

Surface characterization of nano-structured carbon catalysts by adsorption microcalorimetry using reactants as probe molecules

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Introduction

Carbon nanotubes (CNTs) as well as P₂O₅-modified CNTs are active catalysts in oxidative dehydrogenation (ODH) of propane^[1]. Information about surface coverage and heat of adsorption is an important input for mechanistic understanding and kinetic modeling in heterogeneous catalysis. Microcalorimetry allows the measurement of differential heat evolving when known quantities of probe molecules are adsorbed on the catalyst surface. Selecting reactants as probe molecules and investigating quenched catalyst surfaces that were operated under steady state conditions are key issues to attain quantitative information on a catalyst surface that approaches closely the active state. In the present work, we adsorbed propane and propene on the surface of oxidized carbon nanotubes (oCNT), 5 wt% B₂O₅/oCNT, and graphite used as catalysts in ODH of propane in order to study the surface sites relevant for catalytic turnover.

Experimental

An apparatus and a procedure were developed to characterize the adsorption sites on the surface of a catalyst in any state along the reaction profile by microcalorimetry.^[2] The calorimeter cell is used as a fixed bed reactor containing 0.5 g catalyst under propane ODH reaction conditions (673 K, 50 ml min⁻¹, C₃H₈/O₂/He = 10:5:85 vol%) applying a micro-GC (Varian CP-4900) for product analysis. After reaching steady state performance, the cell was cooled to room temperature in 50 ml min⁻¹ He. The sealed cell was transferred into a SETARAM MS 70 calorimeter connected to a volumetric system, and evacuated at 313 K. Adsorption was performed at 313 K.

Results and Discussion

At low equilibrium pressures, propane adsorption occurs on energetically homogeneous adsorption sites with constant heat of adsorption of 45 kJ mol⁻¹ (Fig. 1, A). With increasing coverage the heat of adsorption drops sharply (B-C), reaching a

plateau at approximately 33 kJ mol^{-1} (D) indicating that the most abundant adsorption sites on the surface of oCNT used in oxidative dehydrogenation of propane are characterized by weak interaction with propane. Propane adsorption is fully reversible on all catalysts. The surface modification with B_2O_3 does not affect the general energy profile, however, all heats of adsorption are lowered by $\sim 5 \text{ kJ mol}^{-1}$, which could explain the higher alkene selectivity in propane ODH observed over this catalyst. In contrast to propane, propene is partially irreversibly adsorbed. Re-adsorption experiments shown in Figs. 1 & 2 illustrate that the reaction of propene with the oCNT surface at 313 K significantly modifies the nature of adsorption sites. Combination of microcalorimetry with XPS and TPD allows the assignment of propane adsorption sites of type A to ketone and quinone groups, of type B to carboxylic anhydrides, of type C to lactone/ester, phenol, and ether sites, and of type D to adsorption on the basal plane of graphitic carbon.

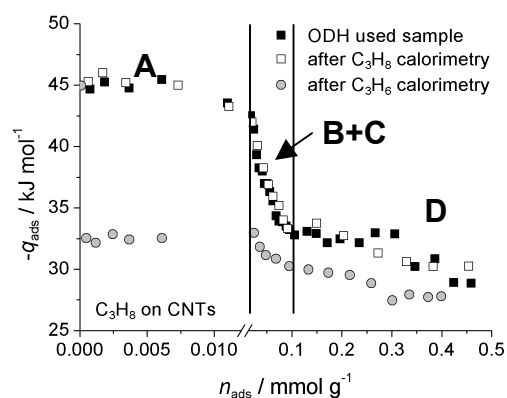


Fig. 1. Differential heats of adsorption of propane on oCNT used in oxidative dehydrogenation of propane.

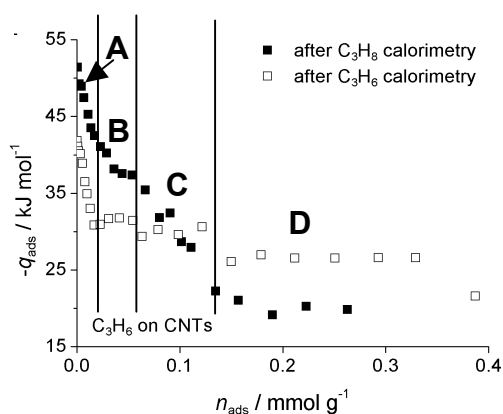


Fig. 2. Differential heats of adsorption of propene on oCNT used in oxidative dehydrogenation of propane.

Summary

The present calorimetric study shows that adsorption of hydrocarbons on carbon surfaces favorably occur on oxygenated sites. The analysis of propane adsorption on quenched active CNT surfaces allows for a quantification of the different adsorption sites and provides experimental evidence for the interpretation of differences in the catalytic activity of CNT catalysts in the oxidative dehydrogenation of propane.

References

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