

Dynamics in heterogeneous Catalysis -monitored by microcalorimetry beyond adsorption-

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For a detailed understanding of complex reaction networks we need thermodynamic data of high accuracy and information about the nature of the catalyst surface. Therefore, we quantitatively study the adsorption, activation, and reaction phenomena close to the reaction parameters. Furthermore, we simulate reactants-induced responses of the surface via adsorption/desorption cycles in order to stepwise create an active surface, and thus can get new insights into the dynamic behaviour of the surface. Since perhaps only a minor fraction of all surface atoms form active sites, the quantification requires a very sensitive analytical method. We focus on microcalorimetry beyond adsorption.[1-4] This is a direct method to determine the number, strengths and energy distribution of adsorption sites, as well as adsorption constants and the active surface area. To facilitate the correlation of microcalorimetric results with the catalytic performance, a molecule similar to the reactant is used.

In this work, we present i) CO chemisorption cycles on a Ni/MgAl oxide catalyst for dry reforming of methane (DRM) [3], ii) propane and ethane adsorption/desorption cycles on a MoV oxide catalyst for oxidative dehydrogenation of alkanes [5] and iii) CO chemisorption on Ir based catalysts for oxygen evolution reaction (OER) [4].

In the first example, the influence of structural and compositional properties of Ni/MgAl catalysts on the catalytic performance in dry reforming of methane (DRM) has been studied.[3] In general, the most active 50wt.-%Ni/MgAl catalyst ($X_{\text{CH}_4,10\text{h}}=73\%$) is characterized by bigger Ni particles (>20nm) due to the high Ni content. The particles are mainly metallic and partially covered by an overgrowth (NiAl_2O_4). Reactant-induced changes of the surface via adsorption/desorption CO cycles are revealed by a drastic change in the differential heat profiles due to restructuring of metallic Ni sites (Fig. 1). This behavior evidences a highly dynamic surface. In contrast, the less active 5wt.-%Ni/MgAl oxide catalyst ($X_{\text{CH}_4,10\text{h}}=50\%$) shows no dynamic features. We can conclude that an active Ni-based catalyst needs metallic Ni sites and has dynamic capabilities to restore deactivated metallic Ni sites. The less active catalyst has a comparably high nickel oxide content, which probably prevents the dynamics.

The second example presents MoV oxide as an active catalyst in the oxidative dehydrogenation of alkanes. In-situ photoelectron spectroscopy has shown that with time on stream the surface of the catalyst is progressively enriched in V^{5+} , which leads to a decrease in selectivity to acrylic acid. [5] Fig. 2 shows adsorption/desorption cycles of propane measured by microcalorimetry. At very low coverages of propane the differential heat increases over the cycles. The newly generated sites might be related to the segregation of V^{5+} . The very strong interaction of propane with these sites explains the decrease in selectivity caused by V-segregation. The MoV catalyst was studied in a corresponding kinetic experiment. The overall barrier for propane activation can be estimated with 133 kJ/mol based on measured adsorption enthalpy (59 kJ/mol) and apparent activation energies (74 kJ/mol). The intrinsic barrier for additional studied V-catalysts increases in the order MoV oxide (133 kJ mol⁻¹) < V_2O_5 (136 kJ mol⁻¹) < MoVTeNb oxide (143 kJ mol⁻¹[1]) < $\text{V}_x\text{O}_y/\text{SBA-15}$ (162/154 kJ mol⁻¹[1]), which is in agreement with a decrease in the normalized consumption rate of propane in the same order. Comparison with DFT calculations [6] interestingly suggests that the cluster size

of the active surface vanadium oxide ensembles decreases in the order MoV oxide > V_2O_5 > MoVTeNb oxide > V_xO_y /SBA-15.

Thirdly: Ir-based catalysts are promising materials to electrocatalyze the oxygen evolution reaction in acidic media. To investigate the electronic structure of iridium metal, rutile-type IrO_2 and an amorphous IrO_x , synchrotron-based X-ray photoemission and absorption spectroscopies were combined with theoretical calculations. Furthermore, we applied CO chemisorption experiments at 40°C using microcalorimetry under reaction conditions to identify surface differences between active amorphous IrO_x and inactive crystalline IrO_2 materials (Fig. 3). Only the active amorphous Ir oxide shows average differential heats of 125 kJ mol^{-1} due to the CO oxidation. The measured differential heats of reaction agree nicely with those calculated for the reaction enthalpies of CO(g) with electrophilic O^+ species. [4]

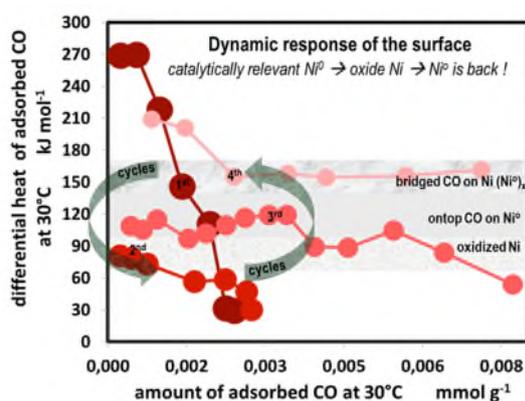


Figure 1: Differential heat of CO adsorbed on 50 wt.-% Ni/MgAl oxide. Adsorption-desorption cycles (4 cycles) at 30°C. [3]

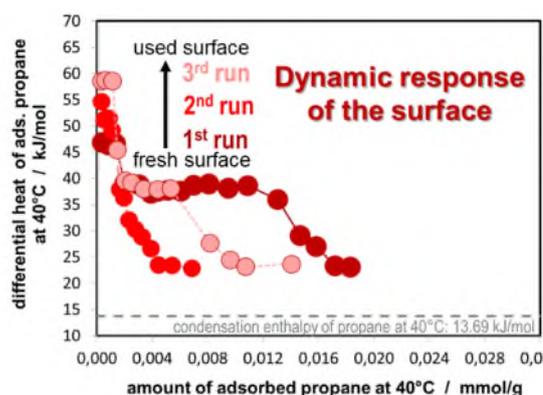


Figure 2: Differential heat profiles of 3 adsorption/desorption C_3H_8 -cycles on fresh MoV oxide at 40°C.

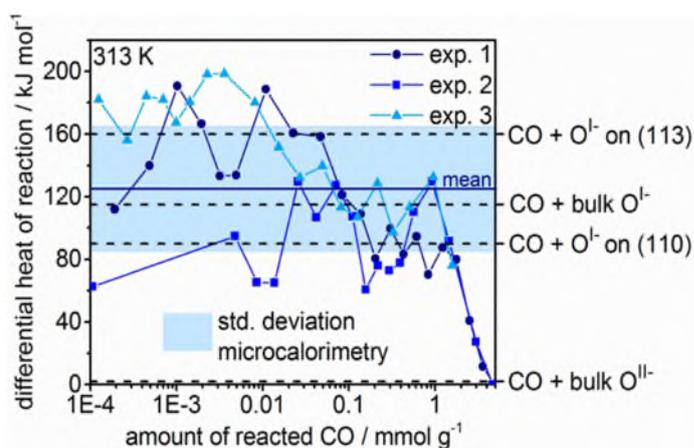


Figure 3: Differential heats over the amount of reacted CO with IrO_x (3 times) at 313 K = T_{reaction} . The dotted lines show the calculated heats (DFT) of reaction for CO with different oxygen species of IrO_x . [4]

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