# 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 for study. Reactants and products of the catalytic reaction can be employed when adsorption of these gases leads to well-defined adsorption species.
The adsorptive microcalorimetry was broadly used in several projects yielding a surprising spread of energetic data for the same molecule on different surfaces. In addition, we observed significant differences of the energetic data for the same molecule on slightly modified surfaces.
Selected calorimetric measurements on supported metals (Pd/N-CNF, Pt/H-Mordenite), supported metal oxides ($FeO_x$/N-CNF, $V_xO_y$/SBA-15, $MoO_x$/SBA-15) and mixed metal oxides (MoVTeNb oxide (M1)) will be presented, such as:

Molybdenum containing oxide catalysts - active in direct oxidation of propane to acrylic acid (aa) - have shown that the prepared state of the surface is different to the post-reaction state of the surface that means dynamic surface during reaction. Structure-selectivity relationship: a remarkable selective (53%) phase-pure M1 surface is characterized by high density of energetically homogeneous propane adsorption sites with a weak acid-base character. Small changes in compositional and structural characteristics of a modified $_{oxidized}$M1 leads to a loss of selectivity to acrylic acid by 37 %, which is associated with a reduced density and enhanced energetic heterogeneity of the propane adsorption site, and also an increased interaction of the propane with the still noticeable active M1 surface (Fig. 1).

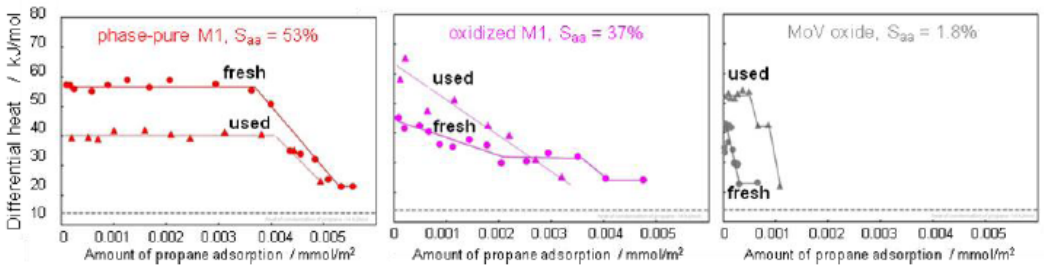


*Figure 1: Differential heats as a function of coverage of propane at 313 K on fresh (red dots) and used M1 (red triangle) fresh (magenta dots) and used $_{oxidized}$M1 (magenta triangle) grey dots) and used MoV (grey triangle) oxide*