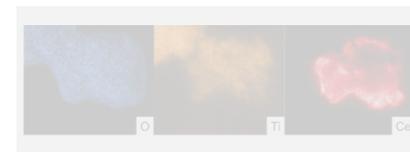
- higher amount of adsorption places for 1-hexyne $190\ \mu\text{mol/g}$
- slightly easier regeneration of the surface after 1-hexyne contact at T_{react} .
- pronounced trapped and phys. state of the adsorbates to find the most suitable place for reaction → dynamic surface is apparently favorable for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

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

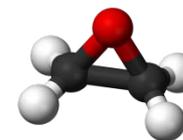
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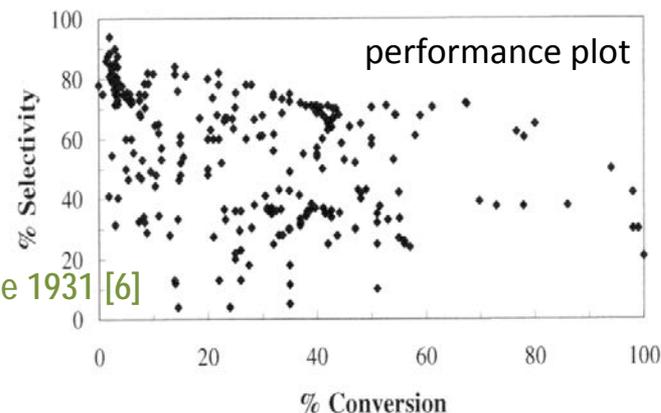


3. Silver as a catalyst for the ethylene epoxidation - Ag-O system in catalysis



- **Ag** is used as a catalyst in two important large scale processes in the chemical industry, the **ethylene epoxidation** and **methanol oxidation**.

The **economic relevance** of these processes motivated the extensive investigation of the Ag-O system in past years. The mechanisms behind the **remarkable selectivity** are still unclear.

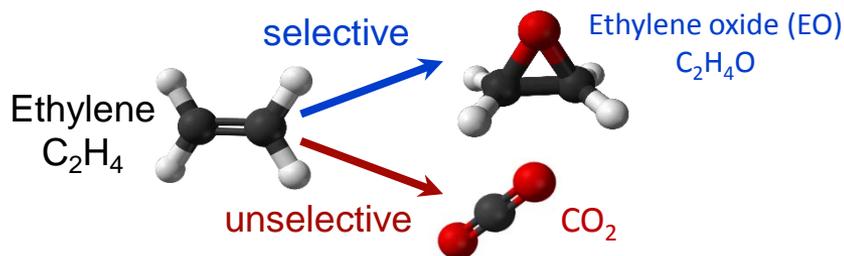


- The current understanding of oxidation reactions on Ag catalysts rely on the knowledge about the **oxygen species formed on silver** [1].
- Final goal is to safely **translate the electronic signatures** obtained by X-ray spectroscopies **into structural information**, which can be used to construct reaction mechanisms [4,5].

- [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.

epoxidation of ethylene over silver catalyst

$T = 180 - 230 \text{ }^\circ\text{C}$



versatile
intermediate

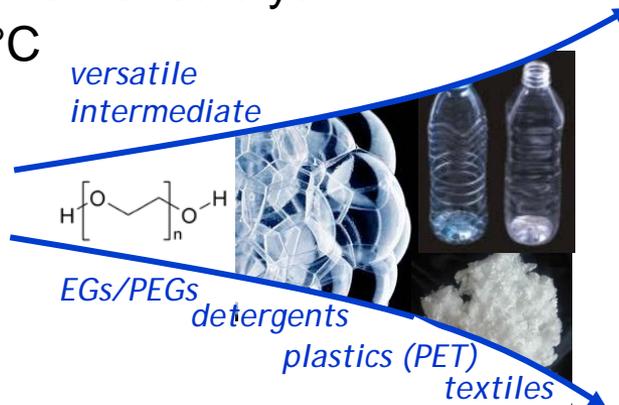


EGs/PEGs

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

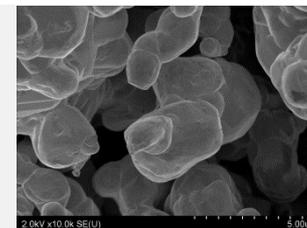
★ Oxygen

Adsorption:

★ $T_{\text{reaction}} = 230 \text{ }^\circ\text{C}$

Microcalorimetry

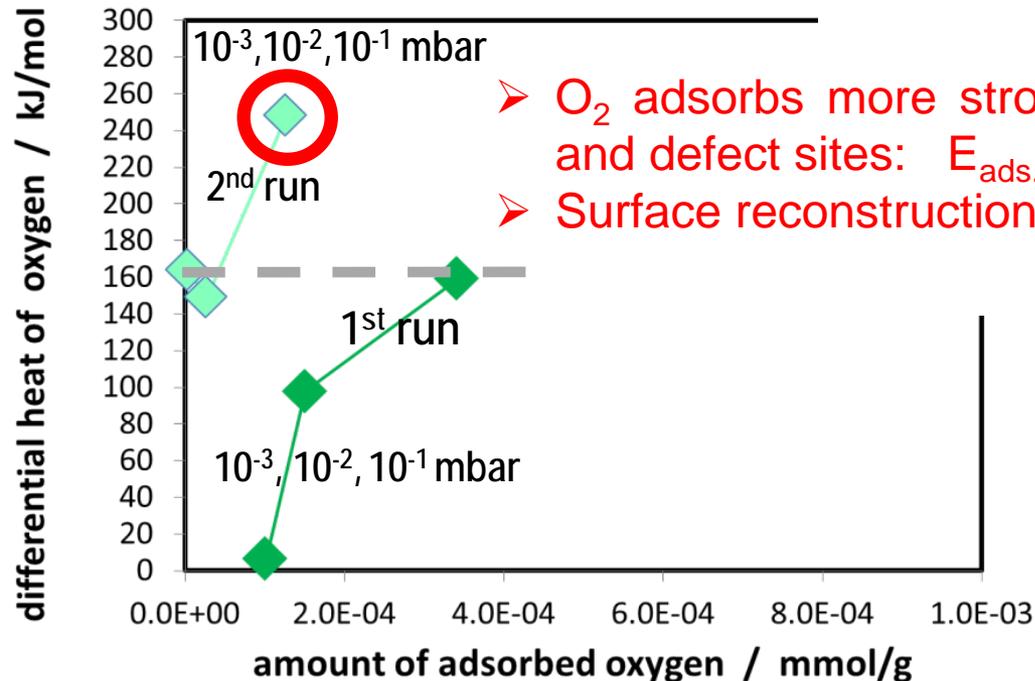
★ selected catalyst: Ag powder <45micron



Initial State

Cleaning of the silver surface observed by calorimetry

Differential heat of O₂ ads. at 150°C



DFT

- O₂ 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

$q_{\text{diff}} \uparrow$ is due to the exothermic reaction of oxygen atoms with the carbon contaminants (CH_x/CO₃).

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

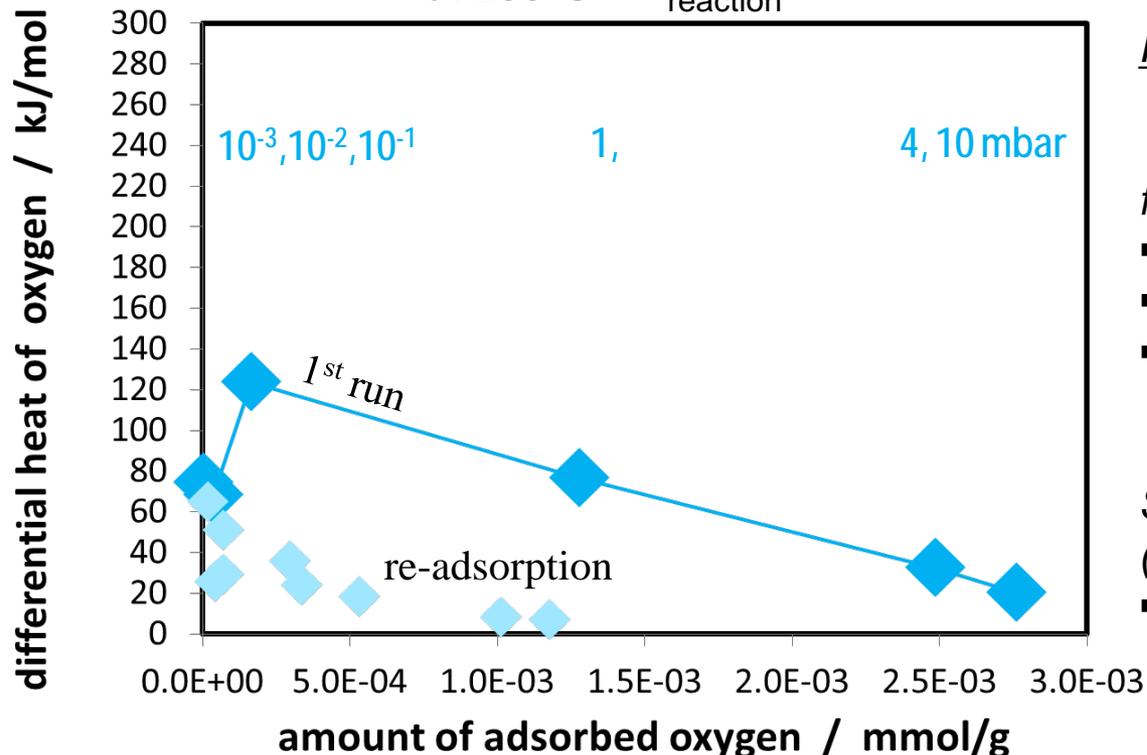
[4] Auroux, A. & Gravelle, P.C., 1981. Comparative study of the bond energy of oxygen at the surface of supported silver catalysts and of the activity of these catalysts for ethylene epoxidation. *Thermochemica Acta*, 47, pp.333–341.

[5] Anderson, K.L., Plischke, J.K. & Vannice, M., 1991. Heats of Adsorption of Oxygen, Ethylene, and Butadiene on Al₂O₃-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 Al₂O₃-Supported Silver. *Journal of Catalysis*, 160, pp.148–160.]

Steady State

Differential heat of O₂ 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_f°) of O adatoms on Pt(111):

- 109 – 99 kJ/mol

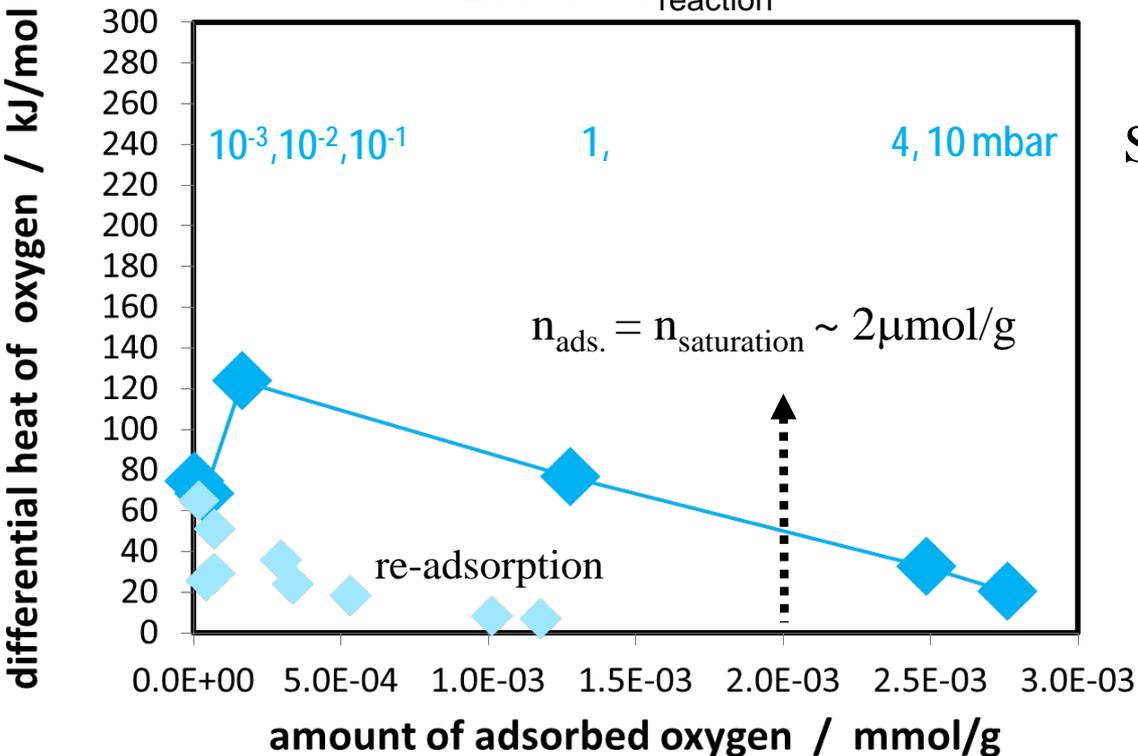
Note: The enthalpy is insignificantly affected by the temperature (DFT)

[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.

Steady State

Differential heat of O₂ ads. on the clean Ag surface
at 230°C = T_{reaction}



Specific surface area of Ag for O₂
at T_{reaction} = 230°C

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

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

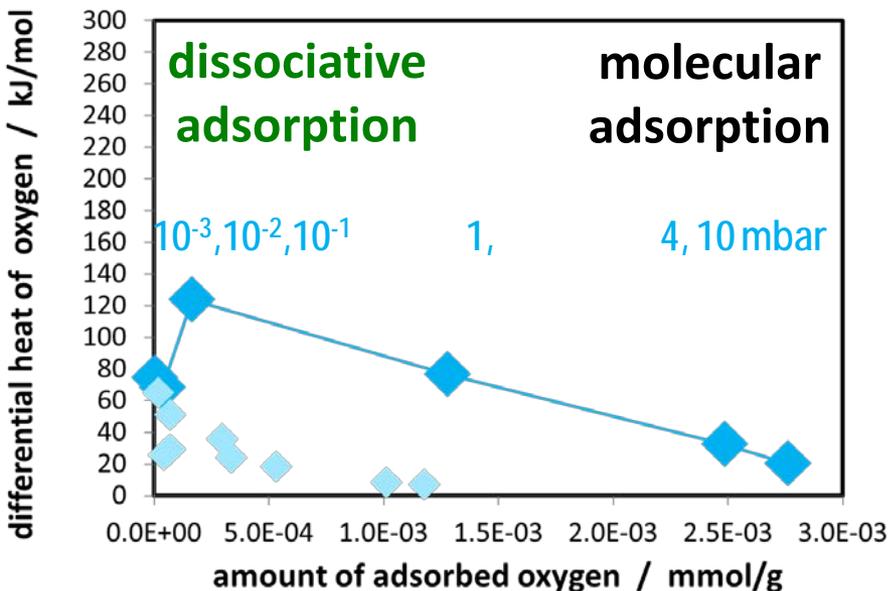
$$S_{\text{Ag-O}} = 0.86 \text{ m}^2/\text{g}$$

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

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

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

Experiment

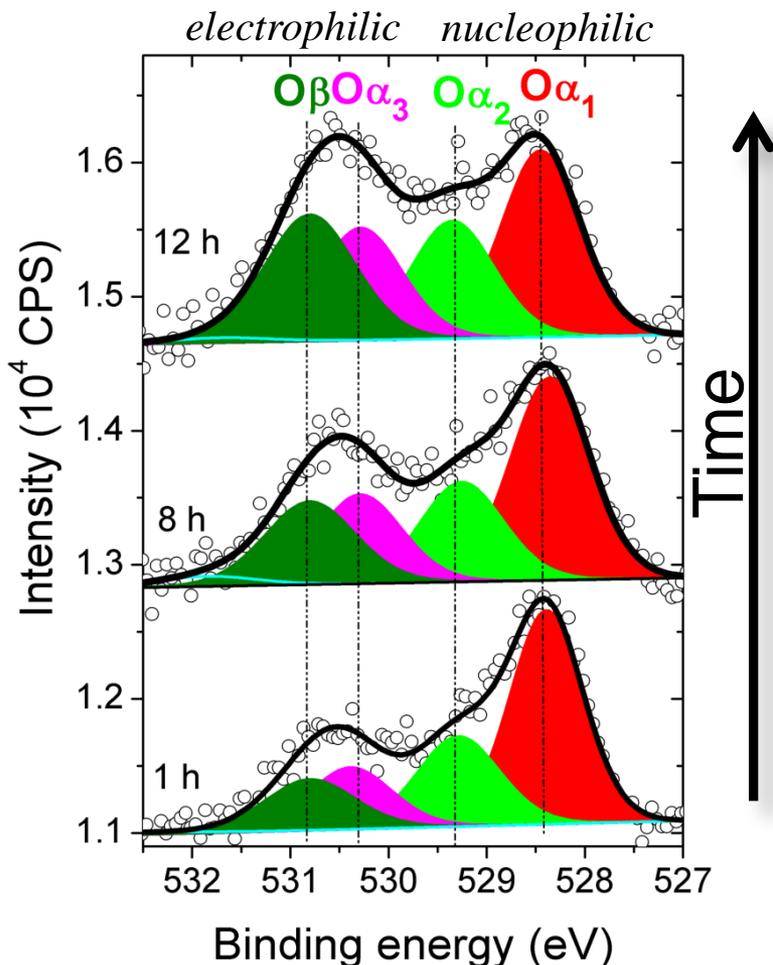


Theory

DFT calculations

system	E _{ads} per 1/2 O ₂ [kJ/mol]	E _{ads} 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
O ₂ clean surface	5-10	10-20
O ₂ on sub O	10-20	20-40
O ₂ on defects	20-30	40-60

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



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

T ° C	p _{O2} mbar	n _{ads.} μmol _{O2} /g _{Ag}	q _{diff} kJ/mol	Ag-O dynamics	DFT
T _{cleaning} 150	< 10 ⁻¹	0.5	>120 - 260	<ul style="list-style-type: none"> ➤ dissociative adsorption ➤ cleaning the surface from CH_x/CO₃ ➤ initial formation of the surface reconstructions 	
T _{reaction} 230	10 ⁻¹ - 1	1.5	>50 - 120	<ul style="list-style-type: none"> ➤ 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	<ul style="list-style-type: none"> ➤ molecular oxygen adsorbed on surface vacancies **** ➤ formation of electrophilic oxygen ***** ➤ O₂ on subsurface oxygen 	

○ Ag_{surf}
 ● Ag_{sub}
 ● O

c(6x2)
 Ag(110)reconstruction

* 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: O₂ stabilized on defects on O covered surface (DFT) or surface oxygen modified by sub-surface species (XPS)



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>

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