Electronic Structure Calculations For Improving Catalyst Design for Use in the Hybrid Sulfur Cycle

Project highlight. No more than one or two sentences to highlight the impact for the nation and overview the technology in "layman's terms." No acronyms. Should include one image that reflects the key achievement or importance of the project.

Awards and Recognition

Provide a concise (100 words or less) description of any awards and/or recognition achieved due to participation in a FY20 LDRD project.

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

SRNL Legal Signature

Signature	**Date**

Electronic Structure Calculations For Improving Catalyst Design for Use in the Hybrid Sulfur Cycle

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Project Type: Seedling

Project Start Date: October 1, 2019
Project End Date: September 30, 2020

The hybrid sulfur cycle is a promising means for efficient production of large quantities of hydrogen with a small carbon footprint. However, many challenges remain in designing catalysts that are stable at high temperatures and have high sulfur tolerance. Theoretical calculations can provide fundamental insights at the electronic scale to improve our understanding of reaction mechanisms and surface energetics, thereby facilitating improved catalyst design. Here, density functional theory was used to explore the reaction energetics of the hybrid sulfur cycle on Pt, Au, and Pt - Au surfaces. A database of information has been built that contains calculations from which adsorption energetics and density of states information can be extracted.

FY2020 Objectives

- Run density functional theory calculations for various HyS steps on the Pt – Au catalyst surface
- Run density functional theory calculations with applied electric fields
- Expand the calculation database from FY2019's LDRD seedling

Introduction

Catalytic materials are used in nearly 80% of all chemical processes and yet are largely developed through trial and error methods of synthesis and evaluation. In order to take a more scientific approach to catalyst design, this work has constructed a database of density functional theory (DFT) calculations (expanding on those completed in FY19) that can be examined to gain a deeper understanding of how the structure of Pt, Au, and Pt – Au catalyst systems affects reactivity in the hybrid sulfur cycle (HyS). Design and control of catalyst structures used in HyS will enable the synthesis of specialty materials at the nanometer scale. Controls in design will help further elucidate the impact of spatial defects in atomic structure to enable the synthesis of new highly reactive species. This will further the understanding of how carbon supported Pt/Au catalysts interact to accelerate SO_2 oxidation. Understanding the mechanism of catalytic processes can be improved by determining deactivation rates, changes in chemical structure involved in each step, and macroscopic rates of conversion.

Incorporating advanced modeling and simulation to our knowledge base for HyS builds upon the research efforts in nano-particulate catalytic material systems to develop methods of fine-tuning catalyst reactivity at the molecular level. This seedling LDRD focused on expanding the database of calculations that were performed in FY2019 and is comprised of systematic investigations that demonstrate how the electronic structure of Pt/Au catalysts affect the adsorption energetics and catalytic activity at the surface.

Approach

Density functional theory as implemented in the VASP code[1-3] was used to calculate the electronic structure and energetics of Pt/Au systems. The two reactions in the HyS cycle are:

$H_2SO_4(aq) \rightarrow H_2O(g) + \frac{1}{2} O_2(g)$ (thermochemical, T > 800 °C)

$SO_2(aq) + 2H_2O(l) \rightarrow H_2SO_4(aq) + H_2(g)$ (electrochemical, T = 80-120 °C)

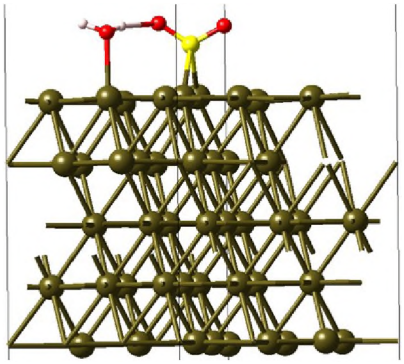

Figure 1. Stabilized structure of SO_2 and H_2O on Pt(111).

A systematic approach was taken to build a database of theoretical calculations containing information that will allow exploration of favorable reaction configurations and the electronic structural changes that promote them. In this approach, the catalyst surfaces and the molecules were structurally optimized in their pure states. Next, various steps in the HyS reaction pathways were iteratively explored by introducing a single molecular species to the surface and subsequently multiple species from various primary and intermediate reaction steps.

Results/Discussion

The primary result of this research effort is a database of 80 structurally optimized density functional theory calculations that have explored various configurations of the primary steps in the HyS reaction pathways. From this, the most stable states can be identified and compared against less stable states to extract configuration-dependent changes in the adsorption energetics and the accompanying electronic structure of both the molecular species and the catalyst surface.

Two key outputs from these models are the total system energies and the partial density of states. Total system energies can be combined in order to compute reaction energetics for the various steps and compare the stability of different configurations. In addition to guiding experiments, the database of energetics can be used to parameterize larger-scale chemical kinetics models. The partial density of states between different configurations containing the same species can be compared to identify, for example, a shift in the d-band states that might promote increased stability or reactivity.

FY2020 Accomplishments

- Construction of a database of 80 density functional theory calculations that can be used to understand various steps in the HyS on Pt, Au, and Pt – Au catalyst surfaces

Future Directions

- Applying the database of information to experimental catalyst design by more precisely analyzing simulation results and identifying key phenomena that promote reactivity
- Identifying and filling in critical gaps of the database (e.g., the inclusion of surface defects)

FY 2020 Peer-reviewed/Non-peer reviewed Publications

None

Presentations

None

References

1. Kresse, G.; Furthmüller, J., Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* **1996,** *6* (1), 15-50.
2. Kresse, G.; Furthmüller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B* **1996,** *54* (16), 11169-11186.
3. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996,** *77* (18), 3865-3868.

Acronyms

DFT	Density Functional Theory
HyS	Hybrid Sulfur
VASP	Vienna ab initio Simulation Package

Intellectual Property

None

Total Number of Post-Doctoral Researchers

None

Total Number of Student Researchers

None

External Collaborators (Universities, etc.)

None