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

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### **Introduction**

In the present work, microcalorimetry is applied to characterize the surface chemical properties of nanocarbon (NC) and NC-based materials for heterogeneously catalyzed and electro-catalyzed reaction.

By a comparative study of differently active materials, the reactivity data can be analyzed with respect to the surface processes occurring on these materials during adsorptive microcalorimetry. Three reaction systems have been studied: CO<sub>2</sub> chemisorption on Fe/CNTs based electrocatalysts for the reduction of CO<sub>2</sub> to fuel; O<sub>2</sub> chemisorption on Pd /CNT catalysts for the selective oxidation; O<sub>2</sub> chemisorption on Pd/Au /CNT catalysts for the synthesis of H<sub>2</sub>O<sub>2</sub>. Additionally, CO chemisorption was carried out on Pd and Pd/Au /CNF catalysts as a tool to determine both, the specific Pd surface area and the nature of the chemisorption sites.

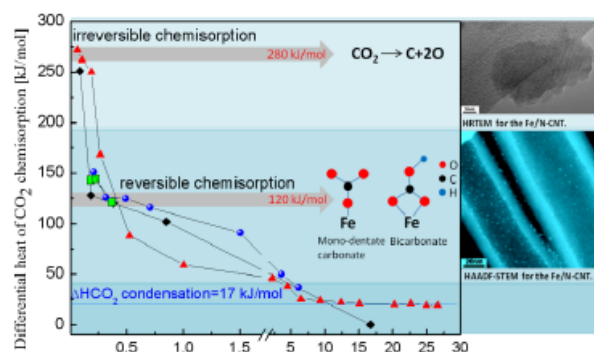
### **Experimental**

A SETARAM MS70 Calvet calorimeter was combined with a custom-designed high vacuum and gas dosing apparatus [1]. CO<sub>2</sub> or O<sub>2</sub> were stepwise adsorbed at reaction temperature 313 K and 353 K, respectively. O<sub>2</sub> and CO chemisorption was performed on the Pd and Pd-Au/N-CNT catalysts. The Pd and at room temperature. Pd/Au catalysts are obtained via sol-immobilization on the CNFs [2], while Fe-based electrocatalyst are prepared via incipient wetness impregnation [3].

### **Results and discussion**

The microcalorimetry CO<sub>2</sub> chemisorption on the Fe-based electrocatalysts shows the presence of special CO<sub>2</sub> chemisorption sites and how they correlated with the N-functionalization of the carbon support [4] 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 characterize [5]. The reversible sites are those relevant for the electrocatalytic CO<sub>2</sub> conversion to fuel. The experiments also show that the surface of CNT<sub>ox</sub> leads to electrocatalysts, that are not stable under CO<sub>2</sub> 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 oxidation [6]. The oxygen chemisorption on the Pd and Pd-Au/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.



**Figure 1: Differential heats of CO<sub>2</sub> adsorption versus amount of CO<sub>2</sub> uptake.**

## Conclusion

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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