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New insights by microcalorimetry on the reactivity of CNT-based materials for catalysis

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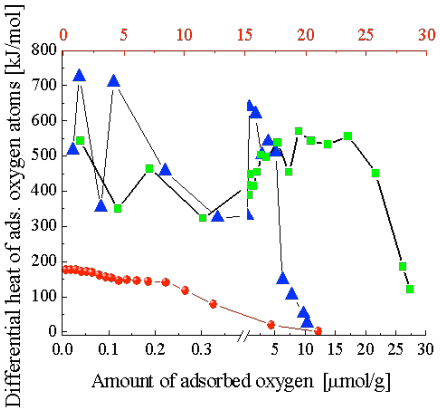
In the present work, adsorption microcalorimetry is applied to characterize the surface chemical properties of nanocarbon (NC) and NC-based materials for heterogeneously catalyzed reaction. In particular, the focus is placed on the interaction of O_2 at the surface of PVA-protected Pd nanoparticles immobilized onto N-CNT for liquid phase oxidation reaction of benzyl alcohol to benzaldehyde at 80 °C.

By monitoring the thermal response of the interaction of the reactant under reaction condition it was possible to gain new insights into the catalyst's surface in its active state. By a comparative analysis of differently performing catalysts in their fresh state and after reaction, it was possible to identify the nature of the relevant active sites for achieving high selectivity. The picture below shows the reaction heat as function of the oxygen coverage for the used Pd samples, which is composed, in part by the heat of oxygen chemisorption and in part by the heat of PVA combustion. In contrast the dissociative oxygen chemisorption is hindered on the fresh samples due to the presence of the PVA. This investigation shades light on the role that the PVA protective shell plays in the application of nanoparticles in catalysis. The PVA shell not only control the particles size during the catalyst preparation but also during the reaction suppresses the total oxidation by inducing specific adsorption geometry for the reactants. Additionally, it is demonstrated in this work that CO adsorption microcalorimetry is a powerful tool to probe the energetic distribution of chemisorptive sites on the topmost layer of Pd and Pd/Au nanoparticles onto N-CNT.



Differential heat of O_2 chemisorption and reaction vs. amount of O_2 uptake at $T_{adsorption}=T_{reaction}$ = 80°C.
Pd-PVA/N-CNF873K (blue triangle) , Pd-PVA/N-CNF473K (green quadrangle) and Ref.: $Pd_{w.i}$ /VGCNF (red circle)