Surface characterization of nano-structured carbon catalysts by adsorption microcalorimetry using reactants as probe molecules

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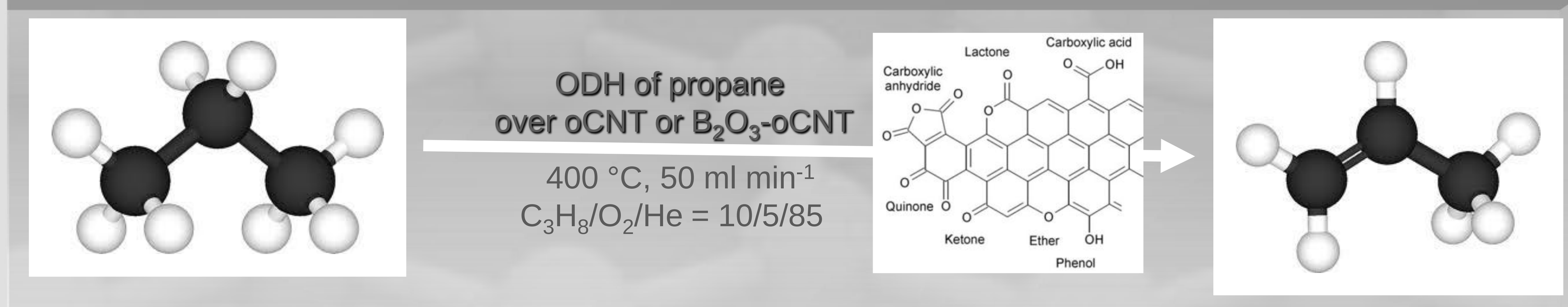
FOCUS

Carbon nanotubes (CNTs) are active catalysts in oxidative dehydrogenation (ODH) of propane [1] . Information about surface coverage and heat of adsorption is an important input for mechanistic understanding and kinetic modeling in heterogeneous catalysis. Microcalorimetry allows the measurement of differential heat evolving when known quantities of probe molecules are adsorbed on the catalyst surface. Selecting reactants as probe molecules and investigating quenched catalyst surfaces that were operated under steady state conditions are key issues to attain quantitative information on a catalyst surface that approaches closely the active state.

In the *present* work, we adsorbed propane and propylene on the surface of oxidized carbon nanotubes (oCNT), 5 wt% B_2O_5/oCNT, and graphite used as catalysts in ODH of propane in order to study the surface sites relevant for catalytic turnover [2] .

CONCLUSION



Adsorption site classification:

Combination of calorimetry, TPD, XPS

<u>type A sites</u> are ketones and quinones with a constant heat of propane ad-sorption (45 kJ mol^{-1}) and irreversible chemisorption of propene. Their amounts are 10 µmol/g (oCNT) and 5-8 µmol/g (B_2O_3-oCNT)

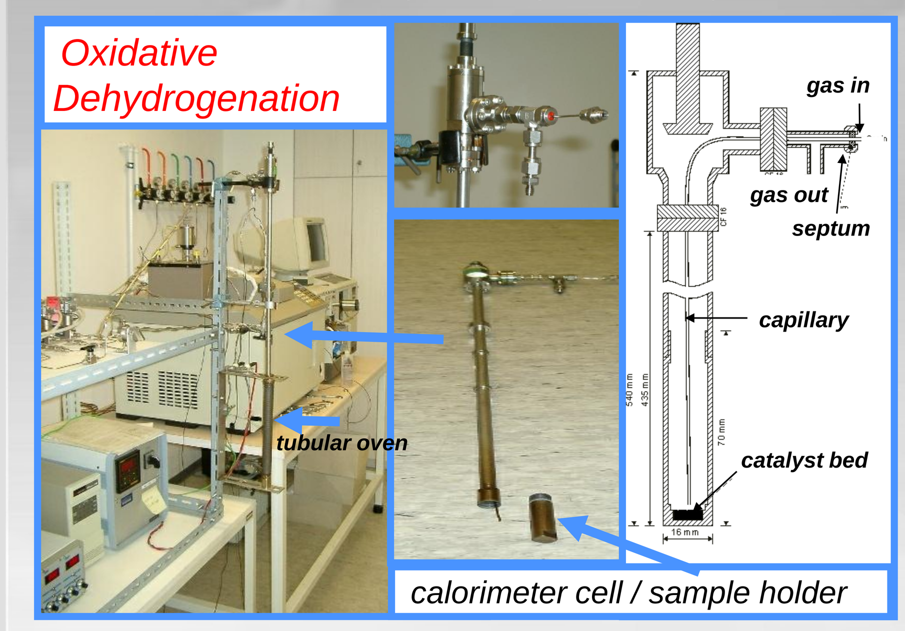
<u>type B sites</u> are carboxylic anhydrides; similar behavior as sites A but with lower energy (45 -35 kJ mol^{-1})
Their amounts are 40-50 µmol/g (oCNT) and 20-30 µmol/g (B_2O_3-oCNT)

<u>type C sites</u> are lactone/ester, phenol, and ether sites; reversible interaction with propane and propene (30 kJ mol^{-1})
Their amounts are 50 µmol/g (oCNT) and 60 µmol/g (B_2O_3-oCNT)

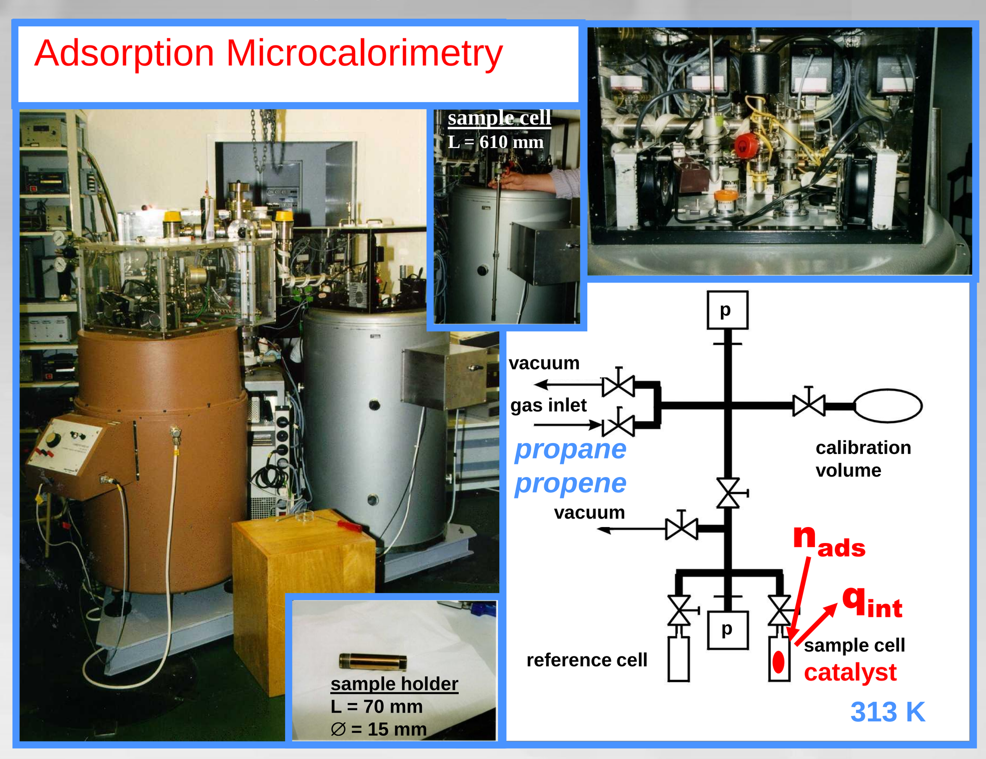
<u>type D sites</u> is the basal plane of graphitic carbon - free of oxygen (< 25 kJ mol^{-1})

quasi *in situ* Adsorption Microcalorimetry [3]

To investigate the catalytically relevant surface sites, the active surface of CNT catalysts under ODH reaction conditions was conserved by switching from the ODH feed to He and subsequent cooling of the reactor prior to its transfer to the calorimeter without getting contact to ambient.



The calorimeter cell is used as a fixed bed flow reactor, wherein the catalytic reaction propane of oxidative dehydrogenation is carried out (0.4 g catalyst, 400°C, 50 ml min^{-1}, C_3H_8/O_2/He = 10/5/85). The feed is introduced through a capillary. The catalytic performance is monitored by an on-line micro-GC (Varian CP-4900) for product analysis. After reaching the steady state performance the reaction is stopped.



The cell is purged with He, then the capillary is removed without exposing the catalyst to atmosphere. Afterwards the cell is placed in an MS 70 Calvet calorimeter of SETARAM combined with an in-house-designed volumetric system [4-6], which enables dosages of probe molecules such as propane or propene in steps as small as 0.02 µmol/g. The instrumentation allows measurements of adsorption isotherm and differential heats of adsorption, and gives the possibility to elucidate the distribution of adsorption sites along the range of adsorption heats [4,5,7].

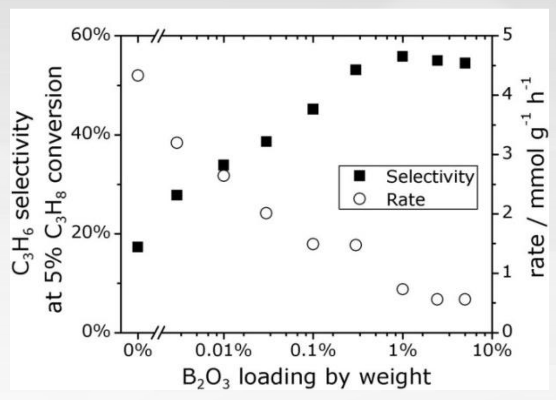
Catalysts and Catalytic Performance

Creation of oxygen functional groups by HNO_3 treatment at 375 K for 2 h
→ oCNT

additional 5 wt% B_2O_3 to reach a sufficient self-oxidation stability
→ B_2O_3 - oCNT

→ graphite

propane —(after 12 h TOS)→ propylene
ODH over oCNT or B_2O_3-oCNT
400 °C, C_3H_8/O_2/He = 10/5/85, 50 ml min^{-1}

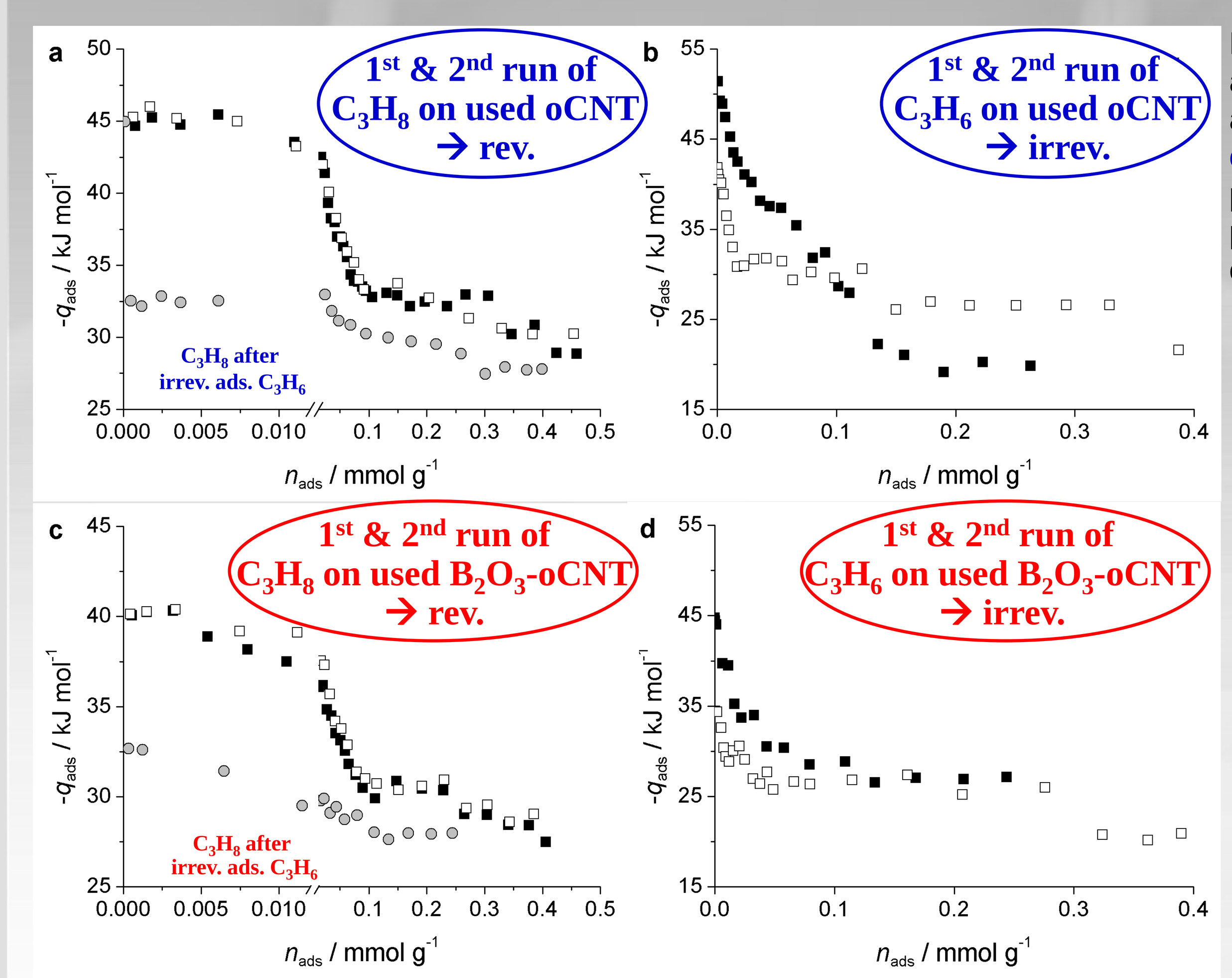


Validation of the flow-type calorimeter cell reactor

	$X(C_3H_8)$	$S(C_3H_6)$
tubular reactor	4.5 / 1.1	19.8 / 79.2
calorimeter cell	5.5 / 1.4	15.4 / 65.4

- Strong improvement of the alkene selectivity by surface modification using boron oxide

Differential heats of propane and propene adsorption [2]



Differential heats of adsorption of (a) propane and (b) propylene on oCNT catalyst and of (c) propane and (d) propylene on B_2O_3-oCNT catalyst.

- **Graphite** shows constant low level of diff. heats for propane (32kJ/mol) and propylene (40kJ/mol). The ads. sites react reversible with propane and propylene.
- No surface reaction, no essential catalytic activity !

Quantitative evaluation of calorimetric measurements

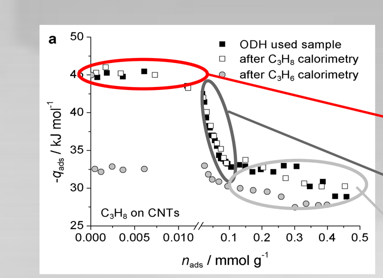
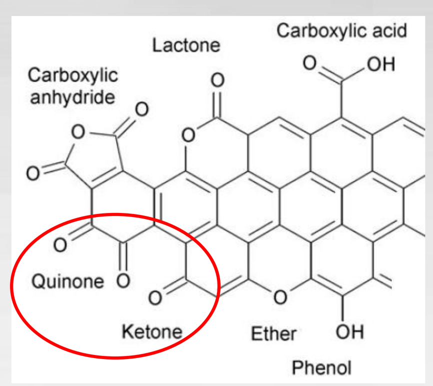


Table 1. Quantitative evaluation of calorimetric measurements of propane and propylene adsorption on CNT and B_2O_3-CNT catalysts (Figure 1).

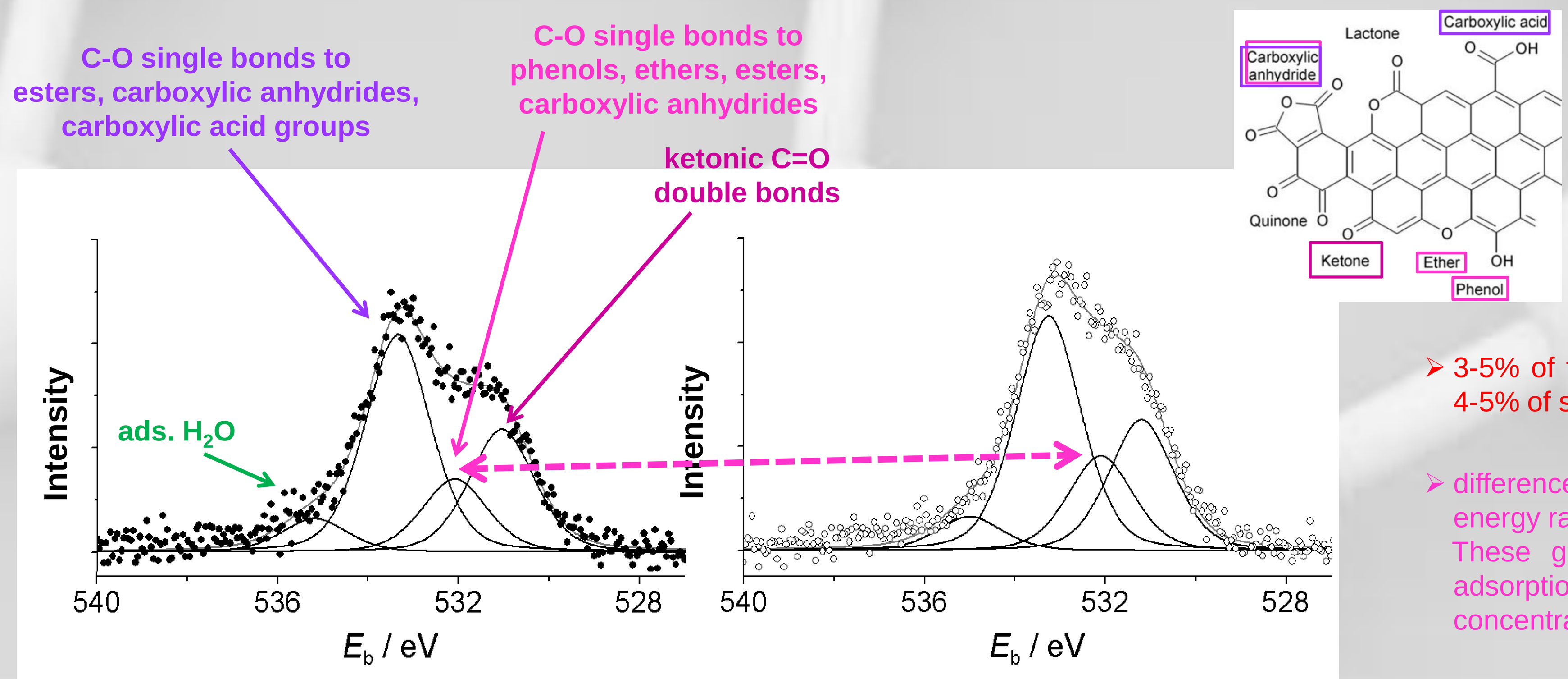
	Sample Adsorbent	CNTs C_3H_8	 C_3H_6	B_2O_3–CNTs C_3H_8	 C_3H_6
	$-q_{ini}$ (kJ mol^{-1})	45	51	40	45
High-Energy Plateau	n_{ads} (µmol m^{-2})	0–0.015	–	0–0.016	–
	$-q_{ads}$ (kJ mol^{-1})	45±0.5	–	39±1	–
Steady-Decay Range	n_{ads} (µmol m^{-2})	0.015–0.18	0–0.27	0.016–0.24	0–0.32
	$-q_{ads}$ (kJ mol^{-1})	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)
  - *Trans. Faraday Soc.* 1967 *63* 455 (C1-C4 alkanes/alkenes)
  - *J. Phys. Chem.* 1969 *73* 2321 (C5-C9 alkanes, aromatics, ethers)
  - *J. Therm. Anal.* 1998 *54* 343 (MeOH, EtOH)
- 3-5% of the surface is covered by high-energy adsorption sites
- Irreversibility of propylene adsorption due to surface reaction with ketones and anhydrides



O1s ranges of XP spectra



<u>used oCNT</u> <u>used B_2O_3-oCNT</u>

- 3-5% of the high-energy adsorption sites correlate to 4-5% of surface oxygen determined by XPS.
- difference between these spectra is in the medium-energy range of 532.1–532.2 eV.
  These groups are assigned to the medium-energy adsorption sites, which were in higher surface concentration on the B_2O_3–CNTs.

References:

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