Catalysts based on cerium oxide are ubiquitous in industrial-scale chemical conversion. Here, a thorough study of their fundamental properties is undertaken via a model system approach with the goal of furthering rational design in heterogeneous catalysis. A focus is put on understanding the behavior of oxygen vacancies in cerium oxide with respect to atomic co-ordination and electronic structure perturbations. Utilizing state-of-the-art probing techniques, a scalable model system framework is developed that allows for control over both the oxygen vacancy concentration and local co-ordination. High precision of the innovative approach facilitated observation of new phases of substoichiometric cerium oxide and lead to a first-of-a-kind investigation of the electronic structure of cerium oxide throughout isostructural transition from CeO_2 to Ce_2O_3. The acquired results advance fundamental understanding of essential properties of cerium oxide that are relevant to its utilization in heterogeneous catalysis and open new pathways for functionalization of cerium oxide-based materials. Furthermore, the methodology developed in the thesis is transferable to other important reducible oxides.