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Density Functional Theory Simulations of MOFs Encapsulated-Catalyzed Systems

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Website: http://www.clemson.edu/ces/computationalcatalysis

Motivation
- The development of new nanoporous materials with improved properties is critical to advances in many areas related to energy and environment.
- New catalysts, new gas storage media, and new sorbents for separations are urgently sought.
- New synthesis methods are needed.

- Driven by these, an enormous number of new nanoporous materials have been developed.
- MOFs are microporous and mesoporous materials synthesized in a building-block approach from metal ‘nodes’ and organic ‘linker’ molecules.
- They feature good mass transfer kinetics, high void volumes, and well-defined structures, and, in principle, tailorable cavities of uniform size.
- One of the grand challenges in catalysis is selectivity, especially when the undesired products are the more thermodynamically stable.

- The incorporation of nanoparticle(NPs) into MOFs has attracted great attention due to the chemical and physical properties exhibited by certain classes of nanoparticle.
- Modeling using Density Functional Theory (DFT) could be used to screen catalyst materials for a cheaper alternative.

Objectives
- Use Density Functional Theory (DFT) to model the reaction from butane oxidation to 5-butanol under certain MOFs encapsulated catalyst.
- Try to figure out all the possible steps involved in the butane oxidation to 5-butanol reaction.
- Analyze the thermodynamic and kinetic properties of the steps involved in the reactions to develop a best reaction mechanism.
- Work on different materials, molecular structures, oxide coverage and pore size to compare with each other in order to identify the material properties that lead to catalytic activity.
- Establish trends for use in future work.

Computational Details
- VASP DFT-O2 package, PAW pseudopotentials, PBE electron exchange and correlation functional
- Fully converged k-point grids (lots of increments for the numerical integration)
- Calculations run on Clemson’s super computer the Palmetto Cluster

Table 1. Parameters used in VASP calculations

<table>
<thead>
<tr>
<th>VASP Computational Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cut off Energy</td>
<td>500 eV</td>
</tr>
<tr>
<td>Electronic Iteration Tolerance</td>
<td>0.0001</td>
</tr>
<tr>
<td>Geometric Iteration Tolerance</td>
<td>0.05 eV</td>
</tr>
<tr>
<td>Pseudopotential</td>
<td>Projector Augmented Wave (PAW)</td>
</tr>
<tr>
<td>Exchange-Correlation Functional</td>
<td>Perdew-Burke-Ernzerhof (PBE)</td>
</tr>
<tr>
<td>6-points for back</td>
<td>11x11x11</td>
</tr>
<tr>
<td>Dispersion F1-Correction</td>
<td>DFT-O2 [Dobson]</td>
</tr>
</tbody>
</table>

Table 2 Reaction properties involved in butane oxidation

<table>
<thead>
<tr>
<th>Reaciton #</th>
<th>Reactants</th>
<th>Products</th>
<th>O config, reacts</th>
<th>O config, prods</th>
<th>Erxn Eact</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2C4H10 + 2O2 + 2O* = 2C4H10 + O2 + O2* + 2O*</td>
<td>X</td>
<td>0.25</td>
<td>0.62</td>
<td>0.24</td>
</tr>
<tr>
<td>25</td>
<td>C4H10 + C4H9OH* + 5O* = C4H10 + C4H9OH + 5O*</td>
<td>X</td>
<td>X</td>
<td>308.81</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Future Work
- We will be continuing working on the thermodynamic and kinetic calculations of the reaction steps to fill out the table which is shown before on the Ag3Pd catalyst.
- Try to figure out the reaction mechanism of the butane oxidation on the Ag3Pd catalysts.
- Develop trends to minimize computational expense for electronic energy calculations.
- Determine the appropriate locations or sites of the reactants and oxygen which is more favorable for the reaction steps.
- Find other potential metal or alloy materials. As a starting point, we are looking at Cu3Pd and Pd/Cu catalysts. Another idea is to look at a metal oxide or mixed metal oxide, which is similar to the active site in methane monooxgenase.
- Find the best structure and coverage for other materials.
- Calculate thermodynamic properties of the reaction steps as on Ag3Pd surface.
- Compare the materials with Ag3Pd and other surface we have done before.

References

Acknowledgements
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- Cyberinfrastructure Technology Integration Group
- Palmetto Cluster Supercomputer
- Northwestern University
- Thanks to Diego Gomez and all the others doing experimental work.
- National Science Foundation under Grant #1334028.

Ongoing Work

As the results shown below, we need to consider other materials to see whether they work for the reaction.

The first alloy we considered is Cu3Pd.

Table 3 Reaction properties involved in butane oxidation

<table>
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<td>0.00</td>
</tr>
</tbody>
</table>

Pd3 is another alloy which we will be looking into in the future. Searching the literature, we found that Pd3 is expected to bind O2 more strongly than Ag3Pd, which should facilitate O2 dissociation. Cu also binds O2 more strongly than Ag, but it should be less favorable for C-H bond activation than Pd, which should prevent overdehydrogenation. What’s more, some researches have been done to these alloy structure.