Hydrogen-atom transfer (HAT) constitutes a key process in a broad range of chemical transformations as it covers heterogeneous, homogeneous, and enzymatic reactions. While open-shell metal oxo species \([\text{MO}]^*\) are no longer regarded as being involved in the heterogeneously catalyzed oxidative coupling of methane \(2\text{CH}_4 + <\text{O}> \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O}\), these reagents are rather versatile in bringing about (gas-phase) hydrogen-atom transfer, even from methane at ambient conditions. In this lecture, various mechanistic scenarios will be presented, and it will be demonstrated how these are affected by the composition of the metal-oxide cluster ions. Examples will be discussed, how ‘doping’ the clusters permits the control of the charge and spin situation at the active site and, thus, the course of the reaction. Also, the interplay between supposedly inert support material and the active site – the so-called ‘aristocratic atoms’ – of the gas-phase catalyst will be addressed. Finally, gas-phase HAT from methane will be analyzed in the broader context of thermal activation of inert C–H bonds by metal-oxo species and it will be shown that the investigation of 'doped' metal oxide clusters as mimics for catalytic processes is about to enter into widely uncharted territory of chemistry, a field in which "each atom counts".