Mechanistic Insights into Hydrogen Peroxide Synthesis using Gold Palladium Clusters: A Density Functional Theory Study

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Hydrogen Peroxide ($\text{H}_2\text{O}_2$) is an important commodity chemical with both industrial and domestic uses. It's an environmentally benign oxidizing agent as compared to chlorinated oxidizers, since the primary by-products are $\text{H}_2\text{O}$ and $\text{O}_2$. Direct synthesis of $\text{H}_2\text{O}_2$ from $\text{H}_2$ and $\text{O}_2$ provides a promising alternative route to current industrial anthraquinone auto-oxidation process which requires energy intensive separation and concentration steps. Gold-palladium based bimetallic catalysts have been previously shown to be active for direct synthesis of $\text{H}_2\text{O}_2$ along with different acid/halide additives and solvents. Many experimental and kinetic studies have been performed on gold and palladium nanoparticles to study the dependence of different reactants but the mechanism of this reaction and active sites remain unclear and has been studied here.

Figure 1. Transition states of synthesis of OOH with different reactants over metallic clusters

In previous studies, $\text{H}_2\text{O}_2$ synthesis has been studied in different solvent media and it was found that protic solvent was necessary to produce $\text{H}_2\text{O}_2$. To understand the reaction mechanism and active site catalysis, we employed DFT study on 38-atom gold and palladium clusters. All calculations were performed using VASP with PBE+ U pseudopotentials with D3 dispersion corrections. Upon optimizing the clusters, $\text{O}_2$ was adsorbed on junction of different facets. $\text{O}_2$ adsorbed at the junction of (100) and (111) facet was found to most stable. With this configuration, then $\text{H}_2$ and $\text{H}_2\text{O}$ were adsorbed at adjacent positions with various configurations and the structures were optimized. These configurations were then used to create endpoint structures with OOH formation to simulate synthesis of hydroperoxy like species over gold and palladium clusters. Transition state search was carried out by performing interpolation and nudged energy barrier calculations using VASP-TST. It was observed the barrier energy was smaller with $\text{H}_2\text{O}$ as the proton source than $\text{H}_2$ (Figure 1a and b). Interestingly, with addition of free $\text{H}_2\text{O}$ molecule to study the effect of protic solvent, the barrier energy was lowered drastically (Figure 1c), which is in agreement with previous experimental studies. Lower barrier energies were also observed with implicit solvation. Similar effect in lowering of barrier energies was observed with palladium cluster as well (Figure 1d).

We have performed density functional theory calculations to understand $\text{H}_2\text{O}_2$ processes mechanism which can be used to understand the role of active site and different additives/solvents and help design better catalyst and process.

References

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