Reactants-induced dynamic responses of heterogeneous catalysts monitored by microcalorimetry beyond adsorption

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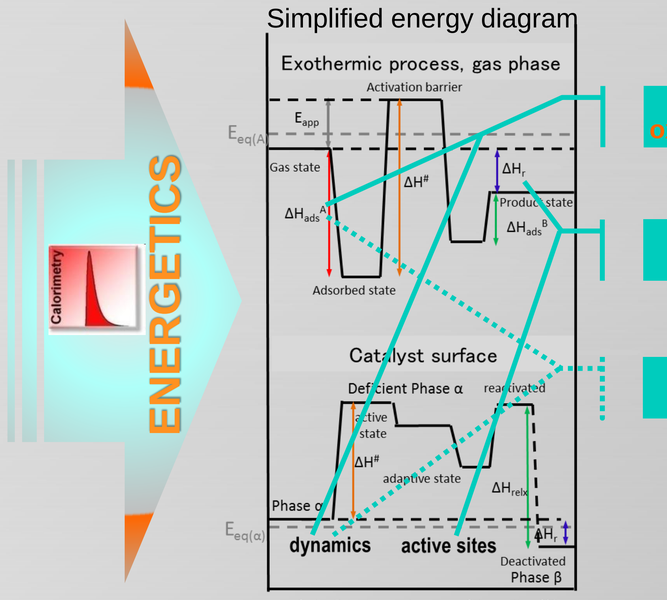
Introduction

- For a detailed understanding of the complex reaction networks, we need quantitative data of high accuracy and information about the **behaviour of the catalyst surface during the reaction process**. → Quantitative data provide a basis for theoretical modelling.

✓ We quantitatively study the adsorption, activation, and reaction phenomena close to the reaction parameters.
✓ We simulate reactants´ induced responses of the surface via adsorption/desorption cycles in order to stepwise create an active surface, and thus get new insights into the dynamic behaviour of the surface.

We focus on microcalorimetry beyond adsorption. [1-6]

$\Sigma\, n_{ads}\ vs\ p_{eq}$, $\frac{mmol\ *g^{-1}}{mmol*m^{-2}}$	Adsorption isotherm
$q_{diff} = \frac{Q_{int}}{n_{ads}} = \Delta H_{ads}$, kJ/mol	Adsorption enthalpy
$q_{diff}\ vs\ n_{ads}$, kJ/mol	Energetic distribution of ads. sites
$K = K_o\, exp\frac{\Delta H_{ads}}{RT}$, hPa^{-1}	Adsorption constant
$S = n_{ads.} \cdot Avogadro\ const. \cdot stoichiometry \cdot cross\text{-}section\ area$	Specific surface area



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

Presented projects

MoV oxide catalyst in oxidative dehydrogenation of alkanes [1]

Ir-based catalysts for the oxygen evolution reaction at r.t. [2]

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

References:
1 P. Kube, B. Frank, S. Wrabetz, J. Kröhnert, M. Hävecker, J. Velasco-Vélez, J. Noack, R. Schlögl, A. Trunschke, ChemCatChem 9 (2017) 1-14.
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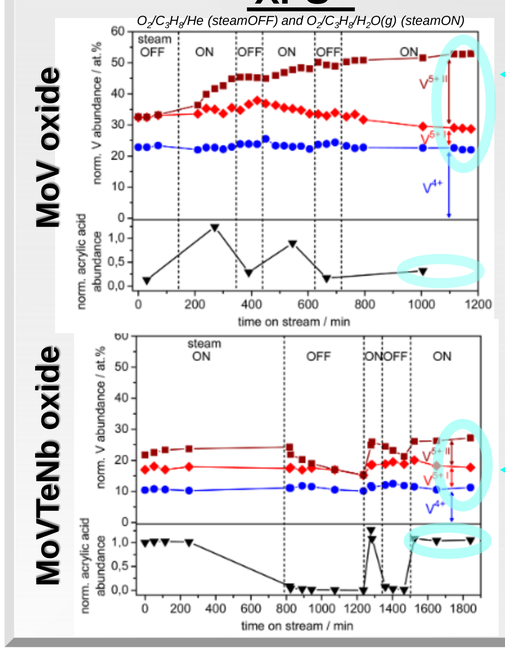
MoV oxide catalyst in oxidative dehydrogenation (ODH) of alkanes [1]

➢ MoV oxide [7] has been studied as a model system for a better understanding of the complex V-containing bulk MoVTeNb oxide catalyst [8] active in ODH of alkanes.

XPS [9]



LINK

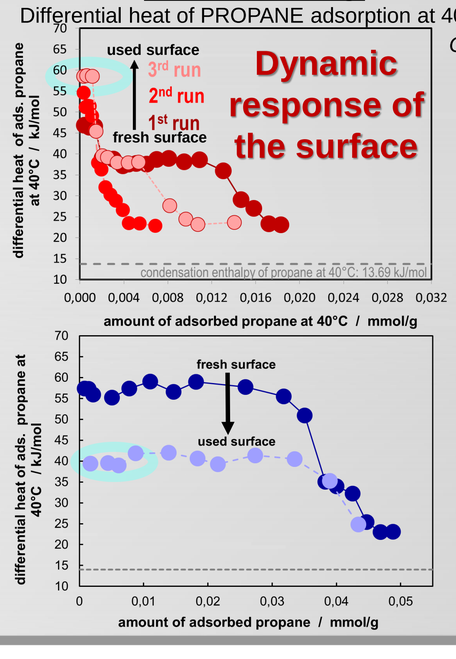
The newly generated very strong sites might be related to the segregated of V^{5+} .

Under working conditions, a substantial enrichment of V^{5+} species at the MoV surface has been observed, which has led to a decrease in selectivity.

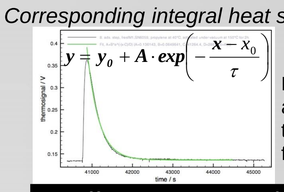
LINK

Calorimetry

Differential heat of PROPANE adsorption at 40°C



Corresponding integral heat signal



$\tau > \tau_0$ indicates :
Propane is activated already at 40°C and consequently traces of H_2O might be formed during the experiment.

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

- **Dynamic nature of the surface**
- **Very strong interaction of propane with the used surface explains the decrease in selectivity caused by V-segregation.**
- **Segregation of V^{5+} occurs already at low temperature and is possible in absence of water.**
- **Alkanes are already activated at r.t.**

References:
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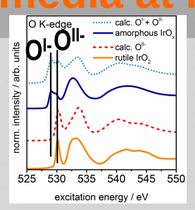
Ir-based catalysts for the oxygen evolution reaction (OER) in acidic media at r.t. [2]

➢ Electrophilic formally O^{I-} species contained in IrOx are expected to be active precursor sites for the OER.
➢ CO titration as a prototype chemical probe reaction to investigate the reactivity of active oxygen species
➢ Catalysts: • X-ray amorphous $Ir^{III/IV}$ oxyhydroxides (IrOx)
• crystalline rutile-type IrO_2

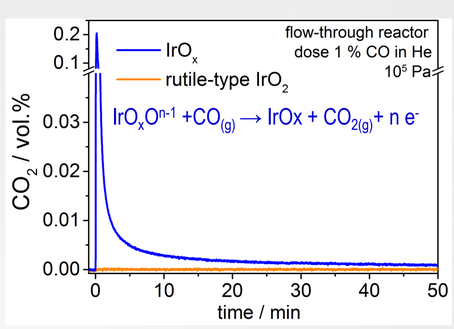
NEXAFS



- **electrophilic formally O^{I-} species is the active oxygen and will be consumed in the CO oxidation reaction**
- **the nature of the catalytic relevant species is a property of the metal and also linked with the electronic structure of oxygen**

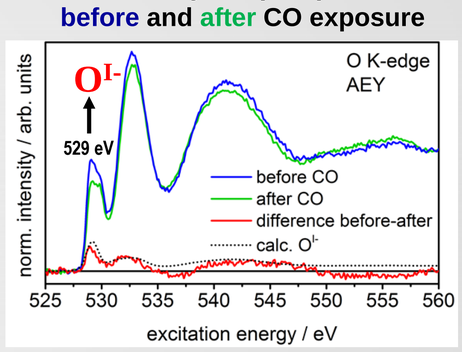
The O^{I-} species plays a crucial role in the O-O bond formation in the electro-catalytic OER on IrO_x.

CO_2 concentration in effluent gas stream over time after CO is introduced at RT



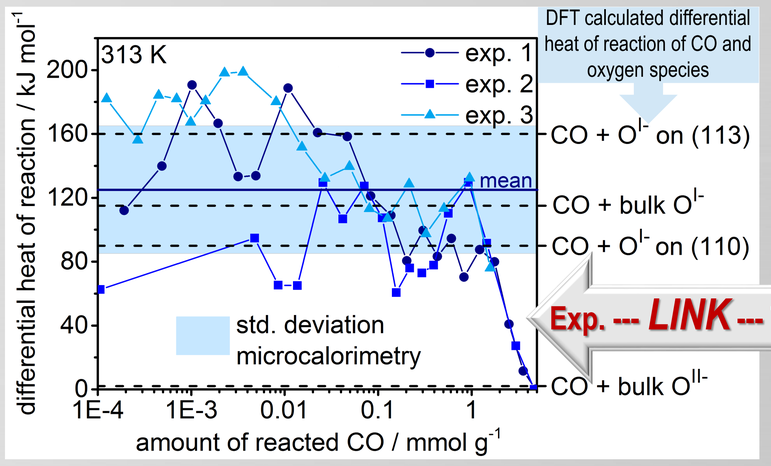
The higher level of activity for the OER of amorphous IrOx as compared to crystalline rutile-type IrO_2 may be connected to more active oxygen species present in IrOx.

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

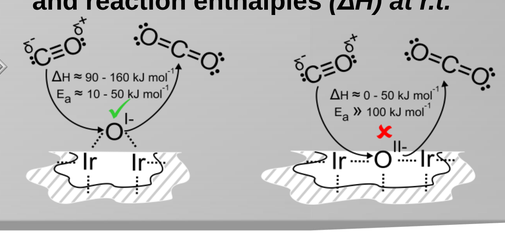


Consumption of electrophilic formally O^{I-} sites in the CO oxidation reaction.

Differential heats over the amount of reacted CO in the microcalorimeter with amorphous IrOx at r.t.

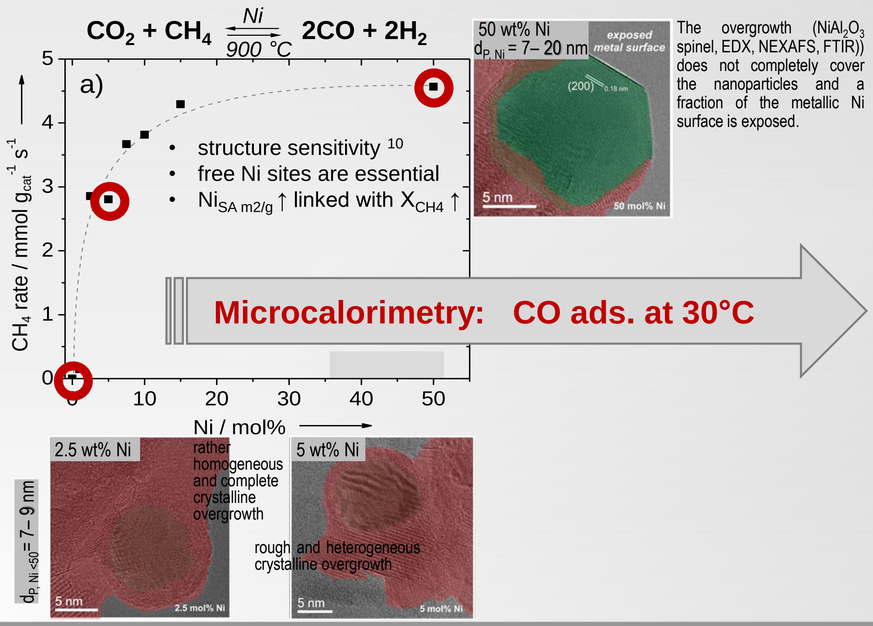


Calculated (DFT) activation barrier (E_a) and reaction enthalpies (ΔH) at r.t.



Ni-based catalysts for the dry reforming of methane (DRM) [3]

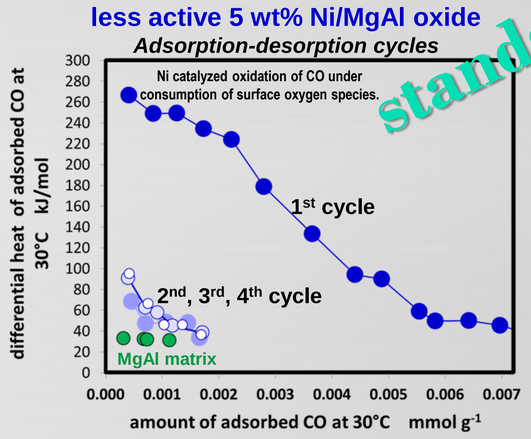
➢ The influence of structural and compositional properties of Ni/MgAl catalysts on the catalytic performance of the dry reforming of methane (DRM) has been studied. We consider a combination of microcalorimetry with FTIR spectroscopy, NEXAFS, HR-TEM, theory calculations and catalytic performance.



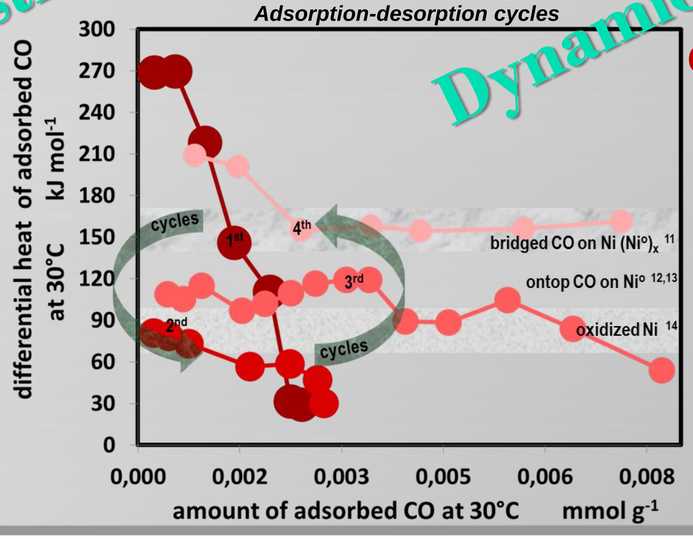
The overgrowth ($NiAl_2O_3$ spinel, EDX, NEXAFS, FTIR)) does not completely cover the nanoparticles and a fraction of the metallic Ni surface is exposed.

Microcalorimetry: CO ads. at 30°C

Differential heat of CO adsorbed on less active 5 wt% Ni/MgAl oxide
Adsorption-desorption cycles



Differential heat of CO adsorbed on most active 50 wt% Ni/MgAl oxide
Adsorption-desorption cycles



Catalytically relevant Ni^0 is back again !

Active Ni/MgAL oxide is characterized by:

- **very dynamic aggregated metallic Ni sites**
- **partial overgrowth**
  Overgrowth ($NiAl_2O_4$) seems to prevent the occurrence of dynamic phenomena on Ni nanoparticles, effectively diminish the formation of coke during the DRM and may act as a rigid scaffold keeping the Ni nanoparticles in shape.

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