

Spring 2015

Density Functional Theory Simulations of MOFs Encapsulated-Catalyzed Systems

Jiazhou Zhu
Clemson University

Rachel B. Getman
Clemson University

Follow this and additional works at: https://tigerprints.clemson.edu/chembio_grs

 Part of the [Chemical Engineering Commons](#)

Recommended Citation

Zhu, Jiazhou and Getman, Rachel B., "Density Functional Theory Simulations of MOFs Encapsulated-Catalyzed Systems" (2015). *Chemical and Biomolecular Graduate Research Symposium*. 7.
https://tigerprints.clemson.edu/chembio_grs/7

This Poster is brought to you for free and open access by the Research and Innovation Month at TigerPrints. It has been accepted for inclusion in Chemical and Biomolecular Graduate Research Symposium by an authorized administrator of TigerPrints. For more information, please contact kokeefe@clemson.edu.



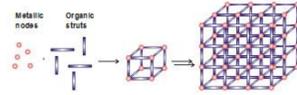
Jiazhou Zhu, Rachel B. Getman

Department of Chemical and Biomolecular Engineering, Clemson University

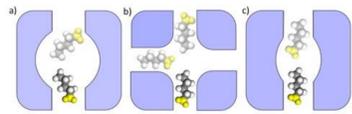
Website: <http://www.clemson.edu/ces/computationalcatalysis>

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 nanoparticles (NPs) into MOFs has attracted great attention due to the chemical and physical properties exhibited by certain classes of nanoparticles.
- 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 1-butanol under certain MOFs encapsulated catalyst.
- Try to figure out all the possible steps involved in the butane oxidation to 1-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-D2 package, PAW pseudopotentials, PBE electron exchange and correlation functional
- Fully converged kpoint grids (lots of increments for the numerical integration)
- Calculations run on Clemson's super computer the Palmetto Cluster

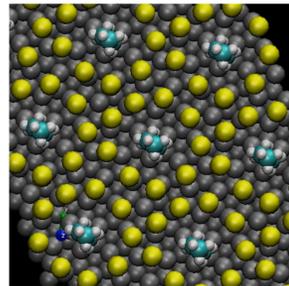
Table 1: Parameters used in VASP calculations

VASP Computational Parameters	
Cutoff Energy	400 eV
Electronic Iteration Tolerance	1×10^{-5} eV
Geometric Iteration Tolerance	0.03 eV/Å
Pseudopotential	Projector Augmented Wave (PAW) ^[2]
Exchange-Correlation Functional	Perdew-Burke-Ernzerhof (PBE) ^[3]
K-points for bulk	11x11x11
Dispersion Force Correction	DFT-D2 (Grimme) ^[4]

Previous Work

Helium Ring Model

Periodic copies of butane within rings of helium on a 4x4 silver surface

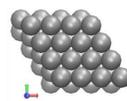
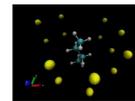
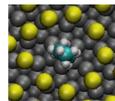


He = Yellow. C = Cyan. H = White. Ag = Silver.

- Choose helium because it is inert and exhibits virtually no chemical reactivity.
- Helium is placed at minimum 3 angstroms from nearest neighbor and C, H atoms.
 - Comparable to a van der Waals bond length, molecular kinetic diameter
 - This is the *minimum* pore size
- Adsorption favored in atop site

- Adsorption energy calculations:

- Ringed Model:**
 - $\Delta E_{\text{adsorption}} = \text{Energy of ringed molecule plus surface} - \text{Energy of ringed molecule} - \text{Energy of surface}$



$$-0.464 \text{ eV} = -271.856 - (-73.668) - (-197.726)$$

Conclusion from Previous Work

We have been working on all the reaction steps on Ag₃Pd surface

Reaction Pathway

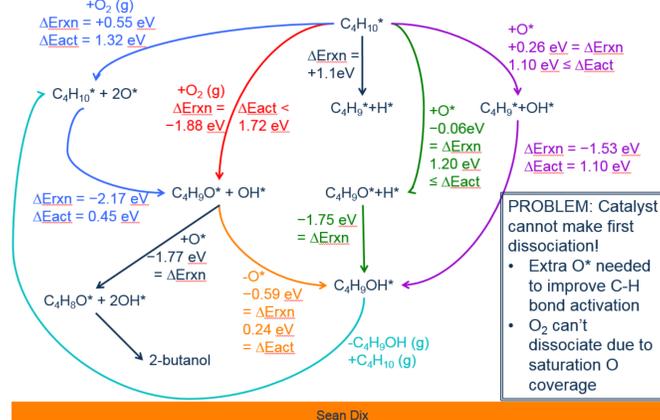


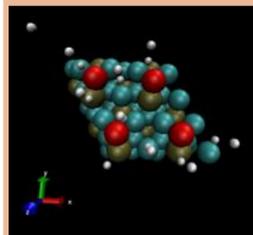
Table 2 Reaction properties involved in butane oxidation

Reaction #	Reactants	Products	config. react	config. prod	Erxn	Eact
1	2C4H10 + O2 + 2O*	2C4H10 + O2 + 2O*	p(2x4)-0	p(2x4)-0	0.00	0.00
2	2C4H10 + O2 + O2* + 2O*	2C4H10 + O2 + 4O*	p(2x4)-0	triangle	0.00	0.00
3	2C4H10 + O2 + 4O*	2C4H10 + O2 + 4O*	triangle	p(2x2)-0	-0.66	0.35
4	2C4H10 + O2 + 4O*	2C4H10 + O2* + 4O*	p(2x2)-0	p(2x2)-0	-0.08	0.00
5	2C4H10 + O2* + 4O*	C4H10 + C4H9OH* + 5O*	p(2x2)-0	X	-2.00	336.20
6	2C4H10 + O2* + 4O*	C4H10 + C4H9OH* + OH* + 4O*	p(2x2)-0	p(2x2)-0	-1.96	336.20
7	2C4H10 + O2* + 4O*	2C4H10 + 6O*	p(2x2)-0	double X	0.63	1.40
8	2C4H10 + O2 + 4O*	C4H10 + O2 + C4H9* + OH* + 3O*	triangle	line	0.26	1.10
9	2C4H10 + O2 + 4O*	C4H10 + O2 + C4H9O* + H* + 3O*	triangle	triangle-10*	-0.06	1.20
10	2C4H10 + O2 + 4O*	2C4H10 + O2* + 4O*	triangle	triangle	-0.27	0.00
11	2C4H10 + O2* + 4O*	2C4H10 + 6O*	triangle	triangle-20*	-0.04	0.47
12	2C4H10 + 6O*	2C4H10 + 6O*	triangle-20*	p(2x2)-0	-2.17	0.45
13	C4H10 + O2 + C4H9* + OH* + 3O*	C4H10 + O2 + C4H9OH* + 3O*	line	line	-1.53	1.10
14	C4H10 + O2 + C4H9OH* + 3O*	C4H10 + O2 + C4H9OH* + 3O*	line	line	0.00	0.00
15	C4H10 + O2 + C4H9OH* + 3O*	C4H10 + C4H9OH* + O2* + 3O*	line	line	-0.32	0.00
16	C4H10 + C4H9OH* + O2* + 3O*	C4H10 + C4H9OH* + O2* + 3O*	line	triangle-10*	-0.16	256.71
17	C4H10 + C4H9OH* + 5O*	C4H10 + C4H9OH* + 5O*	triangle-10*	p(4x4)-30	-2.12	301.03
18	C4H9OH + C4H9O* + OH* + 3O*	2C4H9OH + 4O*	line	line	-0.59	302.67
19	C4H9OH + C4H9O* + OH* + 3O*	C4H9OH + C4H9O* + 2OH* + 2O*	line or p(4x4)-3	p(2x4)-0	0.00	0.00
20	C4H10 + O2 + C4H9O* + H* + 3O*	C4H10 + O2 + C4H9OH* + 3O*	line	line	0.00	0.00
21	C4H10 + O2 + C4H9O* + 3O*	C4H10 + O2 + C4H9OH* + 3O*	line	line	0.00	0.00
22	C4H10 + O2 + C4H9O* + H* + 3O*	C4H10 + O2 + C4H8O* + H* + OH* + 2O*	line	p(2x4)-0	0.00	0.00
23	C4H10 + C4H9O* + OH* + 4O*	C4H10 + C4H9O* + 2OH* + 3O*	p(2x2)-0	p(4x4)-30 (?)	0.00	0.00
24	C4H10 + C4H9O* + OH* + 4O*	C4H10 + C4H9OH* + 5O*	X	X	-0.62	0.24
25	C4H10 + C4H9OH* + 5O*	C4H10 + C4H9OH* + 5O*	X	X	308.81	0.00

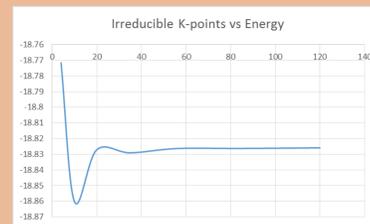
Ongoing Work

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

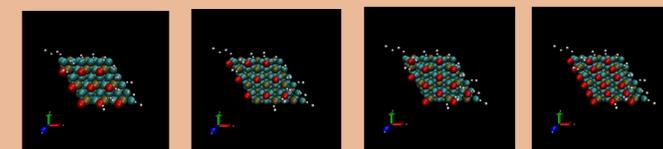


Cu₃Pd blue atoms are copper and green ones are palladium: we use the similar bulk structure as Ag₃Pd, and cut the surface (111)



The best k-points for Cu₃Pd bulk structure is found to be 11x11x11

Oxygen Coverage



The distance between the helium rings and surface is increased a little bit. Since we found in experiment the MOFs pores can not be such close the alloy surface. And in simulation work, the Helium ring will interact with the surface oxygen and lead to some unexpected results.

PdZn is another alloy which we will be looking into in the future. Searching the literature, we found that PdZn 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 overhydrogenation. What's more, some researches have been done to these alloy structure.

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 PdZn catalysts. Another idea is to look at a metal oxide or mixed metal oxide, which is similar to the active site in methane monooxygenase.
- 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

- Lu, G., et al. Nature Chem 4, 310 (2012).
- Li, H., Eddaoudi, M., O'Keeffe, M., and Yaghi, O. M. Nature 402, 276 (1999).
- Kresse, G. and Furthmüller, J. Comput Mat Sci 6, 15 (1996).
- Perdew, J. P., Burke, K., Ernzerhof, M. Phys Rev Lett 77, 3865 (1996).
- Grimme, S. J Comp Chem 27, 1787 (2006).
- Getman, R. B., Xu, Y., and Schneider, W. F. J Phys Chem C 112, 9559 (2008).
- Cavka, J. H. et al. JACS 130, 13850 (2008).
- Getman, R. B., Schneider, W. F., Smeltz, A. D., Delgass, W. N., and Ribeiro, F. H. Phys Rev Lett 102, 076101 (2009).

Acknowledgements

- Clemson University
 - Department of Chemical and Biomolecular Engineering
 - Cyberinfrastructure Technology Integration Group
 - Palmetto Cluster Supercomputer
- Northwestern University
 - Thanks to Diego Gomez and all the others doing experimental work
- External Funding
 - NSF under DMR grant #1334928

