

Adsorption Microcalorimetry in Heterogeneous Catalysis

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Heterogeneous catalysis involves specific chemical interactions between the surface of a solid and the reacting gas molecules. The catalytic cycle is generally composed of adsorption steps, surface reaction processes, and desorption steps. The energetics of these surface chemical events play an important role in the determination of the catalytic properties of the surface.

Adsorption microcalorimetry is a direct method to determine number, strength and energy distribution of adsorption sites on a catalyst. It allows calculation of the differential heats evolving when known amounts of gas probe molecules are adsorbed on the catalyst surface. The released heat is related to the energy of the bonds formed between the adsorbed species and the adsorbent and hence to the nature of the bonds and to the chemical reactivity of the surface. The key to the effective utilization of adsorptive microcalorimetry in heterogeneous catalysis is the judicious choice of gas-phase molecules and adsorption temperature for study. Reactants and products of the catalytic reaction can be employed when adsorption of these gases leads to well-defined adsorption species. Choosing T_{ads} close to T_{reaction} allows studying the reaction mechanism more in detail. If T_{ads} is selected lower than T_{reaction} then the pure adsorption process can be investigated because side reactions are prevented. Selected calorimetric measurements on nano-structured carbon (oCNT, N-CNT), supported metals (Pd/N-CNT, PdAu/N-CNT, Pt/H-Mordenite), supported metal oxides ($\text{FeO}_x/\text{N-CNT}$, $\text{V}_x\text{O}_y/\text{SBA-15}$, $\text{MoO}_x/\text{SBA-15}$, Cu-MOF) and mixed metal oxides (MoVTeNb oxide) will be presented.

A quasi *in-situ* micro-calorimetric study¹ was performed to classify the adsorption sites on the surface of CNT catalysts during ODH of propane.² In agreement with TPD and XPS analyses, the surfaces contain oxygen groups, approximately 3–5% of the total surface area. A small amount of homogeneous high-energy sites, denoted as type A sites, form a plateau with constant heat of propane adsorption of 45 kJ mol^{-1} . These sites react irreversibly with propylene, however, in this case with a decreasing differential heat of adsorption. Their amount is 10 and $5\text{--}8 \text{ }\mu\text{mol g}^{-1}$ on CNTs and boron oxide loaded $\text{B}_2\text{O}_3\text{-CNTs}$, respectively. Sites of somewhat lower energy and heterogeneous composition are classified as type B sites. Again, propane adsorbs reversibly, whereas propylene does not. Their amount is $40\text{--}50 \text{ }\mu\text{mol g}^{-1}$ on CNTs and $20\text{--}30 \text{ }\mu\text{mol g}^{-1}$ on $\text{B}_2\text{O}_3\text{-CNTs}$. Type C sites are oxygenated species with weak and reversible interaction with both propane and propylene (50 and $60 \text{ }\mu\text{mol g}^{-1}$ on CNTs and $\text{B}_2\text{O}_3\text{-CNTs}$, respectively). Finally, type D sites are low energy sites being free of oxygen and present in such abundance that their complete coverage could hardly be obtained in the present study. We suggest to following assignment of the sites: type A sites are ketone and quinone groups; type B sites are carboxylic anhydrides; type C sites are lactone/ester, phenol, and ether sites; type D sites is the basal plane of graphitic carbon.

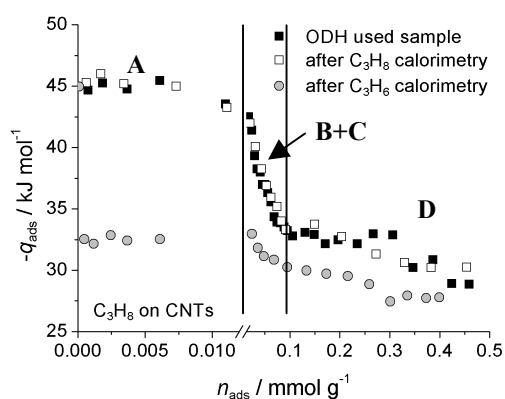


Fig. 1. Differential heats of adsorption of propane on oCNT used in oxidative dehydrogenation of propane.

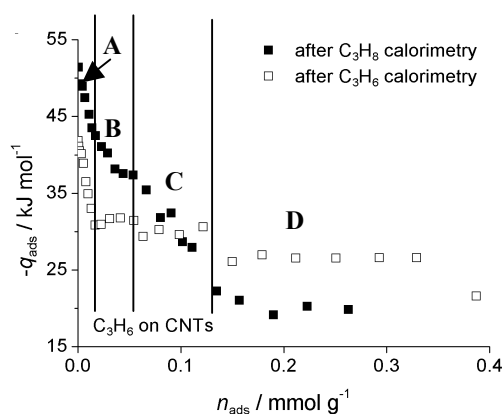


Fig. 2. Differential heats of adsorption of propene on oCNT used in oxidative dehydrogenation of propane.

[1] S. Wrabetz, X. Yang, G. Tzolova-Müller, R. Schlögl, F. Jentoft, J. Catal. **269** (2010) 351-358.

[2] B. Frank, S. Wrabetz, O.V. Khavryuchenko, R. Blume, A. Trunschke, R. Schlögl, ChemPhysChem **12** (2011) 2709-2713.