ENI AWARD 2015

New Frontiers of Hydrocarbons - Downstream Prize

Helmut Schwarz

Winner

Concepts Rather than Recipes: an Unorthodox, Novel Approach to Selectively Activate Inert C-H Bonds

Research Description

Selective activation of inert C–H bonds for the environmentally benign ("green") conversion of ordinary hydrocarbons into valuable products, is one of the "Holy Grails" in contemporary chemistry. The rational approach to develop suitable catalysts for this process is hampered by the fact that conventional experiments carried out with "real" catalysts generally do not allow one to separate the processes at the active site of the catalyst from the influence of the surroundings. This limitation has ingeniously been overcome by the Schwarz group. As an internationally recognized specialist in the field of mass spectrometry, he has developed methods which allowed him to identify the elementary steps of metal-mediated C–H bond activations in the gas phase at a strictly molecular level. By studying the reactions of hydrocarbons, in particular methane, he succeeded to obtain detailed information about intrinsic reactivities of the naked metal ions as well as the influence of the environment. This approach, in combination with quantum chemical calculations, has provided fundamentally new insights on the role of cluster size, charge state, ligand effects, stoichiometry, dimensionality, oxidation state, or degree of coordinative unsaturation in these transformations. By identifying the processes occurring at active sites of catalysts, a breakthrough in contemporary catalysis research was achieved. This unorthodox approach, i.e. using a mass spectrometer as an ideal chemical arena, has been applied by Schwarz et al. to uncover numerous mechanistic features of the challenging activation of small, inert molecules, e.g. NH_3, CO_2, or CH_4, and to solve some fundamental problems of this seemingly simple chemistry, as for example the importance of relativistic effects in metal-mediated dehydrogenation of methane. It was shown that in some bimetallic systems the two metals "share their job": One metal is involved in the formation of metal carbenes, where relativistic effects matter, while the second metal controls the coupling process, e.g. the making of C–N bonds.

The direct, selective, room-temperature conversion methane → methanol is one of the grand challenges in contemporary catalysis, a reaction of enormous societal and technological importance. In a combined experimental/computational investigation the Berlin group proved that excited states may also play a dominant role in thermal reactions, and that the often ignored changes in spin multiplicity are key to understand the puzzling mechanistic details of this seemingly trivial conversion. Based on the "esoteric" gas-phase studies of simple diatomic metal oxides, in collaboration with S. Shaik (Jerusalem) the concept of "Two-State Reactivity" has been formulated; this paradigm is now well accepted in numerous areas of chemistry, and has, for example, resolved some of the controversies associated with the chemistry of Cytochrome P-450 and oxidation catalysis in general.