Mechanism of CO-oxidation on Pd/CeO_2 (100): The unique surface structure of CeO_2 (100) and the role of peroxide

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Understanding the atomic mechanism of low-temperature CO oxidation on a heterogeneous catalyst is challenging. We performed density functional theory (DFT) calculations to identify the surface structure and reaction mechanism responsible for low-temperature CO oxidation on Pd/CeO_2 (100) surfaces. DFT calculations reveal the formation of a unique zigzag chain structure by the oxygen and Ce atoms of the topmost surface of CeO_2(100) with Pd atoms located between the zigzag chains. O_2 adsorbed on such Pd atoms is stable in the presence of CO but plays a very important role in lowering the activation barrier for low-temperature CO oxidation by forming a square-planar PdO_4 structure and facilitating further O_2 adsorption. In-situ Raman spectroscopy studies confirm the adsorbed oxygen species to be peroxides. The calculated activation barrier for CO oxidation, based on the mechanism suggested by these unique structures and peroxides, is 31.2 kJ/mol, in excellent agreement with our experimental results.