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New insights by electron microscopy and microcalorimetry on the reactivity of CNT-based materials for catalysis and electrocatalysis

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To get insight into the nature of the relevant surface processes, two reaction systems have been studied by reactive microcalorimetry on differently active catalysts: O₂ chemisorption at 80°C on Pd/CNT catalyst for selective oxidation of alcohols to valuable compounds;¹ CO₂ chemisorption at 40°C on Fe/CNTs based electrocatalysts for the reduction of CO₂ to long chain hydrocarbons.² Additionally, the surface basicity of N-CNTs was investigated by CO₂ chemisorption at 40°C.³ The beneficial effect of the N-functionalization of the carbon support can be described in terms of population and strength of the defective sites.

The microcalorimetry CO₂ chemisorption on the Fe-based electrocatalysts shows the presence of special CO₂ chemisorption sites and how they correlated with the N-functionalization of the carbon support³ which allows higher electrocatalytic performance. The sample Fe/N-CNT shown in Figure 1 is characterized by few irreversible chemisorption sites at the uncoordinated sites of the facets out of the majority of reversible chemisorption sites at the hydrated oxide surface of the small nanoparticles characterize². The reversible sites are those relevant for the electrocatalytic CO₂ conversion to fuel. The experiments also show that the surface of CNTox leads to electrocatalysts, that are not stable under CO₂ chemisorption because the metal nanoparticles are agglomerating and the carbon surface is damaged during the chemisorption process.

The oxygen chemisorption on Pd/N-CNT at 353K occurs on relatively few surface sites, however is characterized by oscillating and by very high differential heats. (~750 kJ/mol for Pd/N-CNT873K). Both phenomena indicate that the high differential heat is due to dissociative oxygen chemisorption and the oxidation reactions of the protective agent (PVA) covering the Pd nanoparticles. The contribution of heat of oxidation reaction is differs among the samples investigated and correlates with the reactivity of the catalysts in the liquid phase oxidation¹. The oxygen chemisorption on the Pd/N-CNT catalyst at room temperature is characterized by a very small amount of adsorbed oxygen and corresponding integral heat signals of very low intensity. Thus, the differential heat could not be determined with sufficient accuracy.

The CO chemisorption on Pd and Pd-Au/N-CNT has shown a different specific surface area among all the samples investigated. Furthermore, a different energetic distribution of the CO chemisorption sites was observed among the samples investigated. CO does not chemisorb on Au/N-CNT catalysts.

In this work we demonstrate that microcalorimetry chemisorption of the reactant at reaction condition is a useful tool to obtain insight into a catalytic and electrocatalytic process. The differential heat of chemisorption is an evaluation parameter to estimate the performance of the catalyst/electrocatalyst. Also, CO chemisorption by microcalorimetry allows, apart from the determination of the metal surface area, to obtain structural information on the nature of the surface sites through the differential heat of chemisorption. Such values are of relevance for comparing theoretical reaction pathways with numerical experimental observables.

References

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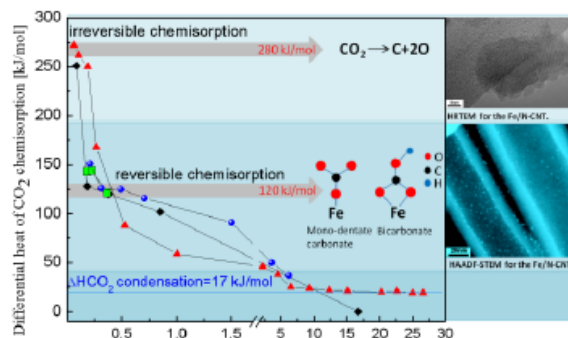


Figure 1: Differential heats of CO₂ adsorption versus amount of CO₂ uptake.