

# New insights on active sites of key catalyst materials using microcalorimetry at close to the reaction conditions

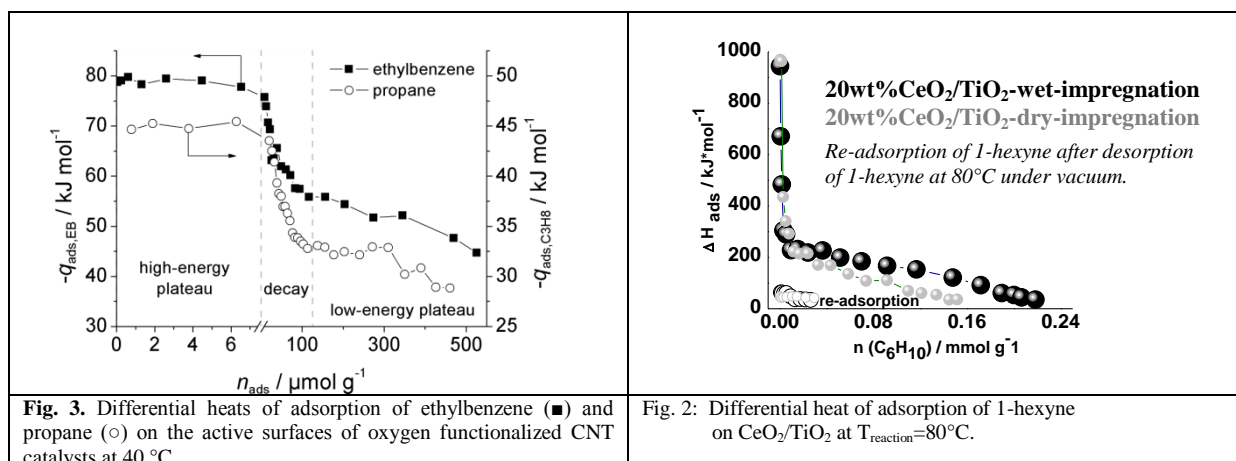
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Adsorption phenomena play an important role in heterogeneous catalysis. The knowledge about heat of adsorption of reactant on the surface of a catalyst can contribute to a better understanding of the complex microkinetics. Since perhaps only a minor fraction of all surface atoms form active centers, the determination of their number and strength requires a sensitive analytical method. We focus on adsorption microcalorimetry [1]. To facilitate the correlation of microcalorimetric results with the catalytic performance, a molecule similar to the reactant, or the reactant itself, was used.  $T_{\text{ads}}$  was chosen lower than  $T_{\text{reaction}}$  to separate the adsorption process from the catalytic reactions or closely related to  $T_{\text{reaction}}$  to study the surface chemical events during reaction.

In this work, we will demonstrate how structure-activity correlations can be established by combining microcalorimetry with electron microscopy, spectroscopic techniques, DFT calculations and catalytic test reactions. The power of these complementary methods will be illustrated by choosing the following examples:

- (i) propene metathesis over MoOx/SBA-15 [2],
- (ii) pure-phase MoVTaNb oxide for selective oxidation of propane to acrylic acid [3],
- (iii) 1-hexyne adsorption at  $80^{\circ}\text{C} = T_{\text{react}}$  on supported ceria, being unexpectedly active in the three-phase semi-hydrogenation of 1-hexyne: The more active catalyst is characterized by a higher amount of adsorption places for 1-hexyne, a dynamic surface and a slightly easier regeneration of the surface after 1-hexyne contact at reaction temperature. The key-note is that a very small number of surface sites is active and selective in alkyne hydrogenation (Fig.2) [4].
- (iv) supported ceria for HCl oxidation [5],
- (v) carbon-based catalyst (oCNT) for oxidative dehydrogenation of propane or ethylbenzene: A two-site redox kinetic approach was chosen to separate the reaction of the hydrocarbon with the quinone sites from the subsequent reoxidation of formed phenol groups by  $\text{O}_2$  (Fig.1) [6].
- vi) Ag-O dynamics during thermal treatments and ethylene epoxidation
- vii) Ni based catalysts for the dry reforming of methane [7]



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Fig. 2: Differential heat of adsorption of 1-hexyne on  $\text{CeO}_2/\text{TiO}_2$  at  $T_{\text{reaction}} = 80^{\circ}\text{C}$ .

Fig. 3. Differential heats of adsorption of ethylbenzene (■) and propane (○) on the active surfaces of oxygen functionalized CNT catalysts at  $40^{\circ}\text{C}$ .