AB INITIO MODELING OF CHEMICAL PROCESSES ON SURFACES

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Understanding the fundamental aspects of the interactions of molecules with surfaces underpins many advanced technologies, such as molecular electronics, sensors, heterogeneous catalysis etc.

Palladium oxides are renowned for their high activity in catalytic reactions. We have investigated the complex reaction mechanisms of methane combustion on the PdO(100) surface within the framework of density functional theory. From an analysis of the calculated driving forces and activation energies for the dissociative adsorption of methane and the successive dehydrogenation of adsorbed hydrocarbons, we conclude that the experimentally observed conversion rates at temperatures of about 600 K cannot be explained in terms of direct dehydrogenation processes. Investigations of alternative reaction routes reveal that the reaction of oxygen molecules from the gas phase with hydrogen previously adsorbed on the catalyst surface can efficiently produce water.

According to combined ab initio molecular dynamics and static total energy calculations, the combustion reaction proceeds through the spontaneous formation of H₂O₂ followed by its dissociation and water formation. Following an analogous mechanism, oxygen molecules from the gas phase can also react with adsorbed CH₃ groups to produce CH₂O as an intermediate reaction product.