QM/MM Study of Isolated Surface Defects on Ceria

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Abstract

The ability to rapidly store/release oxygen atoms via a reversible oxidation/reduction mechanism has instigated ceria's technologically significant role in several industrial catalytic processes; such as its use in automobile three-way catalytic converters to remove environmentally harmful molecules from exhaust fumes. The processes involved in the simultaneous creation of an oxygen vacancy (defect) and the formation of two neighbouring formally charged Ce^{3+} ions, producing no difference in overall charge, are pivotal to the oxygen storage capacity (OSC) properties that give ceria its catalytic importance;

$$O^{2-} + 2Ce^{4+} \leftrightarrow \text{Oxygen Vacancy} + 2Ce^{3+} + \frac{1}{2}O_2(g).$$

Based on the OSC properties previously observed experimentally and theoretically for low index surfaces of ceria, it is important that we understand the mechanisms involved during the formation of surface defects. Within the literature, high level calculations focus on surfaces containing a large concentration of defects, requiring periodic low index crystal surfaces, where adjacent oxygen vacancy sites have the ability to influence each other. However, few high level computational studies are available with respect to low-concentration / isolated oxygen vacancies.

We will use a quantum mechanics / molecular mechanics (QM/MM) embedded-cluster approach to study a small cluster of atoms containing the isolated defect using high level computational techniques – Hartree-Fock, Density Functional Theory (DFT) and hybrid-DFT – while the surrounding structure is modeled using lower accuracy atomistic simulation methods. This QM/MM technique allows us the opportunity to model materials with a large nanostructure in a non periodic environment. By examining embedded-clusters of different size and shape, with the computational techniques described above, we hope to gain a better understanding of the reactions involved in the OSC mechanism on low index surfaces of ceria containing isolated (low concentration) defect sites. In this manner, we will be able to compare the accuracy of the different computational approaches in modeling isolated oxygen vacancies on the reduced surface of ceria and be able to compare the OSC process within low- and high- concentration defect environments.