Mikrokalorimetrische Untersuchungen zum dynamischen Verhalten von heterogenen Katalysatoren unter quasi-realen Reaktionsbedingungen

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Introduction

- heterogeneous catalysis involves specific chemical interactions between the surface of a solid and the reacting gas molecules

- the catalytic cycle is generally composed of adsorption step, 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 - to get a better understanding of the complex microkinetics

- subsequent reaction and desorption processes are confirmed partially irreversible events and prove the dynamic nature of the catalyst surface.
  → Reactants Induced Dynamic Responses simulated *via* ads./des. cycles

- since perhaps only a minor fraction of all surface atoms form active centers

Adsorption Isothermal Microcalorimetry

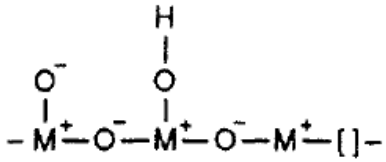
- direct method to determine number, strength and energy distribution of the adsorption sites

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

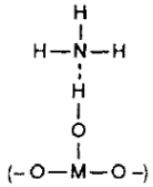
surface sites

careful choice of probe molecules and the adsorption temperature

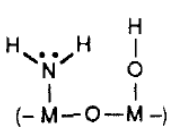
metal oxide catalysts provide acid/base properties

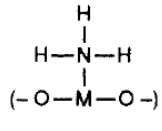


Brønsted acid sites:
transfer of H^+ from OH to Adsorbate

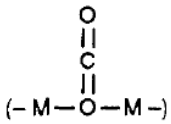


Lewis acid sites:
coordination to an electron-deficient metal atom $_{cus}Me^{n+}$

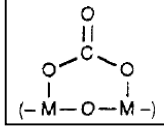


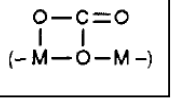


oxygen vacancy: O^{2-}

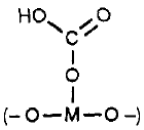


metall cations under participation of oxygen: $Me_xO^-_y$





OH^-



strong basic NH_3 at RT

weak basic CO at 77 K

acidic CO_2 at RT

Focus

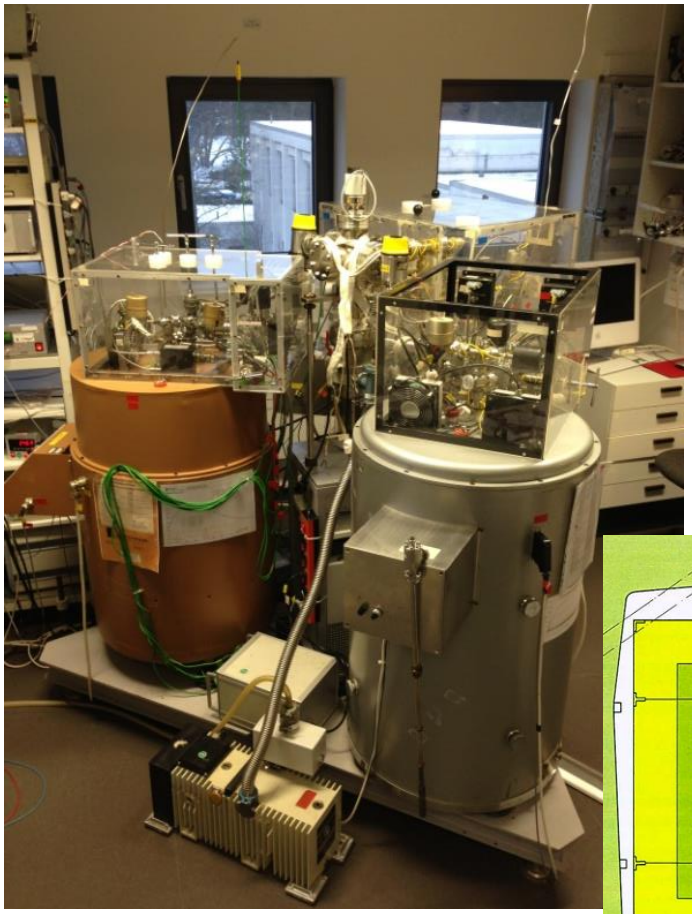
use of probe molecules such as educt, intermediate, product or molecules closely related to the reactants is an elegant method to study the surface sites relevant for catalytic reaction

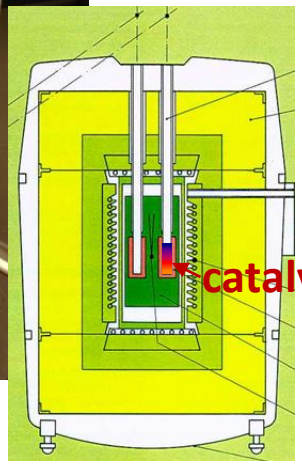
$T_{adsorption} < T_{reaction}$ → study of the pure ads. processes
$T_{adsorption} = T_{reaction}$ → study of the surface chemical events during the reaction

- the study of adsorption-desorption cycles gives new insights into the **dynamic behavior of the catalyst surface**

Equipment

Micro-calorimeters

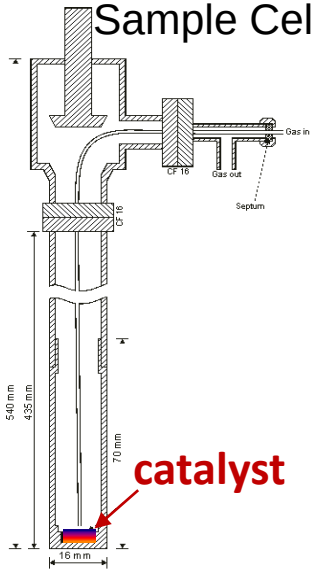




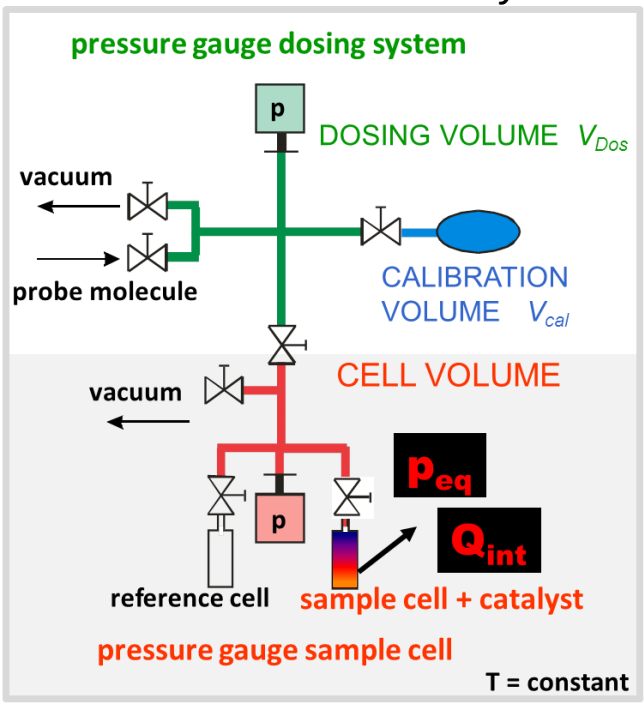
HT1000 (rt-1000°C) and **MS 70** (rt-100°C) Tian-Calvet calorimeter of SETARAM combined with a custom-designed high vacuum and gas dosing apparatus.

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

Sample Cell



Volumetric-Barometric System



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

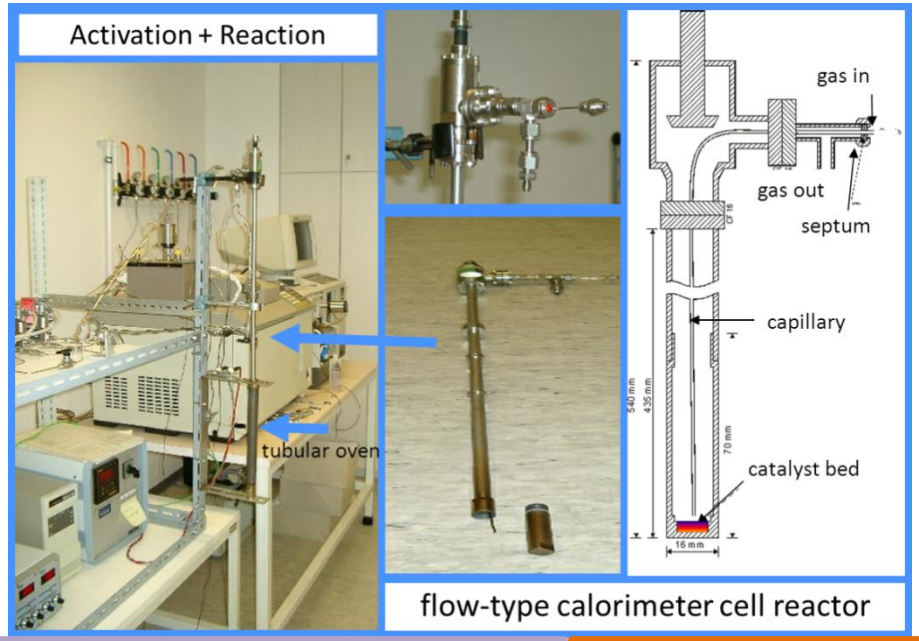
$$q_{diff} = \frac{Q_{int}}{n_{ads}} = \Delta H_{ads} \quad , \quad kJ/mol$$

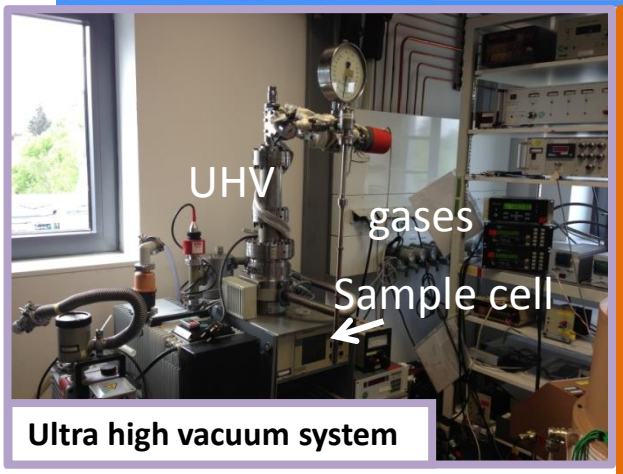
q_{diff} *vs* n_{ads} , kJ/mol

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

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

Experimental procedure





Activation:
UHV (10^{-8}hPa), gases (H_2, O_2 .....),
rt - 600°C

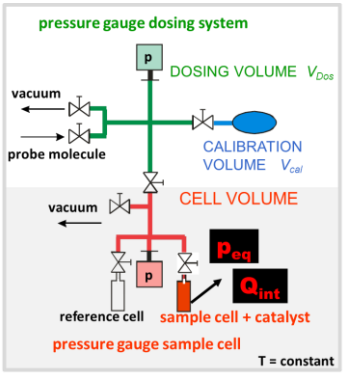
Reaction:
Calorimeter cell can used as a flow-type reactor.
Catalyst is used in the selected reaction until stady-state performance, rt - 600°C

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

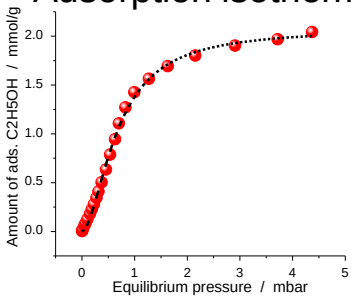
Adsorptive microcalorimetric experiment:
Stepwise adsorption, desorption and re-adsorption of the selected probe molecule at the selected temperature.

Adsorption Calorimetry - Standard procedure

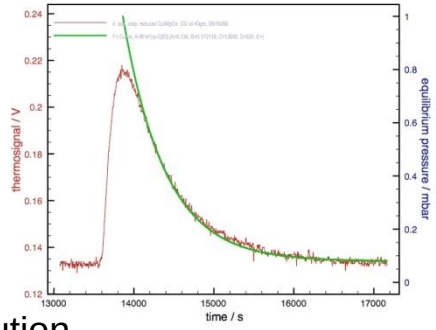
- The probe molecule must be introduced **stepwise** at **constant temperature**, the pressure is increased slowly
- For each adsorption step, the **adsorbed amount** must be determined (isotherm)
- For each adsorption step, the **evolved heat** must be determined (integral heat of adsorption)
- The **differential heat (ΔH_{ads})** can then be determined by dividing the evolved heat through the number of molecules adsorbed in a particular step



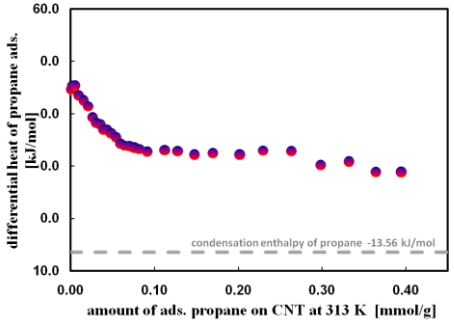
Adsorption isotherm



Integral heat of ads.



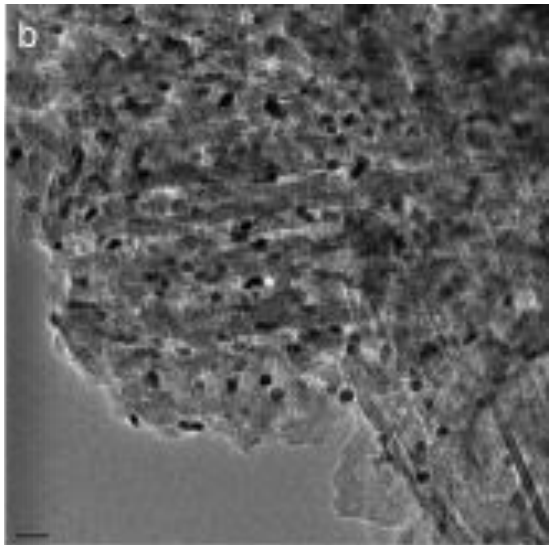
ΔH_{ads} / energy distribution



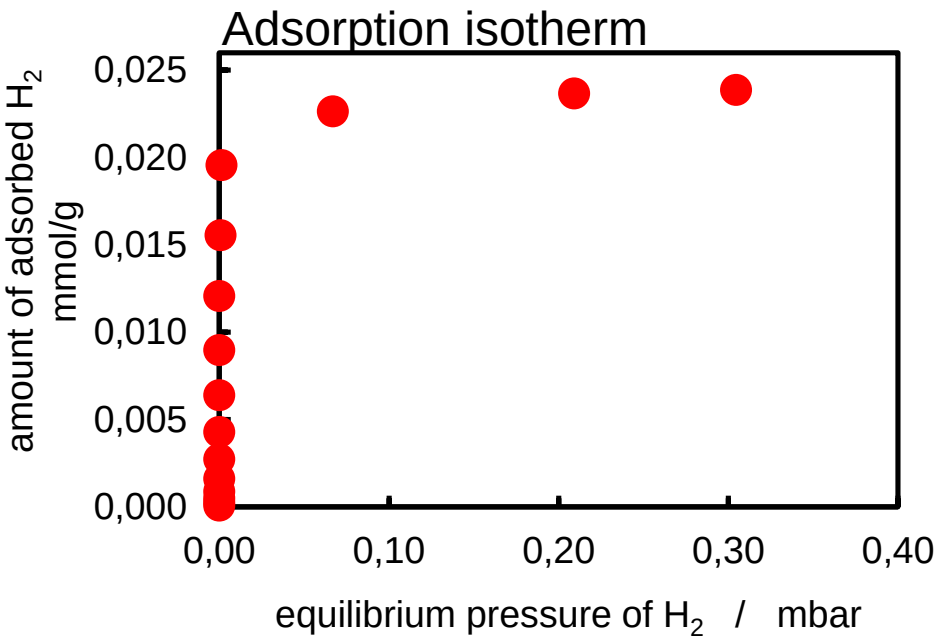
Validation

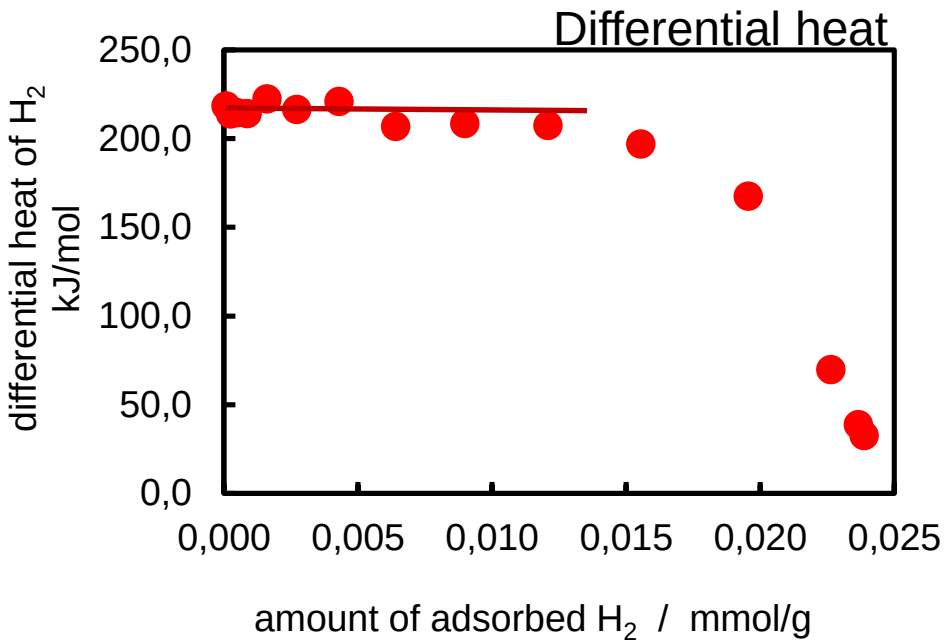
of the SETARAM calorimeter combined with a custom-designed volumetric system

H_2 adsorption on $Pt_{H2\text{-}673K\text{-}2h}/Al_2O_3$ *Quantachrome Instr., Ref.-material, Cat.No.7001* at 40°C



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





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

q_{diff} = 215 kJ/mol : 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

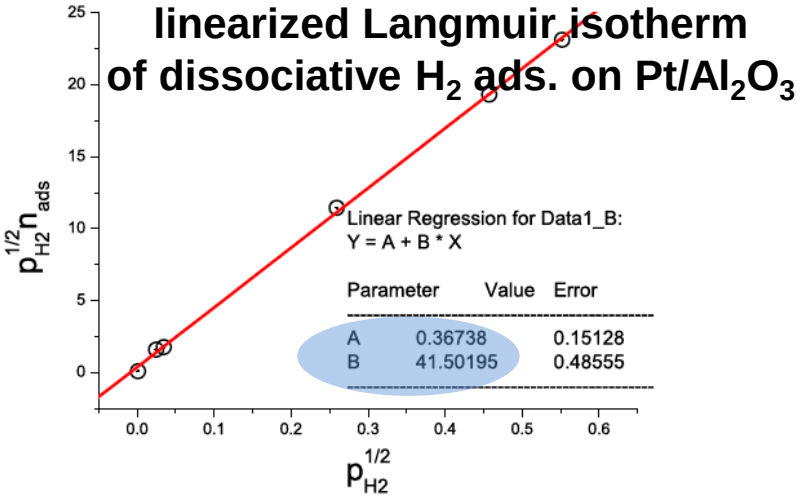
Linearization

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

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

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

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



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}

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

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

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

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

Final Results

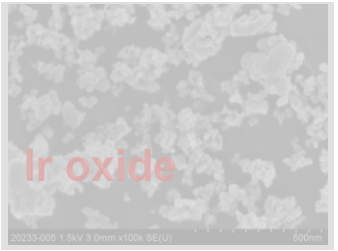
Kinetic parameters determined for the H_2 ads. on Pt/Al_2O_3

n_{mono}	=	$24 * 10^{-6}$ mol · g^{-1}	=	$26 * 10^{-6}$	mol · g^{-1}
K_{ads}	=	10851 mbar^{-1}	=	3946	mbar^{-1}
$\Delta H_{ads.}$	=	215 ±4 kJ · mol^{-1}	=	200 ±4	kJ · mol^{-1}
S_{Pt}	≈	1.0 m^2 · g^{-1}	≈	1.1	m^2 · g^{-1}

CO

Selected applications

1. Ni based catalysts for the dry reforming of methane



2. Reactive oxygen species in iridium-based oxygen evolution reaction (OER) catalysts

3. Dynamic response of a MoV oxide catalyst in propane and ethane adsorption

Ni based catalysts for the dry reforming of methane

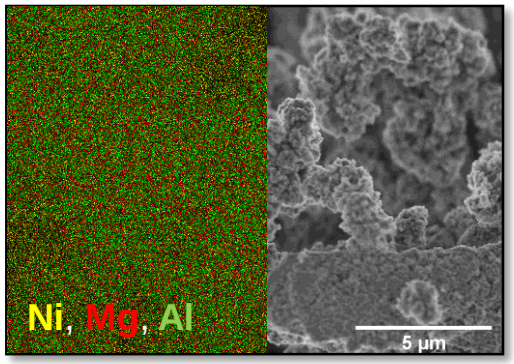
Dry reforming (DRM): $CO_2 + CH_4 \underset{900\ °C}{\overset{Ni}{\rightleftharpoons}} 2\ CO + 2\ H_2$ $\quad \Delta H^0 = 247$ kJ/mol

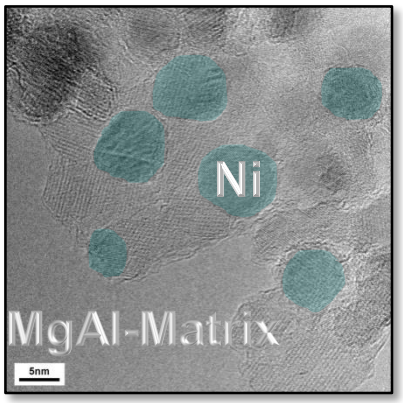
side reactions (⇨ coking):

- Methane pyrolysis: $CH_4 \rightleftharpoons \mathbf{C} + 2H_2$ $\quad \Delta H^0 = 75$ kJ/mol
- Boudouard reaction: $2\ CO \rightleftharpoons \mathbf{C} + CO_2$ $\quad \Delta H^0 = -171$ kJ/mol
- reverse coal gasification: $CO + H_2 \rightleftharpoons \mathbf{C} + H_2O$ $\quad \Delta H^0 = -131$ 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





The catalyst:
Ni/MgAl oxide
by reduction at 1000°C

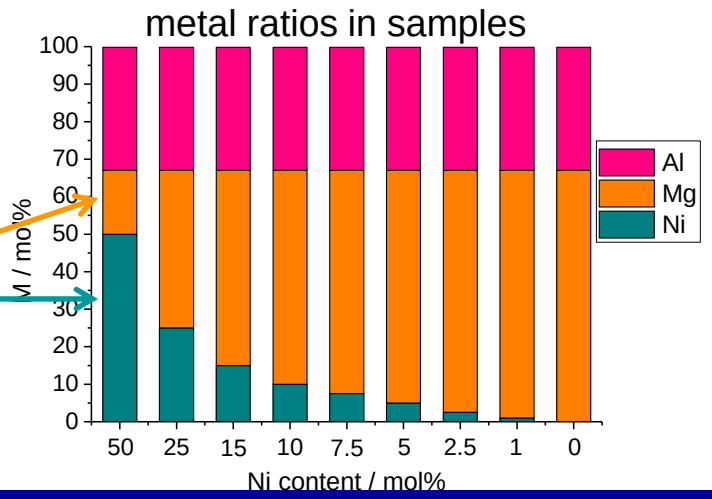
- $d_{P,\ Ni}$ = 7 – 20 nm in all samples

Ni/MgAl oxide catalysts:

- 0-55 wt.-% Ni

50 mol% Ni: **Mg : Al = 1:2 (spinel stoichiometry)**
XRD: metallic Ni in spinel matrix (+ MgO)

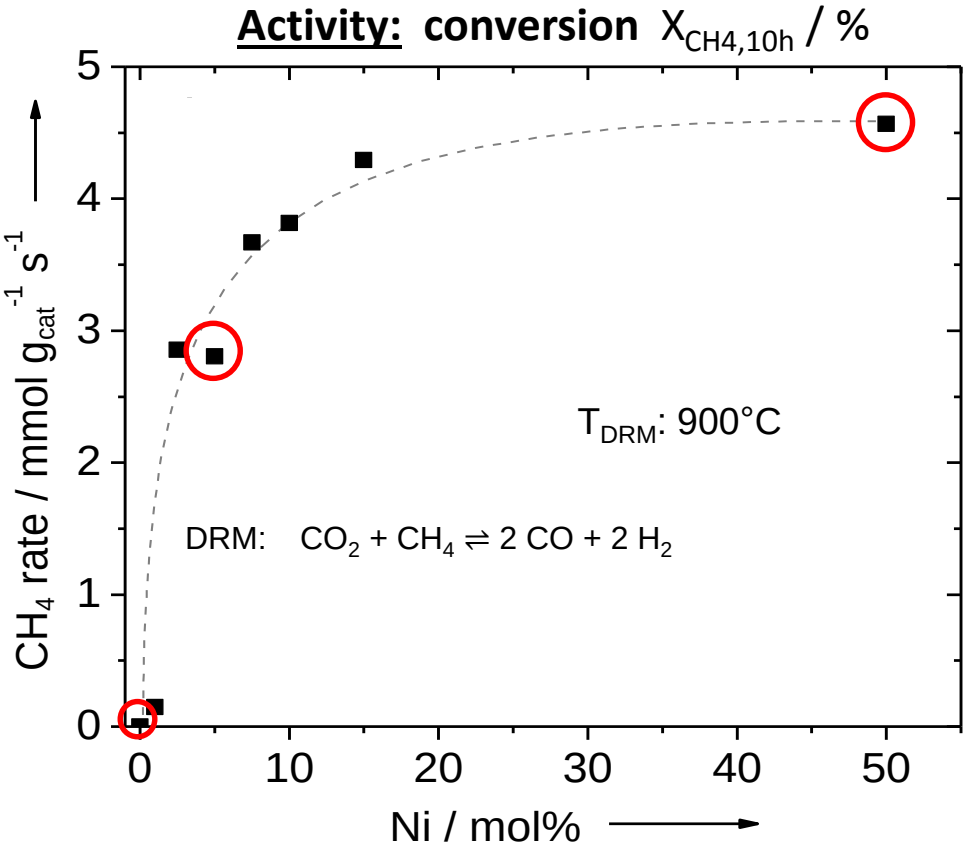
< 50 mol% Ni: exess of Mg



M. Mette, S. Wrabetz, M. Behrens et.al., submitted Jan 2015.

Ni based catalysts for the dry reforming of methane

Intention: In order to define a **structure-activity-relationship,** the properties of the Ni based catalyst were studied by adsorption microcalorimetry using **CO (product) at 30°C**. [2]



Sample	$X_{CH4,10h}$ / %
Ni50	**73**
Ni15	68
Ni10	61
Ni7.5	59
Ni5	**50**
Ni2.5	46
Ni1	3
Ni0	**0**

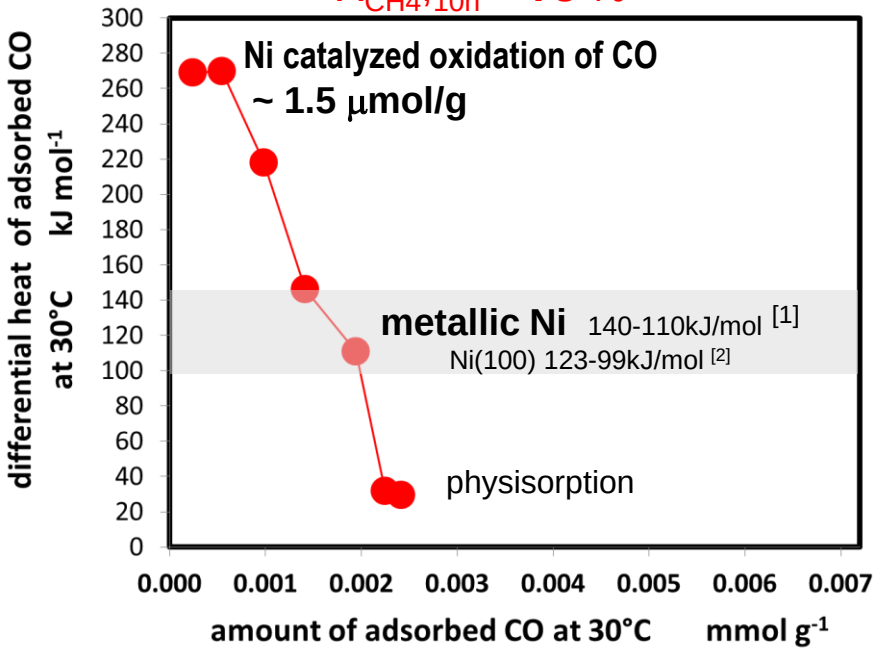
- free Ni sites are essential
- relationship is not linear
- structure sensitivity [1]

1 J. Wei, E. Iglesia, *J. Phys. Chem. B* **2004**, 108, 4094-4103.
2 *M. Mette, …..S. Wrabetz…..M. Behrens, submitted Dec. 2015.*

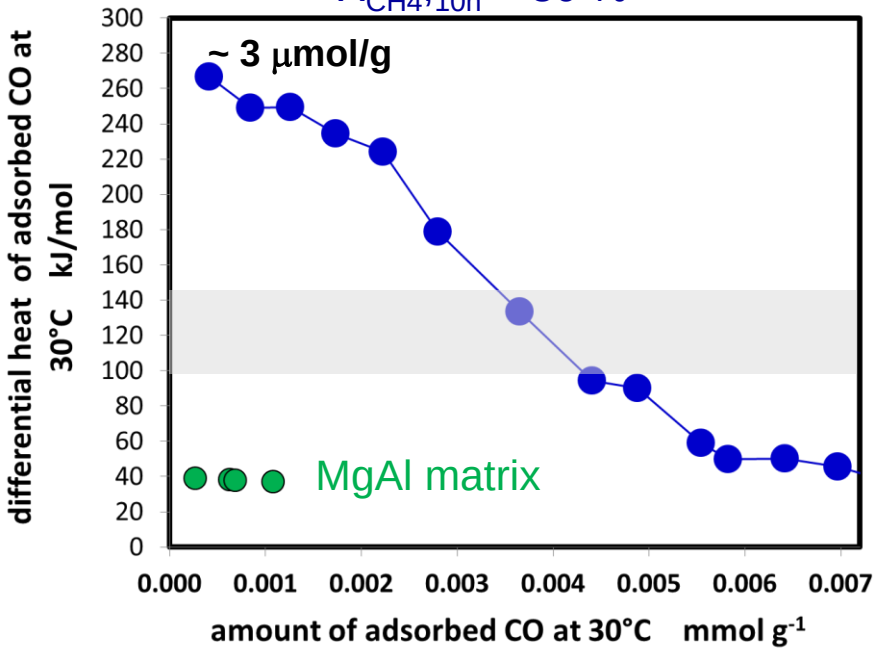
Ni based catalysts for the dry reforming of methane

Microcalorimetry
CO at 30°C

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



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



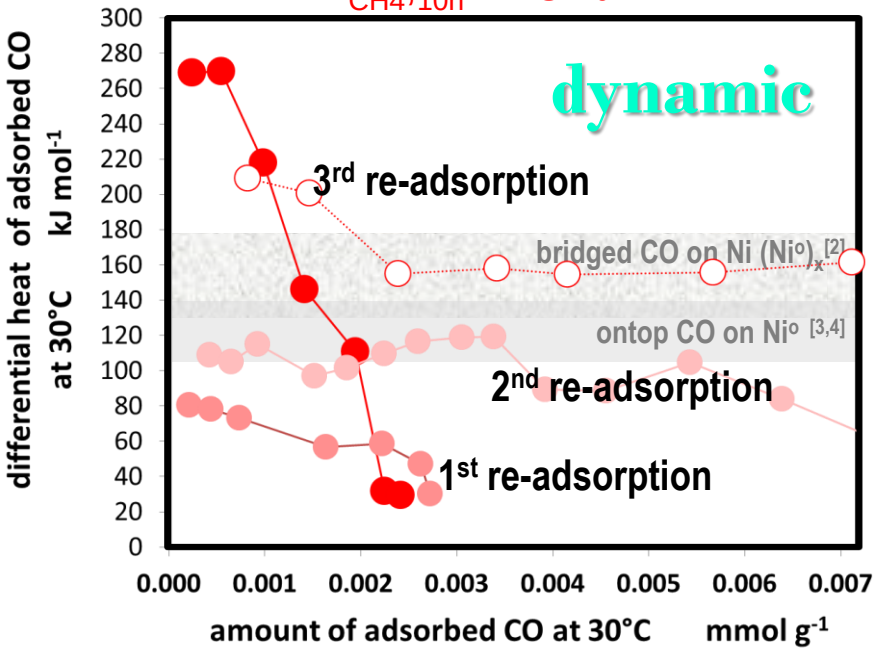
- ***Δn ~ 4μmol/g***
- ~270 kJ/mol: Ni catalyzed oxidation reactions of CO with the oxidic matrix are more pronounced for the catalyst with less Ni and therefore a higher MgO content in the oxidic matrix.

[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.*
M. Mette,S. Wrabetz, M. Behrens , R. Schlögl et.al., submitted Jan 2015.

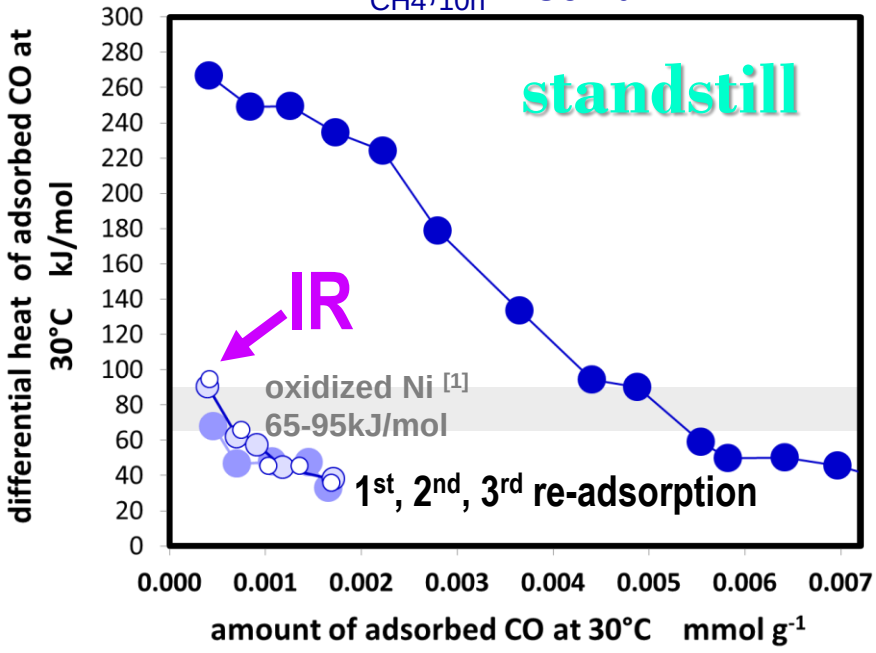
Ni based catalysts for the dry reforming of methane

Microcalorimetry
Adsorption/Desorption cycles
CO at 30°C

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



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



- The mobile character of the Ni-based adsorption sites of the most active surface is apparently favorable for the catalytic performance; perhaps because of generation and/or regeneration of the used active sites.

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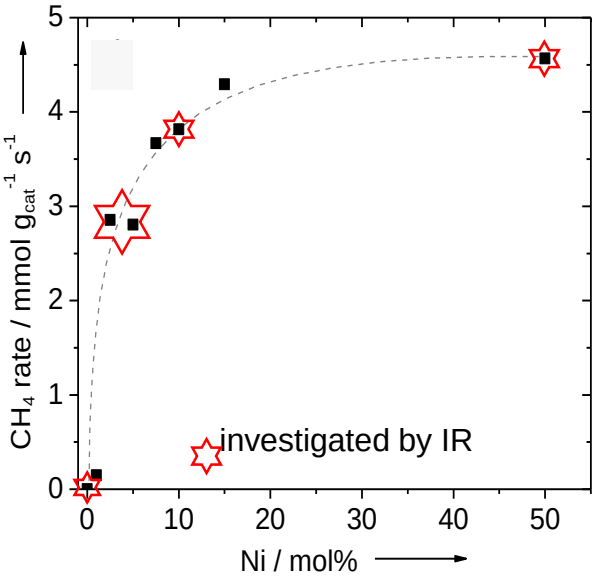
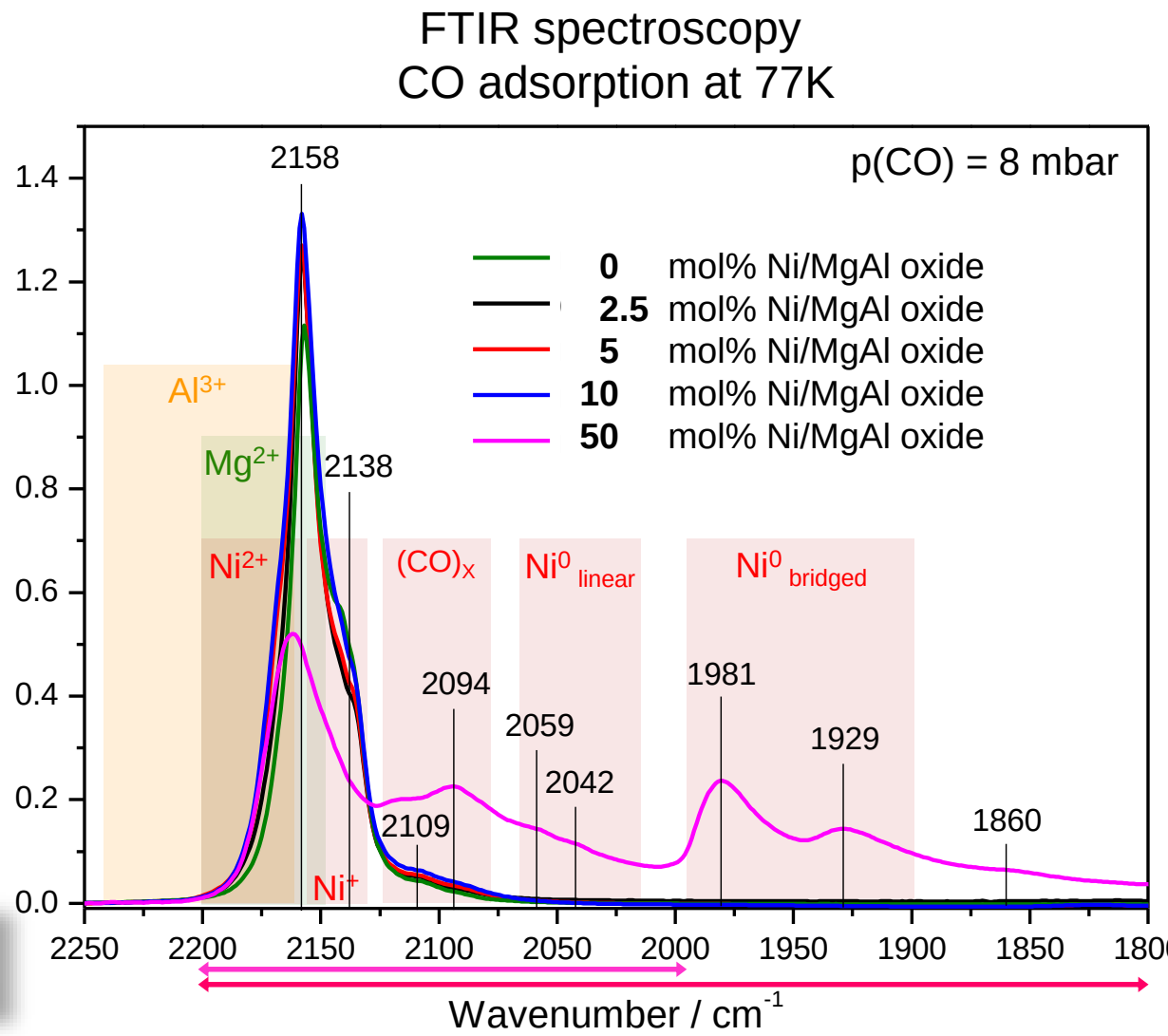
Ni based catalysts for the dry reforming of methane



- spectra of CO adsorbed on NiMgAl samples taken at full CO coverage
- reference band positions taken from literature [1]



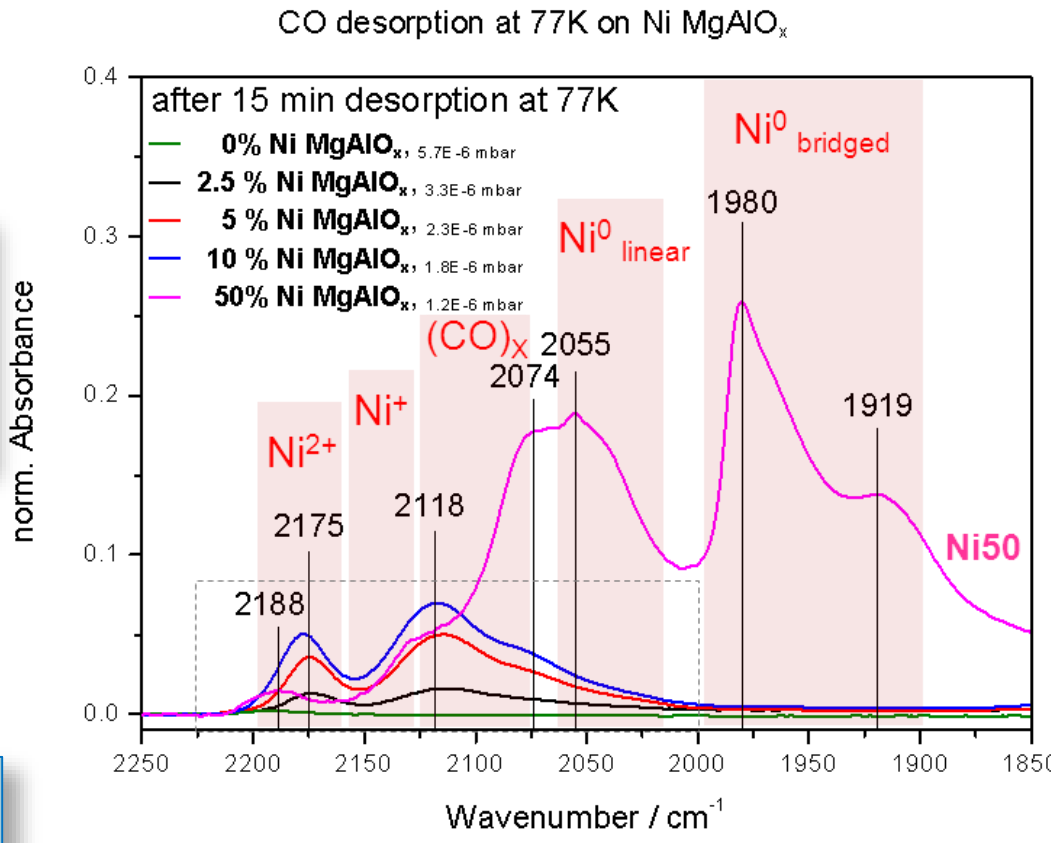
- metallic Ni sites in Ni50 only
- mainly cationic Ni in <50mol% Ni

[1] K. I. Hadjiivanov, G, N. Vayssilov, *Adv. Catal*. **2002**, 47, 307-511

Ni based catalysts for the dry reforming of methane

spectra after evacuation

- amount of residual CO ads. complexes correlates with Ni content
- Ni^0 agglomerates in Ni50 sample
- some isolated Ni^0 sites also in 2.5-10% Ni
- mainly Ni^{x+} in 2.5-10% Ni



- **Results correlates very well with the calorimetric observations**

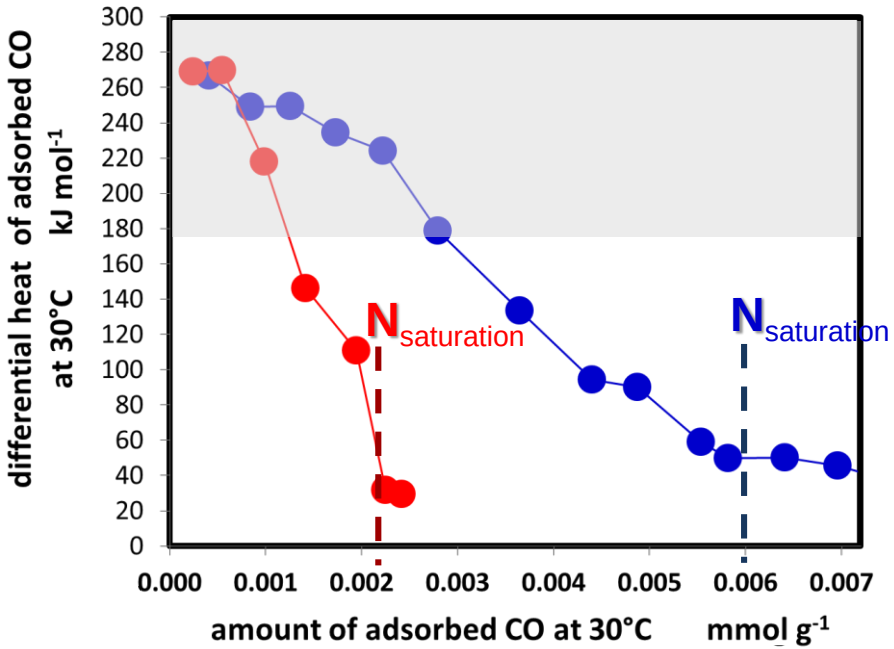
weak interaction
oxidized Ni
65-95kJ/mol

stronger interaction
metallic Ni
140-110kJ/mol
Ni(100) 123-99kJ/mol

Ni based catalysts for the dry reforming of methane

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

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



Metal surface area of Ni for CO at 30°C

$S_{Ni\text{-}CO}$ = 0.09 m²/g
$S_{Ni\text{-}BET\text{-}Calc.,N2\text{-}77K}$ = 226 m²/g
$S_{Ni\text{-}H2\text{-}TPR}$ = 6 m²/g

$S_{Ni\text{-}CO}$ = 0.24 m²/g
$S_{Ni\text{-}BET\text{-}Calc.,N2\text{-}77K}$ = 205 m²/g
$S_{Ni\text{-}H2\text{-}TPR}$ = 3 m²/g

$$S_{Ni,\,CO,\,30grd} = N_{saturation} \cdot \text{stoichiometric factor} \cdot \text{Avogadro´s number} \cdot \text{atomic cross section of the metal}$$

$$= 2.2 / 6*10^{-6}\ \text{mol} \cdot 1 \cdot 6.023*10^{23} \cdot 0.0649*10^{-18}\ \text{m}^2$$

$$= 0.086 / 0.235\ \text{m}^2/\text{g}$$

Ni based catalysts for the dry reforming of methane

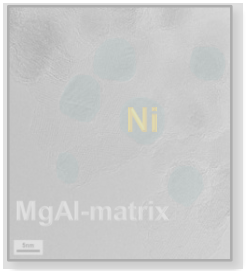
- **The most active catalyst is characterized by:**
  - big Ni^0 agglomerates
  - in the presence of CO an additional notable amount of Ni^0 is formed
  - dynamic character of the Ni-based adsorption sites
  - relatively low amount of Ni free *or* slightly affected MgAl-matrix and hence less degree of oxidation of CO
  - relatively small amount of cationic Ni

$d_{P,\ TEM} = 19.4 \pm 7.1\ nm$
$n_{Ni0} \sim 5 – 7\ \mu mol\ /g$
$q_{diff} = 170 - 110\ kJ/mol$

$n_{matrix} \sim 1.5\ \mu mol\ /g$
$q_{diff} = 270 - 170\ kJ/mol$
$n_{Nix+} \sim 1 – 2\ \mu mol\ /g$

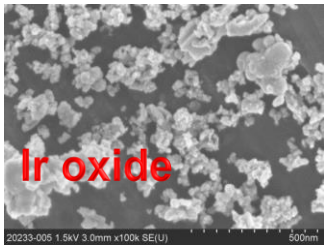
- **Catalytic aspect:**
  -The ***mobile character of the Ni-based adsorption sites*** of the most active surface is apparently favorable for the catalytic performance; perhaps because of generation and/or regeneration of the used active sites.

Selected applications



1. Ni based catalysts for the dry reforming of methane

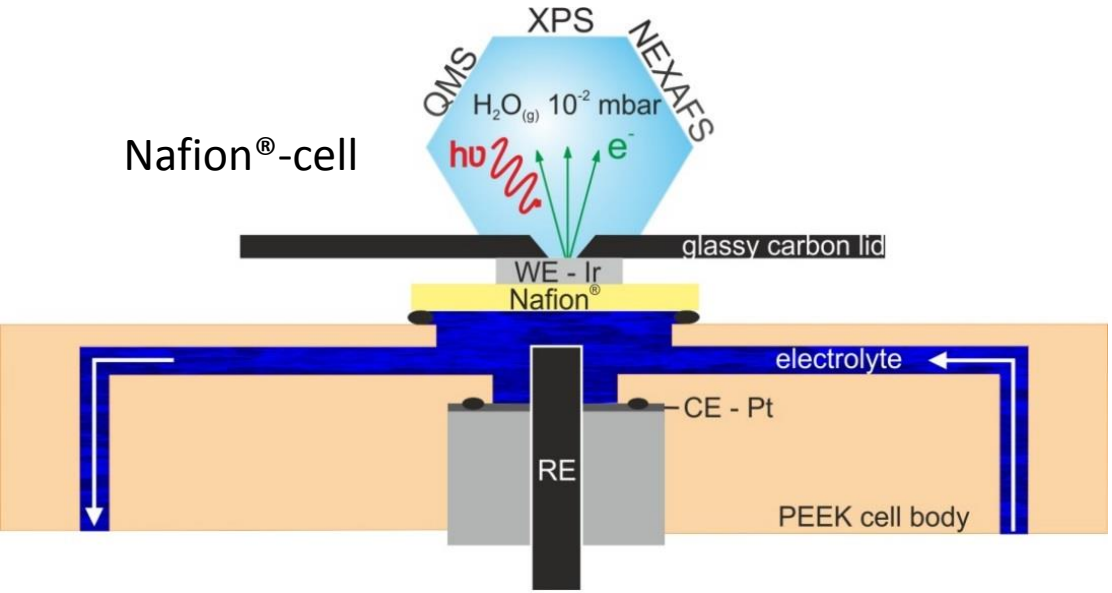
2. Reactive oxygen species in iridium-based oxygen evolution reaction (OER) catalysts



3. Dynamic response of a MoV oxide catalyst in propane and ethane adsorption

Ir-based catalysts are promising materials to electrocatalyze the oxygen evolution reaction (OER) in acidic media.

Nafion®-cell



XPS in-situ cell is operated at BESSY

Aim:

➥Monitor changes in the electronic structure during the oxygen evolution reaction (OER)

Note:

- ➥ X-rayNear Edge X-ray Absorption Fine Structure (NEXAFS)
- ➥ photoelectron spectroscopy (XPS)
- ➥ The FHI high pressure XPS set-up is operated at BESSY
  (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H.)

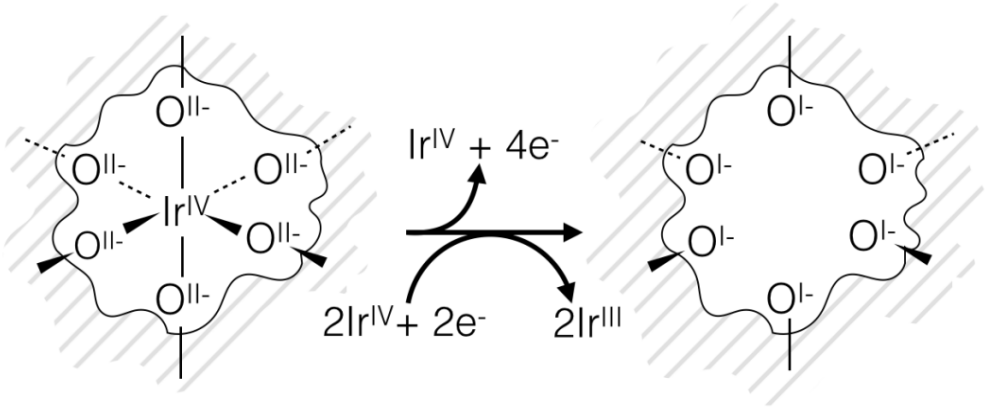
Pfeifer, V.; Jones, T.; Wrabetz, S.; Massué, C.; Velasco-Velez, J.; Arrigo, R.; Scherzer, M.; Piccinin, S.; Hävecker, M. Knop-Gericke, A.; Schlögl, R., Journal of the American Chemical Society , accepted March, 21 2016

Introduction

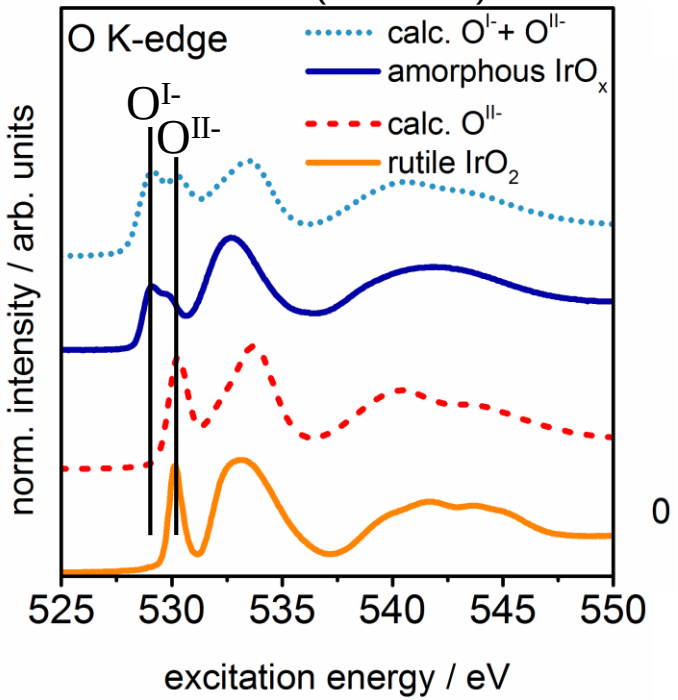
→ We expect the formally O^{I-} species contained in IrO_x as an active site in the OER

Catalyst: • amorphous $Ir^{III/IV}$ oxyhydoxides (IrOx)
• crystalline rutile-type IrO_2

Defect model for iridium oxide



X-rayNear Edge X-ray Absorption Fine Structure (NEXAFS)

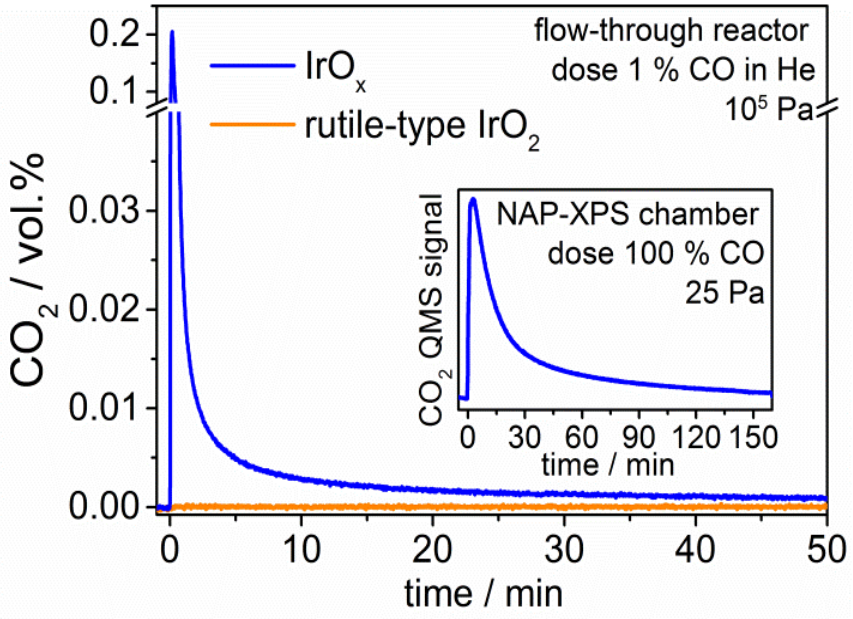


Pfeifer, V.; Jones, T.; Wrabetz, S.; Massué, C.; Velasco-Velez, J.; Arrigo, R.; Scherzer, M.; Piccinin, S.; Hävecker, M. Knop-Gericke, A.; Schlögl, R., Journal of the American Chemical Society , accepted March, 21 2016

CO titration of two IrOx

➥ We use CO titration as a prototype chemical probe reaction to investigate the reactivity of active oxygen species $IrO_x + CO_{(g)} \rightarrow CO_{2(g)} + IrO_{x-1}$ @RT

CO_2 concentration in effluent gas stream over time after CO is introduced (r.t.)



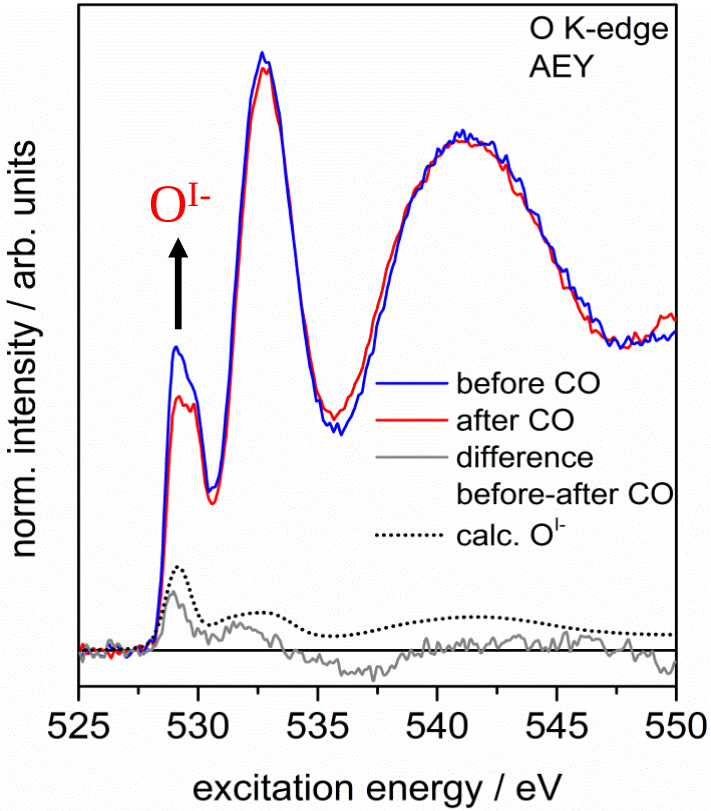
The higher level of activity for the OER of X-ray amorphous $Ir^{III/IV}$ oxyhydoxides (IrOx) as compared to crystalline rutile-type IrO_2 may be connected to more active oxygen species present in IrOx.

Pfeifer, V.; Jones, T.; Wrabetz, S.; Massué, C.; Velasco-Velez, J.; Arrigo, R.; Scherzer, M.; Piccinin, S.; Hävecker, M. Knop-Gericke, A.; Schlögl, R., Journal of the American Chemical Society , accepted March, 21 2016

O K-edge measured by Auger electron yield (AEY) mode before and after CO exposure

- To test this hypothesis "*O^{I-} species the active site*" , we employ XPS and NEXAFS and monitor the regions characteristic for the O^{I}- species (~529 eV).

Comparison of our theoretical and experimental O K-edge spectra



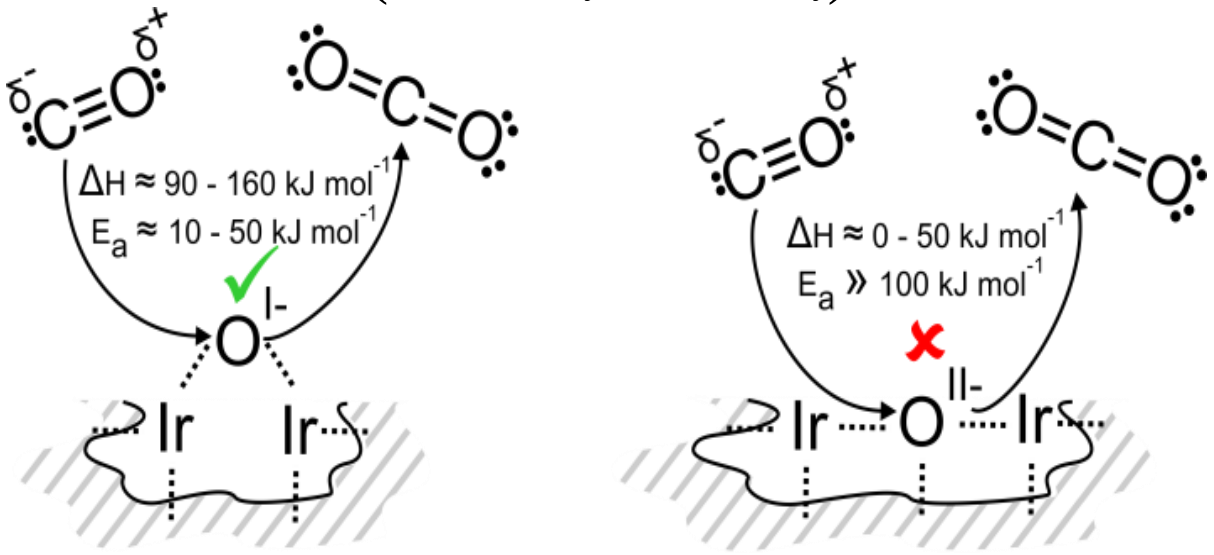
- only IrO_x contains a large abundance of formally **O^{I-} species**,
- the difference spectrum shows the considerable decrease of the 529 eV feature

→ this O^{I-} type of oxygen is a likely candidate for the oxygen active in CO oxidation

Pfeifer, V.; Jones, T.; Wrabetz, S.; Massué, C.; Velasco-Velez, J.; Arrigo, R.; Scherzer, M.; Piccinin, S.; Hävecker, M. Knop-Gericke, A.; Schlögl, R., Journal of the American Chemical Society , accepted March, 21 2016

CO titration of different oxygen species on iridium oxide surfaces

Calculated activation barrier (E_a) and reaction enthalpies (ΔH)
(DFT Density functional theory)



RT

The schemes summarize the CO titration of different oxygen species on iridium oxide surfaces with respect to their calculated activation barrier and reaction enthalpies.

Energetically, the reaction of CO with O^{I-} seems feasible, while the reaction with O^{II-} seems not possible to take place at room temperature.

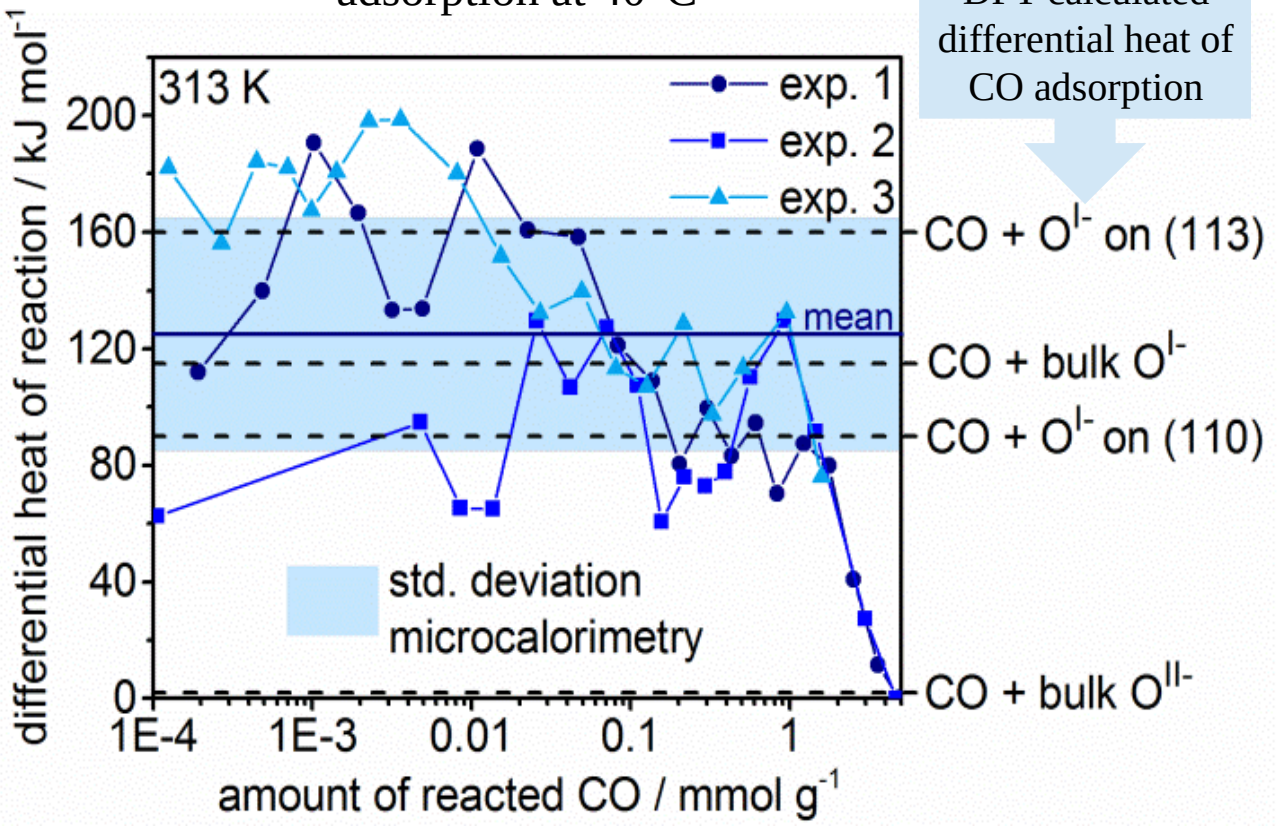
Microcalorimetry – the corresponding experiment

Pfeifer, V.; Jones, T.; Wrabetz, S.; Massué, C.; Velasco-Velez, J.; Arrigo, R.; Scherzer, M.; Piccinin, S.; Hävecker, M. Knop-Gericke, A.; Schlögl, R., Journal of the American Chemical Society , accepted March, 21 2016

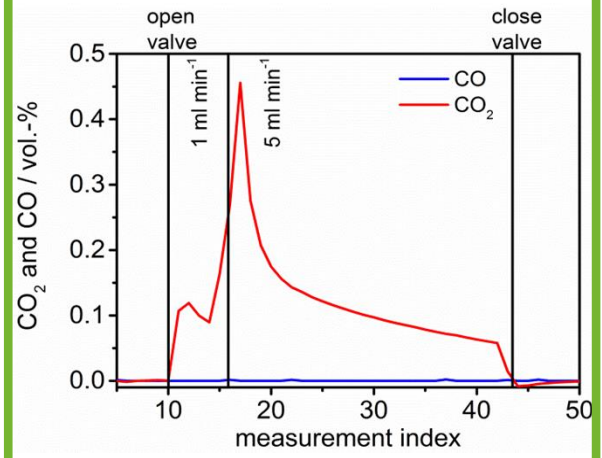
Microcalorimetric study of CO adsorption on IrOx at 40°C

Differential heat of CO adsorption at 40°C

DFT calculated differential heat of CO adsorption



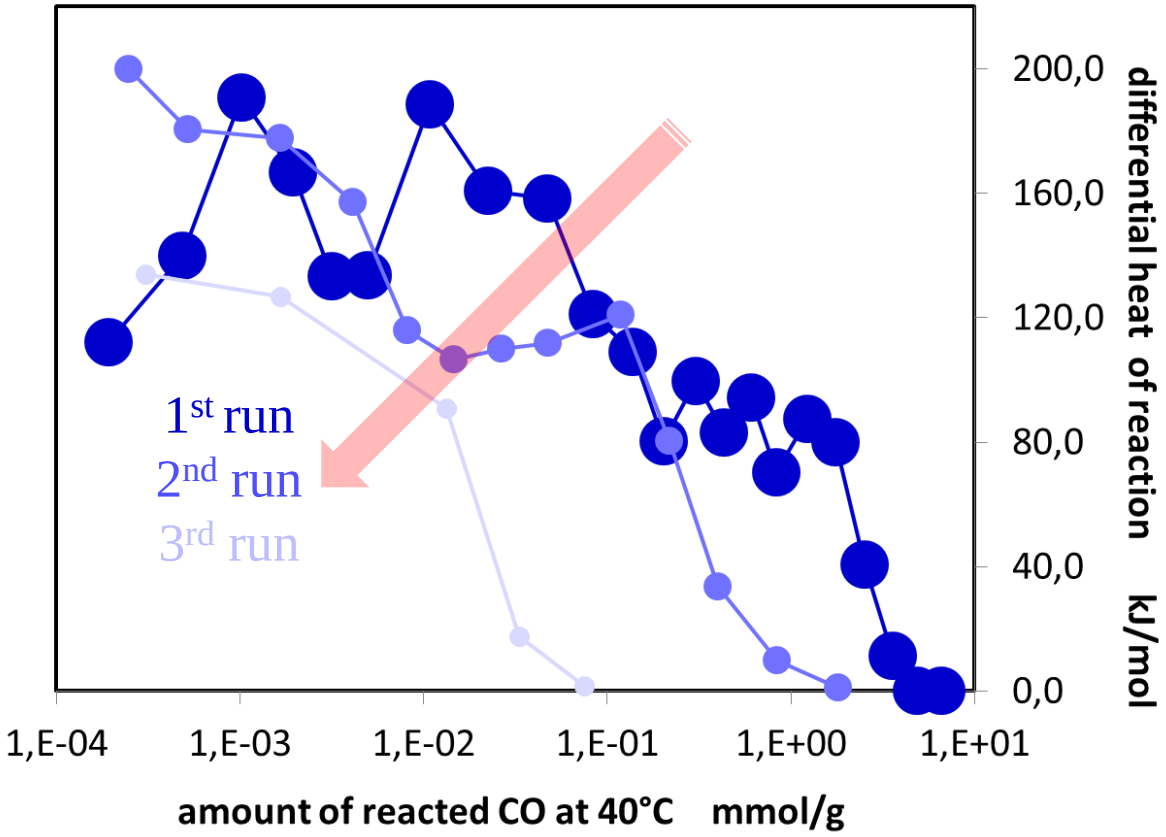
Gas analysis after saturation of CO oxidation



Pfeifer, V.; Jones, T.; Wrabetz, S.; Massué, C.; Velasco-Velez, J.; Arrigo, R.; Scherzer, M.; Piccinin, S.; Hävecker, M. Knop-Gericke, A.; Schlögl, R., Journal of the American Chemical Society , accepted March, 21 2016

Microcalorimetry
Dynamic response of the IrOx catalyst in CO adsorption at 40°C

……..monitored by CO adsorption-desorption cycles



→ **Irreversible consumption of active O^{I-} sites**

Regeneration of active O^{I-} species by ozone treatment

Pfeifer, V.; Jones, T.; Wrabetz, S.; Massué, C.; Velasco-Velez, J.; Arrigo, R.; Scherzer, M.; Piccinin, S.; Hävecker, M. Knop-Gericke, A.; Schlögl, R., Journal of the American Chemical Society , accepted March, 21 2016

Conclusion

- Our experiments outline a facile chemical probe reaction for active oxygen species on Ir-based OER catalysts.

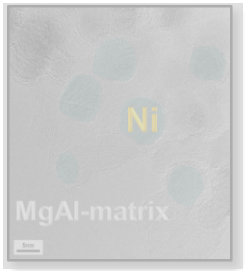
- ✓ Ab initio calculations combined with microcalorimetry confirmed that these defective O^{I-} species may act as sacrificial oxygen in a stoichiometric reaction with CO to form CO_2.
- ✓ XPS and XAS, revealing that electrophilic O^{I-} species were consumed in this process
- ✓ Adsorption-desorption cycles of CO using microcalorimetry show the dynamic character of the catalyst and confirmed the consumption of active sites.

- ➥ These observations explain the increased OER activity (r.t.) of amorphous IrOx structures containing such electronic defects in the anionic framework when compared to stoichiometric rutile-type IrO_2 lacking such defects.

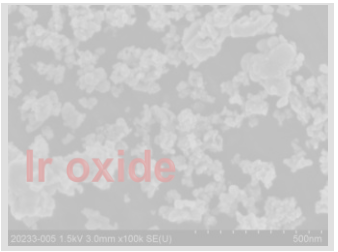
Pfeifer, V.; Jones, T.; Wrabetz, S.; Massué, C.; Velasco-Velez, J.; Arrigo, R.; Scherzer, M.; Piccinin, S.; Hävecker, M. Knop-Gericke, A.; Schlögl, R., Journal of the American Chemical Society , accepted March, 21 2016

Selected applications

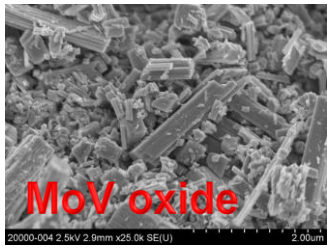
1. Ni based catalysts for the dry reforming of methane



2. Reactive oxygen species in iridium-based oxygen evolution reaction (OER) catalysts



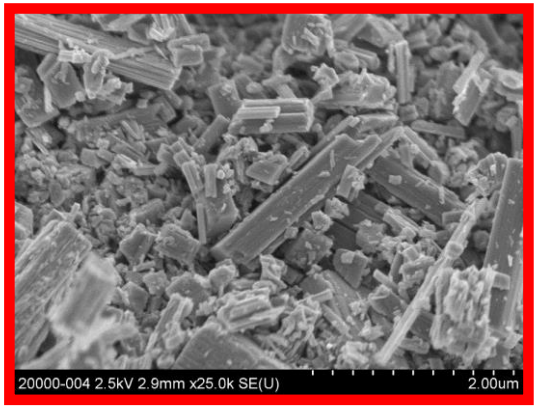
3. Dynamic response of a MoV oxide catalyst in propane and ethane adsorption



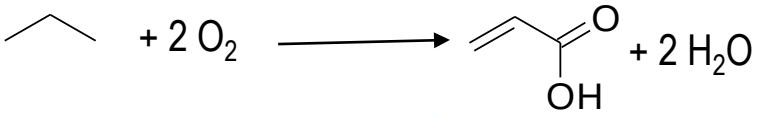
Dynamic response of a MoV oxide catalyst in propane and ethane adsorption

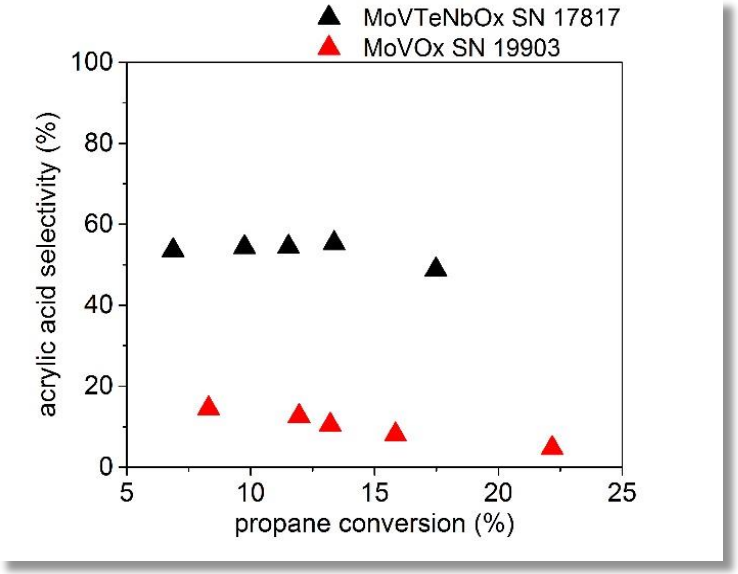
MoV oxide #20000

- Synthesis: hydrothermal method and subsequent washing procedure [1]
- Structure: M1
- Selectivity to acrylic acid: S_{aa}= 5-10mol-%
- BET = 25.52 m^2/g
- Particle size: multimodale distribution



Low selectivity of MoV oxide in oxidation of propane to acrylic acid.





In contrast

MoV oxide, which is a versatile oxidation catalyst in liquid-phase oxidation reactions or in the oxidative dehydrogenation of ethane.

[1] Naumann D'Alnoncourt, R.; Csepei, L. I.; Hävecker, M.; Girgsdies, F.; Schuster, M. E.; Schlögl, R.; Trunschke, A. Journal of Catalysis 2014, 311, 369.

Dynamic response of a MoV oxide catalyst in propane and ethane adsorption

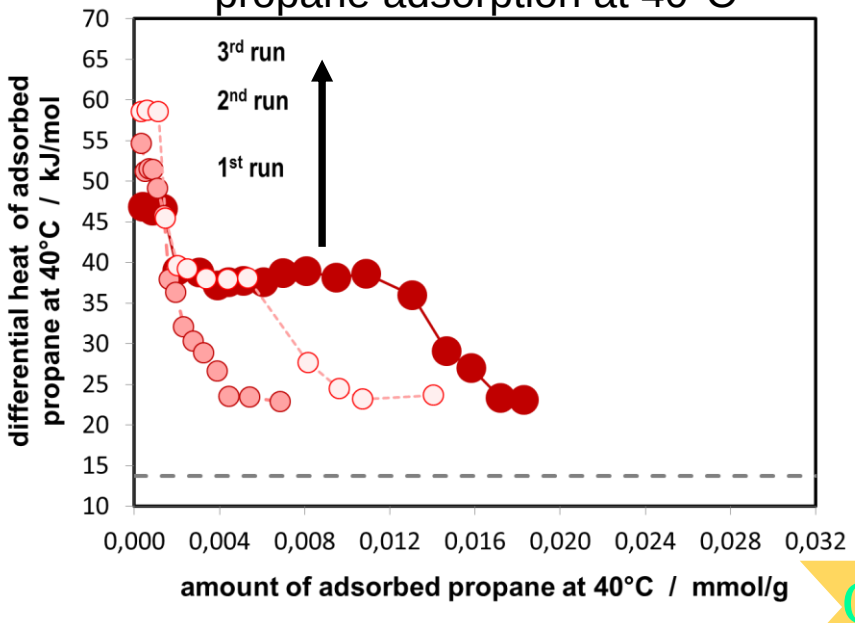
We favor on the study of adsorption-desorption cycles which can gives new insights into the dynamic behavior of the catalyst surface.

Dynamic response of the catalyst to the reactants

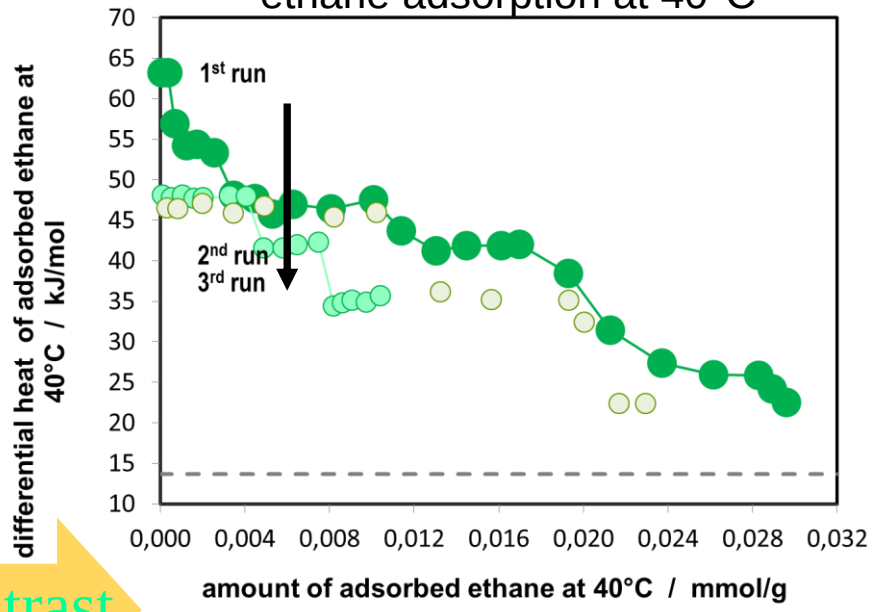
PROPANE and ETHANE as an indicator of activity !

Dynamic response of a MoV oxide catalyst in propane and ethane adsorption

Differential heat of propane adsorption at 40°C



Differential heat of ethane adsorption at 40°C



Contrast

- re-adsorption of propane reveals a drastic reduction of the adsorption capacity and the formation of energetically stronger adsorption sites at r.t.
- $S_{\text{specific for propane}}$ ~ 3.6 m^2/g

- ethane interacts relatively strong *65kJ/mol* with the surface adsorption sites of MoV oxide
- adsorption enthalpy as well as the number of adsorption sites is reduced during the second cycle. Further adsorption-desorption cycles cause no change.
- $S_{\text{specific for ethane}}$ ~ 2.9 m^2/g

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

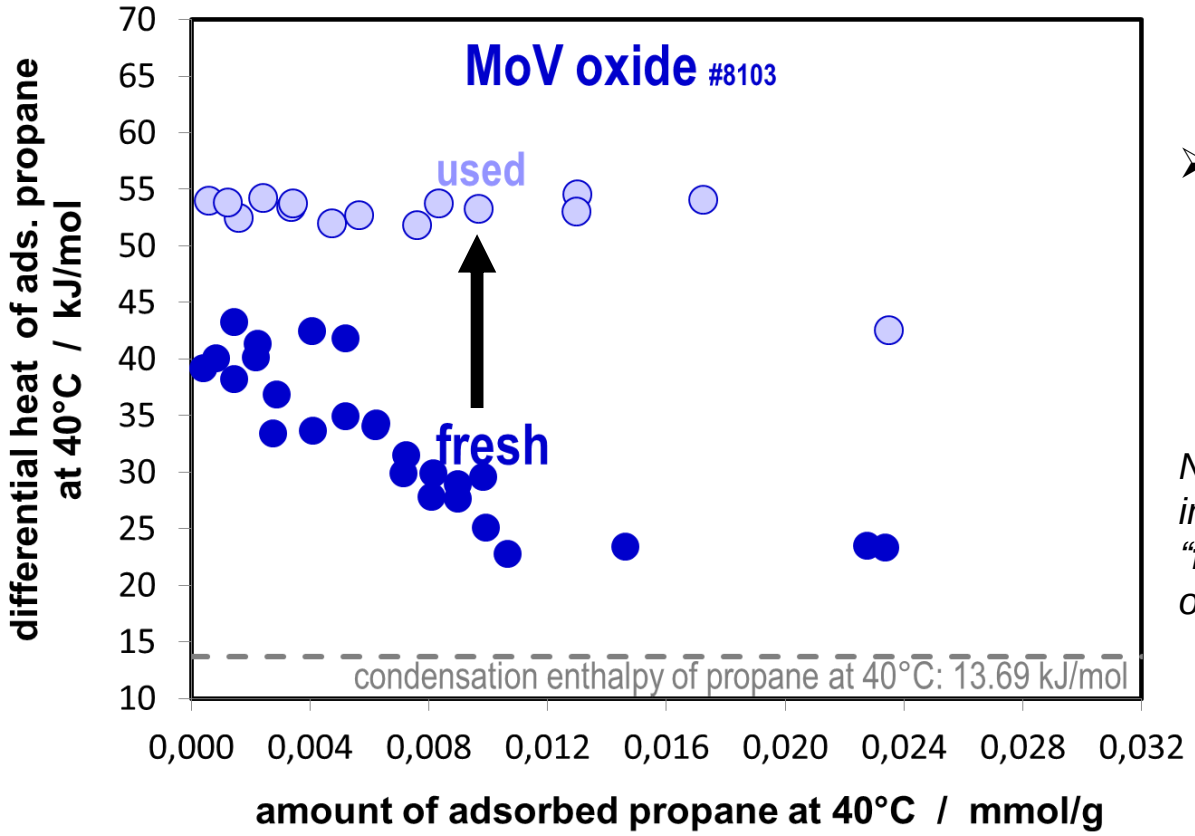
Sabine Wrabetz, Electronic Structure and Adsorption, Dept. of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Dynamic response of a MoV oxide catalyst in propane adsorption

Surface dynamics studied ***in situ***

in agreement

Surface dynamics studied ***ex situ***



- Formation of energetically stronger surface adsorption sites for propane during oxidation reaction of propane.

Note: The MoV oxide catalyst was investigated in the prepared state "fresh" and post-reaction state "used" of the surface.

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

Dynamic response of a MoV oxide catalyst in propane and ethane adsorption

- different behavior of different educts on the surface of the MoV oxide catalyst
- The low selectivity of the MoV oxide in propane oxidation may be attributed to the dynamic generation of strong adsorption sites provoked by the reactant itself.
- *in situ* and *ex situ* studies reveal the same trend

Thank you for your attention

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