The Methane Challenge: Selective C–H bond Activation and C–C Coupling by Metal Oxides and Metal Carbides

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In this lecture we will discuss a story of one molecule (methane), a few metal-oxide cationic clusters (MOCCs), dopants, metal-carbide cations, oriented-electric fields (OEFs), and a dizzying mechanistic landscape of methane activation. One mechanism corresponds to hydrogen atom transfer (HAT), which occurs whenever the MOCC possesses a localized oxyl radical ($M{-}O^{\bullet}$). If the radical is delocalized e.g., in oligomeric $[MgO]_n^{\bullet+}$ ($n \geq 2$) the HAT barrier increases due to the penalty of radical localization. Adding a dopant (Ga_2O_3) to $[MgO]_2^{\bullet+}$ localizes the radical and HAT transpires. Whenever the radical is located on the metal and Lewis-acidic centers are present as in $[Al_2O_2]^{\bullet+}$ the mechanism crosses-over to proton-coupled electron transfer (PCET); here the positive Al center acts as a Lewis acid that coordinates the methane molecule, while one of the bridging oxygen atoms abstracts a proton, and the emerging negatively charged CH_3 moiety relocates to the metal fragment. We provide a diagnostic plot of barriers vs. reactants-distortion energies, which allows the chemist to distinguish HAT from PCET. Thus, doping of $[MgO]_2^{\bullet+}$ by Al_2O_3 enables HAT and PCET to compete. Similarly, pristine $[ZnO]^{\bullet+}$ activates methane by PCET generating many products. Adding a CH_3CN ligand to form $[(CH_3CN)ZnO]^{\bullet+}$ leads to a single HAT product. The CH_3CN dipole acts as an OEF that switches off PCET. Diatomic $[MC]^+$ cations (M = Au, Cu) react with CH_4 by different mechanisms, dictated by the nature and strength of the $M^+{-}C$ bond. For example, Cu^+, which bonds the carbon atom mostly electrostatically, performs coupling of C to methane to yield ethylene, in a single almost barrier-free step, with an unprecedented atomic choreography catalyzed by the OEF of Cu^+.