Catalytic Partial Oxidation of Alkanes Investigated by Molecular Beam Mass Spectrometry

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The catalytic partial oxidation (CPO) of hydrocarbons to synthesis gas, alkenes and oxygenates is an attractive route for the production of valuable chemicals. The formation of synthesis gas via methane CPO on Rh and the oxidative dehydrogenation of ethane to ethene on Pt have economic advantages in comparison to steam reforming. The challenge in performing CPO is to avoid the thermodynamically favored total oxidation. Factors influencing the selectivity and mechanistic detail are thus of great interest. CPO reactions are insufficiently described by surface reaction steps only; they may proceed via heterogeneous-homogeneous mechanisms, with coupling of surface and gas phase reactions by exchange of energy and reactive species. Radicals have been postulated as key intermediates [1]. Our goal is to identify reactive species in the catalyst-gas phase boundary layer.

In order to sample and detect reactive species near the catalyst surface we have developed a novel type of Molecular Beam Mass Spectrometer (MBMS). Heterogeneous catalytic oxidations are performed under atmospheric pressure in a catalytic wall reactor (Rh-doped Pt tube, 4.4 mm ID), which is placed in a high vacuum chamber. The molecules in the surface-gas phase boundary are continuously sampled through a small orifice (100 µm) in the reactor wall. Adiabatic expansion into the vacuum generates a supersonic beam, and reactive species like radicals can be quenched. A quadrupole MS (millisecond timescale) allows identifying the molecular beam constituents arising from the reaction zone by their mass numbers and their ionization- and appearance potentials. Methane CPO experiments reveal formation of ethane, consistent with coupling of methyl fragments. Variation of the flow conditions shifts the reaction zone along the reactor such that axial profiles can be obtained. Results obtained with a model gas mixture (CO/N₂) let us expect that ppm concentrations of radicals can be detected and discriminated from interfering ions of the same mass.