

Unveiling the hydrogen-assisted surface reduction mechanism of cerium-gallium mixed oxide: A theoretical-experimental approach

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The relevance of the cerium based catalytic supports is primarily based on the remarkable oxygen storage capacity of these materials, which is linked to the creation, stabilization and diffusion of oxygen vacancies, especially in the oxide surface, due to the reversible redox property of the Ce(IV)/Ce(III) pair. Temperature-programmed reduction in H₂ and in CO results showed that the redox behavior is noticeably enhanced in the gallium-doped ceria materials as compared to pure cerium oxide. These last results were in agreement with ultimate oxygen storage capacity, in situ time-resolved XRD and x-ray absorption near edge measurements, which further confirmed the reduction state of cerium. In this work, the redox properties of the cerium-gallium oxide are evaluated in-situ using time-resolved infrared spectroscopy in transmittance and diffuse reflectance mode. Two characteristic infrared bands were analyzed: A peak at 2127 cm⁻¹, which is assigned to the forbidden electronic transition $^2F_{5/2} \rightarrow ^2F_{7/2}$ of Ce(III) cations, and a band at approximately 2000 cm⁻¹ attributed to the stretching mode of the Ga-H surface bond. Theoretical calculations by periodic density functional theory (DFT) confirm the higher reducibility of Ga-doped ceria oxides and give a molecular description of the stabilization of the doped material. Based on these combined spectroscopic and theoretical studies, a novel mechanism is proposed for the reduction of Ce(IV) to Ce(III) where Ga-H species are suggested to be directly involved in this surface process.