

Calorimetric Study of Propane and Ethylbenzene Adsorption on the Active Surface on Carbon-Based Catalysts

S. Wrabetz^{1,*}, O. Khavryuchenko^{1,2}, B. Frank¹, R. Blume⁴, J. Zhang³, A. Trunschke¹, R. Schlögl¹

¹ Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of Inorganic Chemistry, 14195 Berlin (Germany)

² Chemical Department, National Taras Shevchenko University of Kiev, Kiev 01033 (Ukraine)

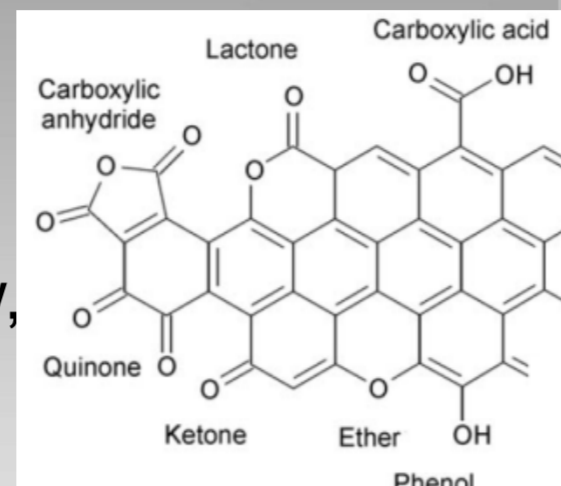
³ Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Zhejiang 315201 (China)

⁴ Division Solar Energy Research, BESSY II, Helmholtz-Zentrum Berlin für Materialien und Energie, 12489 Berlin (Germany)



INTRODUCTION

Carbon based materials are active catalysts for the oxidative dehydrogenation (ODH) reaction.^[1] Low dimensional carbon allotropes such as multiwalled carbon nanotubes (MW CNTs) with high structural homogeneity provide the characteristics of model catalysts. The well defined active surface sites will be created by oxygen functionalization of the CNTs with HNO₃ (MW oCNT). From the mechanistic point of view, quinone groups are believed to be the active sites.^[2-5] These nucleophilic oxygen species can selectively abstract hydrogen atoms and the formed phenol groups are subsequently reoxidized by O₂.



We choose the ODH of propane and ethylbenzene (EB) as the model reactions in order to establish a mechanistic model for carbon-catalyzed ODH.

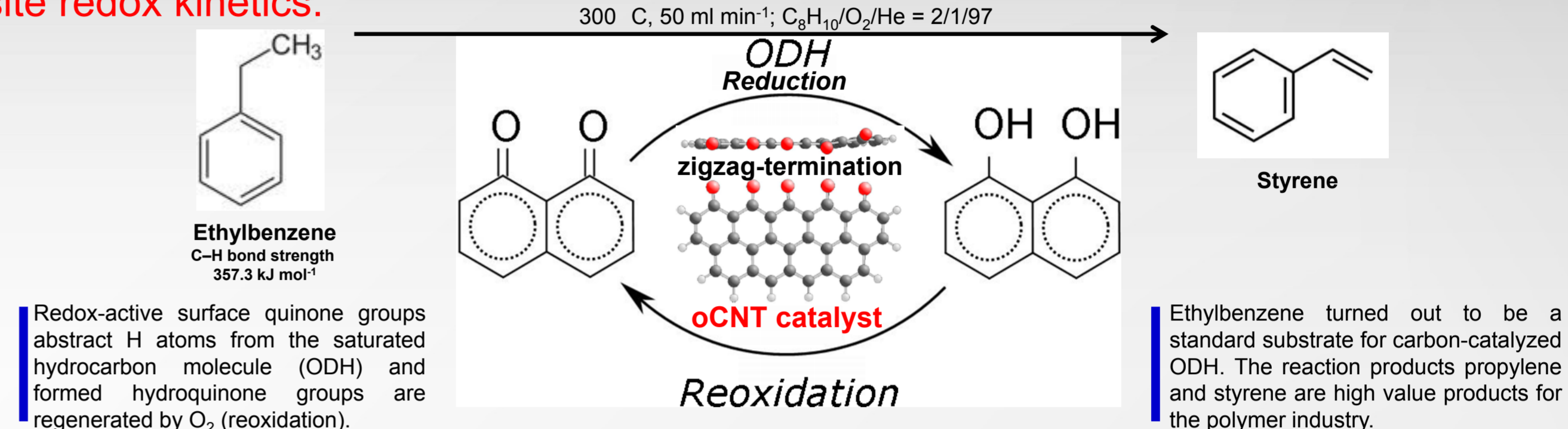
The knowledge about coverage and heat of adsorption of reactants on the surface of a catalyst can contribute to a better understanding of the complex microkinetics. We focus on quasi in situ adsorption microcalorimetry, wherein the adsorption of propane and EB on the active catalyst surface are investigated. A broad-based multidisciplinary study (microcalorimetry, in situ XPS, kinetic measurements, DFT calculations) led to a comprehensive model for carbon-catalyzed ODH.

CONCLUSION

Basic features of the reaction mechanism as well as the state of the catalyst surface are similar for hydrocarbon substrates of alkylbenzene and alkane types.

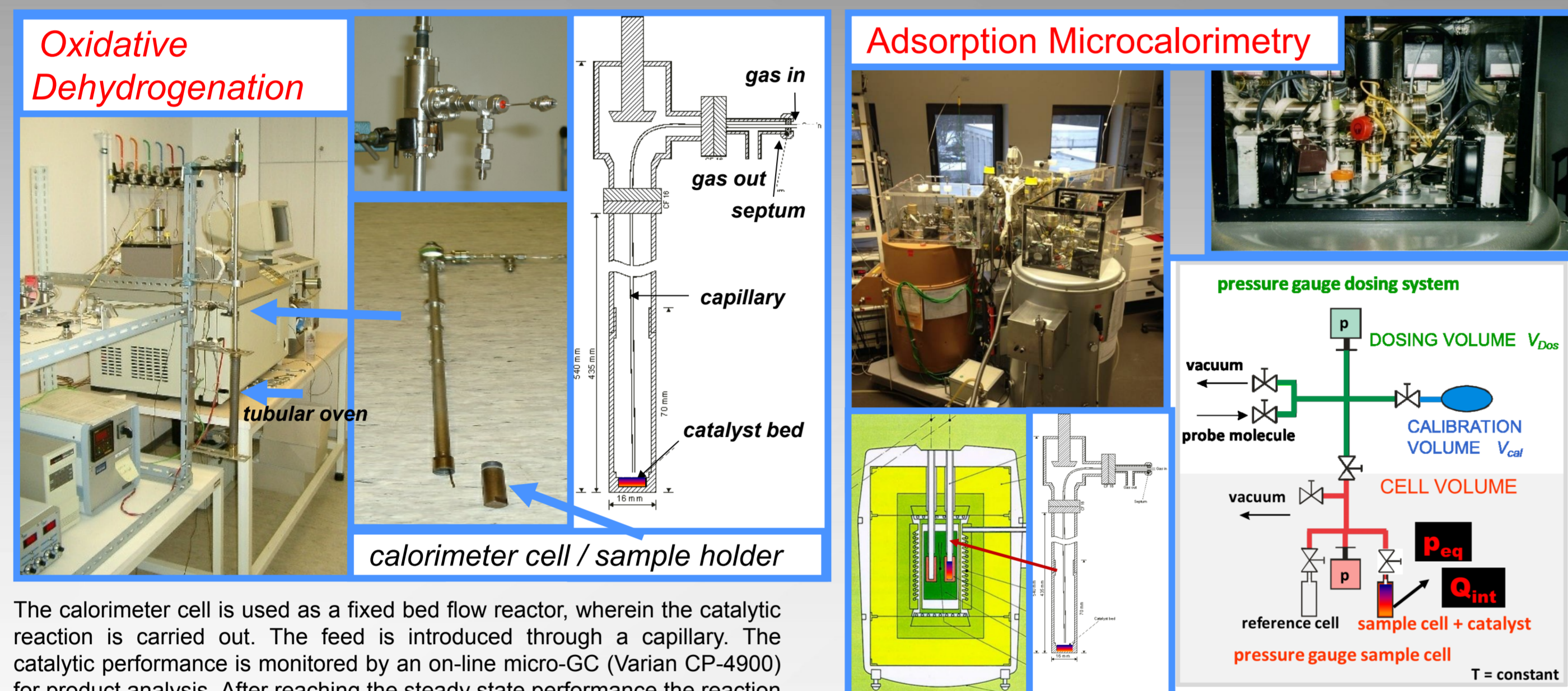
The redox cycle of surface C=O and C-OH groups is the key process, which includes only a small fraction of surface O species and favourably occurs at the zigzag-termination of sp² carbon planes. Higher activation barriers in the reduction step well correlate with the higher stability of the aliphatic C-H bond in propane over the benzylic C-H bond in EB.

two-site redox kinetics:



quasi in situ Adsorption Microcalorimetry^[10]

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 is carried out. 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 [6-8], which enables dosages of probe molecules such as propane or propene in steps as small as 0.02 mmol/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 [6,7,9].

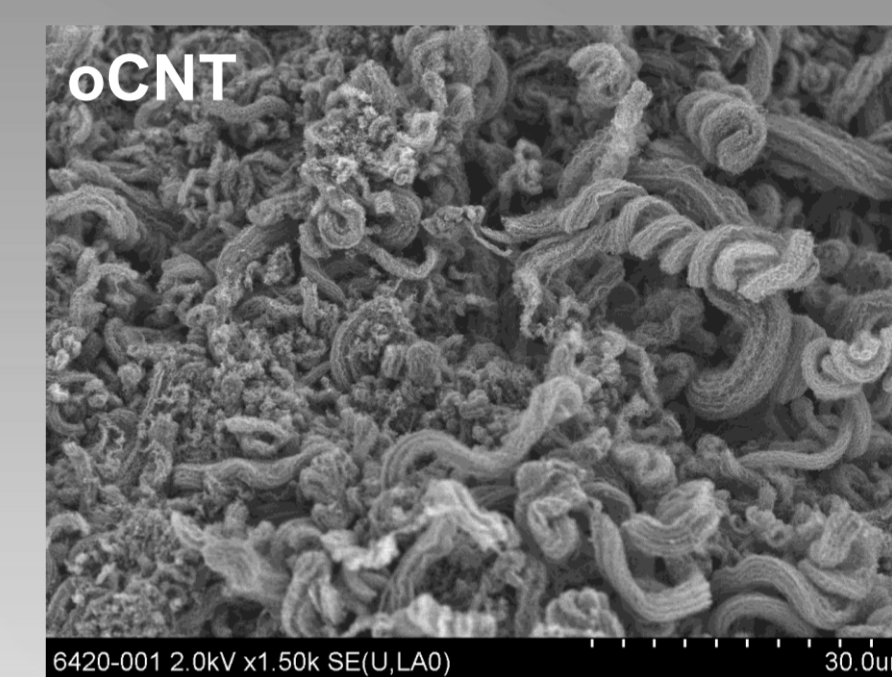
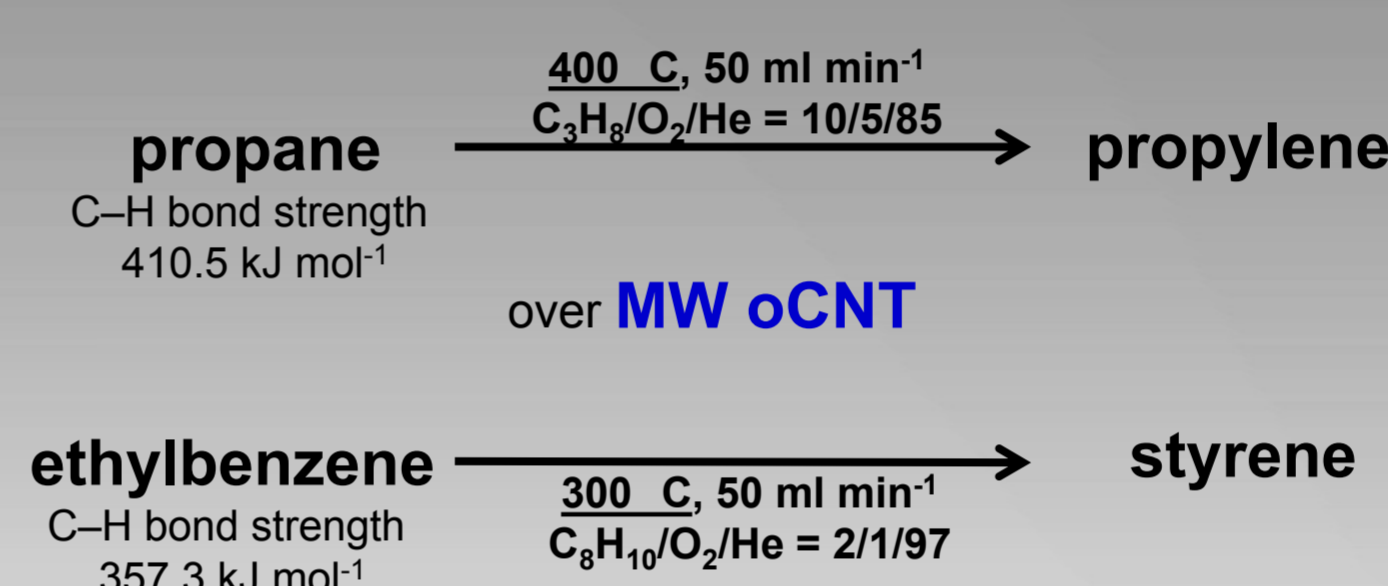
$$\Sigma n_{ads} \text{ vs } p_{eq} \quad , \quad \frac{\text{mmol} \cdot \text{g}^{-1}}{\text{mmol} \cdot \text{m}^{-2}}$$

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

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

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

Catalyst^[11] and Catalytic Performance



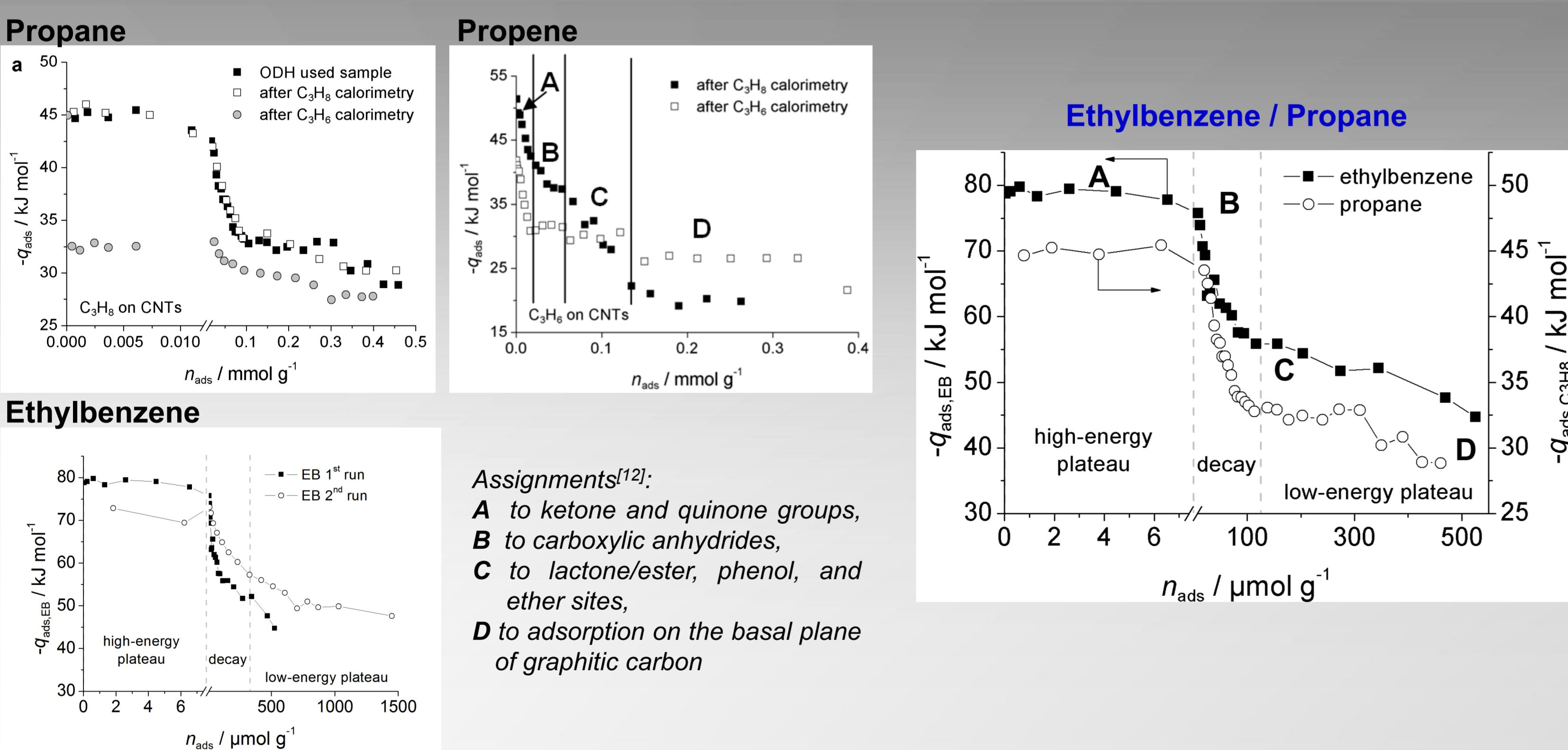
	propane	EB
E _a ¹ reduction kJ/mol	90	62
E _a ¹ reoxidation kJ/mol	72	69
X %	5	5
S %	15	98

Note: Validation of the flow-type calorimeter cell reactor

ODH of propane	X(C ₃ H ₆)	S(C ₃ H ₆)
tubular reactor	4.5	19.8
calorimeter cell	5.5	15.4

EB is much more reactive than propane.
EB reacts much more selective than propane.

Differential heats of propane/propene^[12] and EB adsorption



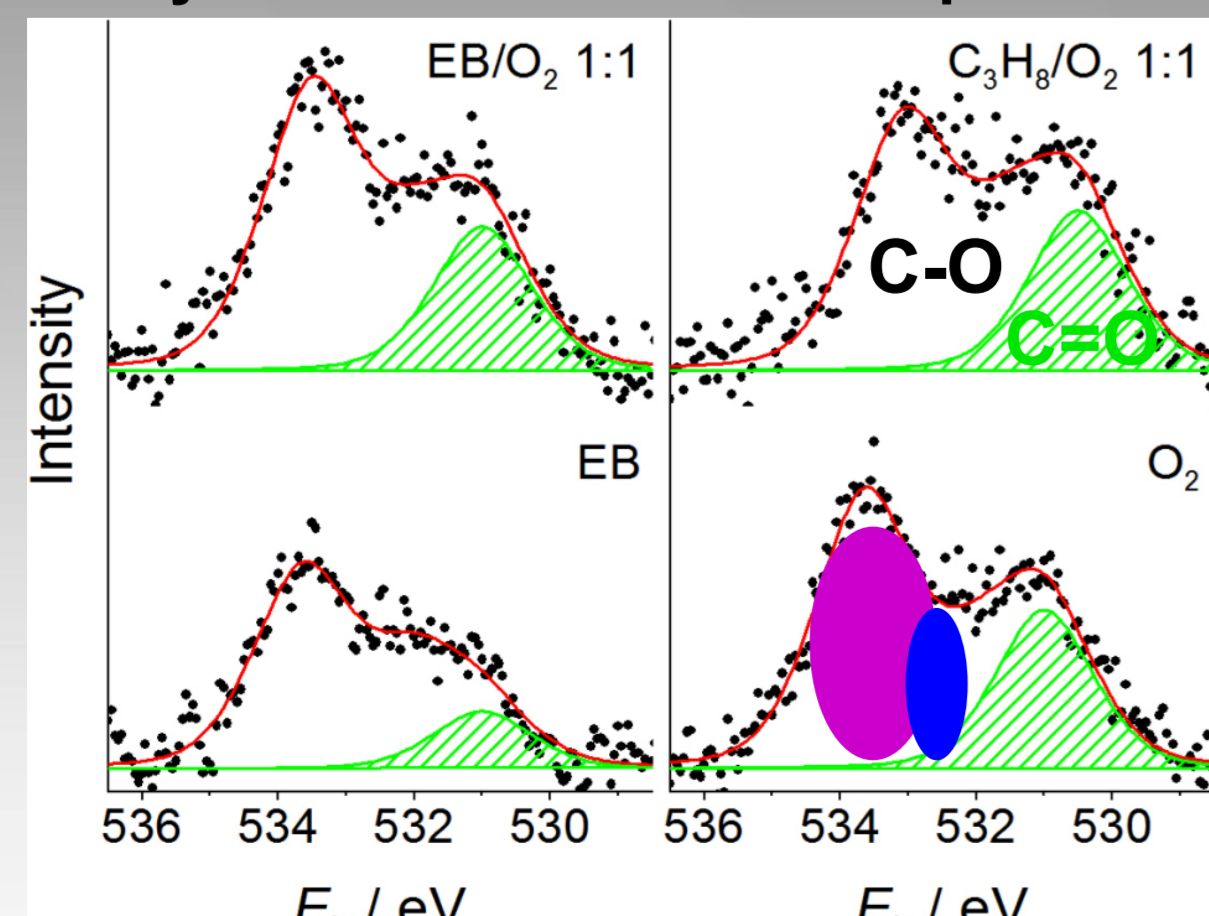
- Propane adsorbs completely reversible on oCNT.
- In contrast, EB and propene is partially irreversible adsorbed in the high-energy range because of the higher reactivity of the benzylic and allylic C-H bond.
- EB reacts stronger (80 kJ/mol) with the C=O double bonds (ketone/quinone) than propane (45 kJ/mol).
→ EB is more reactive than propane.
- From the quantitative point of view microcalorimetry reveals an astonishing analogy of active surface equilibrated in EB and propane ODH reaction.

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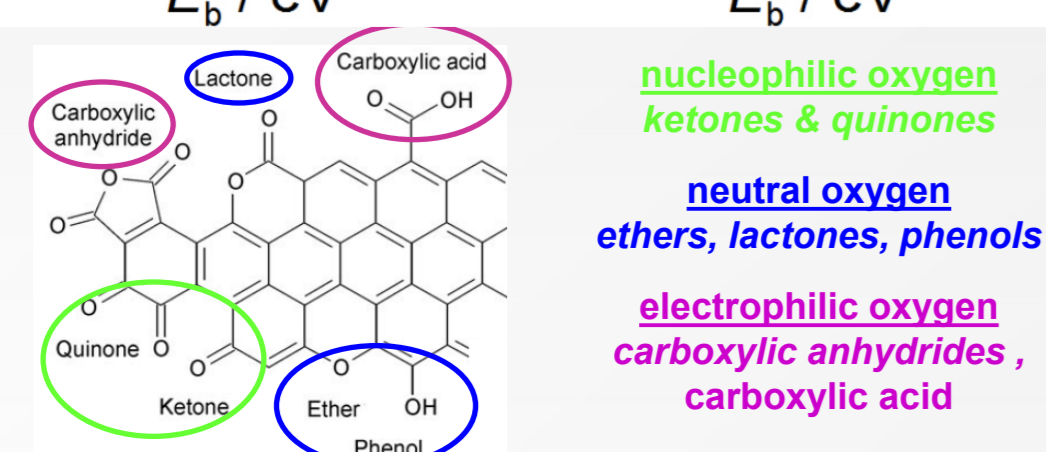
O1s ranges of XP spectra

CNT catalyst under different atmospheres and 350 C.



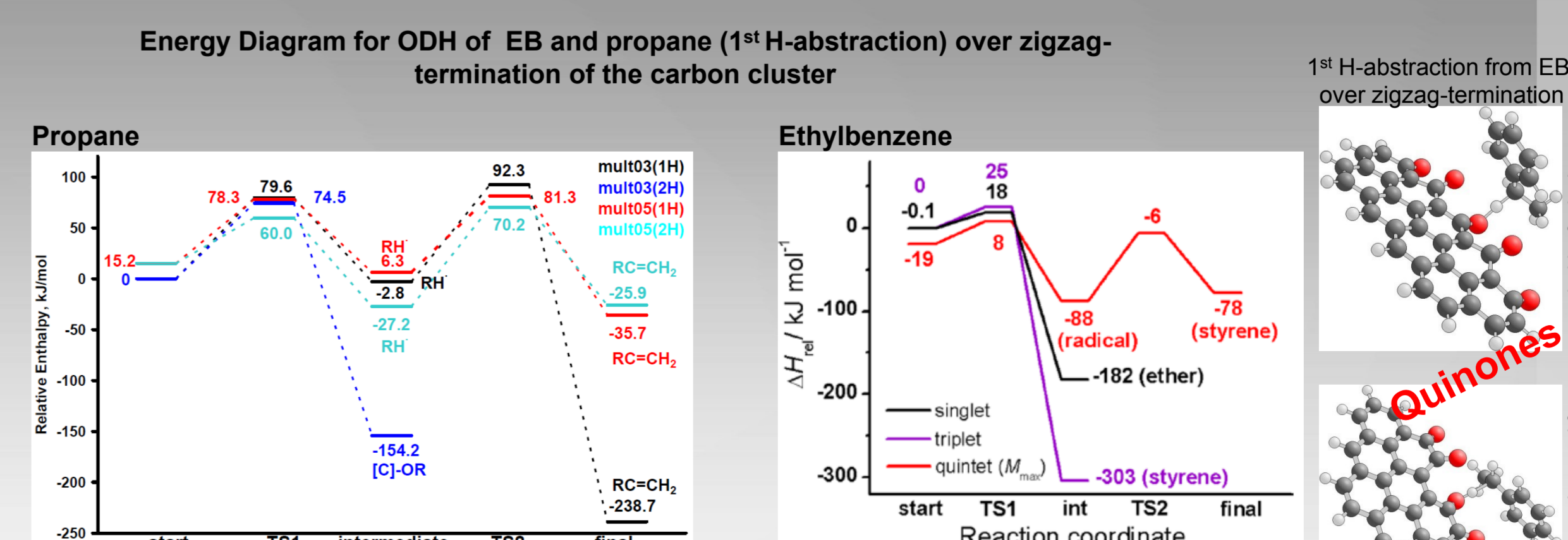
Atmosphere	I _{C=O} / I _{C-O}
EB	0.168
EB/O ₂	0.283
C ₈ H ₁₀ /O ₂	0.313
O ₂	0.315

- The higher the reactivity of the hydrocarbon molecules, the lower the concentration of the active sites in steady state.
- indication for consumption of nucleophilic oxygen (Ketones/Quinones)
- Furthermore, increase of C-O groups are associated with reactivity.



Electronic structure theory calculations by DFT^[13]

density-functional theory



- the barrier for activation of propane is higher than for EB
 - the zigzag-termination is much more active than the armchair geometry
- The armchair-edge carbon cluster is much less reactive for neutral hydrocarbon molecules than the zigzag terminated ones. Surface ethers are formed in the case of ethane and ethylbenzene ODH with activation energies equal to 148 and 128 kJ/mol, respectively. This suggests that the armchair edge can be considered passive compared with the zigzag termination.