Ab initio molecular dynamics of the electrocatalytic decomposition of hydrogen peroxide in the presence of a silver cluster

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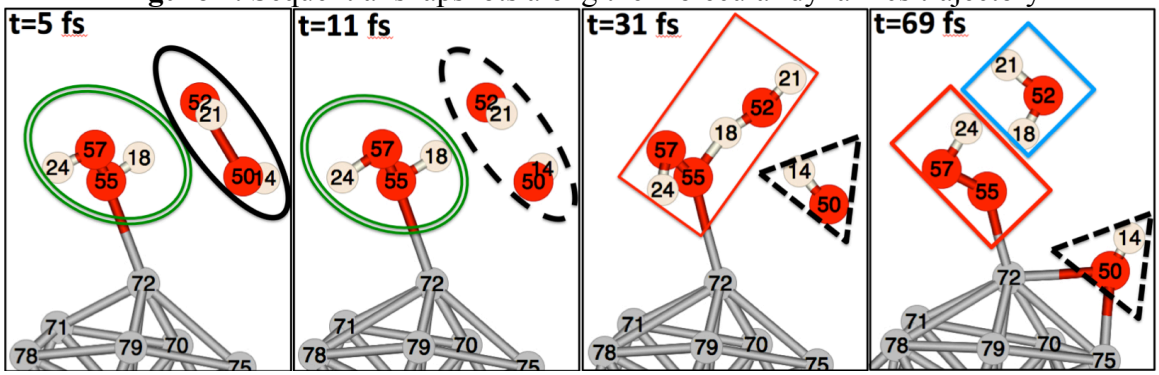
The interest in H_2O_2 propulsion systems has rekindled because H_2O_2 is more environmentally friendly than alternative fuel propellants, has a high density to maximize the oxidizer-to-fuel ratio,[1] and is stored non-cryogenically.[2] For this work, an atomic model of seventeen gaseous H_2O_2 molecules in the vicinity of an Ag_{13} cluster was explored by density functional theory utilizing the Kohn-Sham equation implemented in Vienna Ab initio Simulation Package for ground, excited, and ionized electronic configurations.[3] The system was equilibrated to higher temperatures to induce trajectories of atomic positions for the duration of 100 fs.[4] Molecular dynamics[5] used to explore the mechanisms of H_2O_2 decomposition show that the Ag catalyst expedites the exothermic H_2O_2 decomposition into H_2O and O_2 by providing alternative intermediate pathways containing metastable radicals, which lower the activation energy. Figure 1 shows the donation of electrons by Ag to HO• after the dissociation of H_2O_2 to form the more stable OH^-, allowing the other HO• to bond to the hydrogen of nearby H_2O_2, and form an unstable, intermediate H_3O_3 that quickly converts to H_2O.

Figure 1: Sequential snapshots along the molecular dynamics trajectory



Although the evolution of O_2 was not precisely observed in referenced simulation, we propose that HO• would accept the hydrogen from HO_2• to produce O_2, and would likely be demonstrated in an expanded time interval. As a result of the insight into the mechanism of the catalytic decomposition of H_2O_2 from the molecular dynamics, this computational study could be essential in optimizing the conditions for the electrocatalytic decomposition and propulsion performance of H_2O_2.

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