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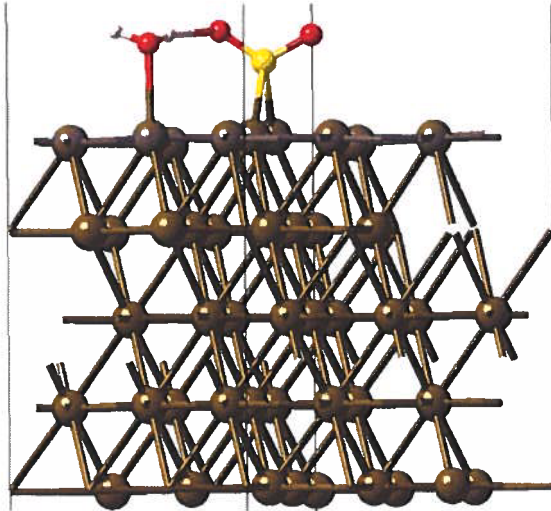
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Title: Electronic Structure Calculations for Improving Catalyst Design for Use in the Hybrid Sulfur Cycle



The hybrid sulfur cycle is a promising means for efficient production of large quantities of hydrogen with a small carbon footprint. Furthermore, there is a demonstrated need to design catalysts that are sulfur tolerant and have stability at high temperatures and reduced activation energies. Theoretical calculations can serve as a blueprint for fulfilling these needs by providing fundamental mechanistic insights to guide future experimental studies. Density functional theory was used to calculate the energetics of Pt-Au systems. Adsorption

energetics for the unary and binary structures were investigated to provide mechanistic insights for improved catalyst design. Results conclude that adsorption of the SO_2 molecule is further stabilized on the Pt surface with a Pt-O dative bond compared to Au. Energetics suggest that the adsorbates are more stabilized in the Pt surface due to a stabilization of the S p bands in the electronic structure. Examination of the density of states support the postulation that SO_2 is more weakly bound to Au, thereby leading to better catalytic performance compared to Pt. These results are encouraging and we expect there to be a weakening effect of ligand adsorption on the Pt/Au surfaces when an electric field is applied.

Awards and Recognition

None

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.

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Signature

10/1/19

Date

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

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Thrust Area: SEM

Project Start Date: February 1, 2019

Project End Date: September 30, 2019

The hybrid sulfur cycle is a promising means for efficient production of large quantities of hydrogen with a small carbon footprint. Furthermore, there is a demonstrated need to design catalysts that are sulfur tolerant and have stability at high temperatures and reduced activation energies. Theoretical calculations can serve as a blueprint for fulfilling these needs by providing

fundamental mechanistic insights to guide future experimental studies. Density functional theory (DFT) was used to calculate the energetics of Pt–Au systems. Adsorption energetics for the unary and binary structures were investigated to provide mechanistic insights for improved catalyst design. Calculations show that while the binding of SO₂ and H₂O are similar in both Pt, Au, and binary Pt–Au systems, the catalyst activity still needs to be explored using an applied electric field to capture the mechanistic reactivity.

FY2019 Objectives

- Installation of Quantum Espresso and benchmark calculations
- Systematic investigation of Pt–Au systems to understand the differences in the electronic structure – particularly the shape and width of the d bands and how this may impact catalyst reactivity
- Investigation of adsorption energetics and electronic structure in the transition states
- Organize the results for publication

Introduction

Catalytic materials are used in nearly 80% of all chemical processes 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 examined the hybrid sulfur cycle (HyS) to gain a deeper understanding of how catalyst structure affects reactivity and reactant adsorption. 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 SO₂ 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 is comprised of systematic investigations of how the electronic structure of Pt/Au catalysts affect the adsorption energetics and catalytic activity at the surface. Results show that while SO₂ and H₂O adsorb to the surface at relatively the same energy, mechanistic understanding of the governing reaction is not straight-forward and more work is needed in this area.

Approach

Density functional theory approaches were used to calculate the electronic structure and adsorption energetics of the Pt/Au systems. The theoretical calculations were first carried out using Quantum Espresso then transitioned to Vienna ab initio Simulation Package (VASP). To describe the electron-core interaction, the projector-augmented wave (PAW) method was utilized within the frozen-core approximations for Pt and Au.^{1,2} For the exchange-correlation, the structures were first optimized using Local Density Approximation (LDA) then further optimized using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized-gradient approximation (GGA).³ The Monkhorst-Pack k-points were 4x4x4 and cutoff energies for the plane waves were chosen to be 500 eV based on previous convergence tests. The convergence tolerance of force on each atom during structure relaxation was set to 0.01 eV/Å, and all atoms were allowed to relax in the crystal structure. The parameters for Pt, Au, O, H and S are the default values given in VASP. The optimized lattice parameters for the face-centered cubic Pt (3.95 Å) and Au (4.16 Å) agree well with the structural data of 3.92 and 4.07 Å, respectively. The calculated adsorption energies between M (M=Pt, Au, Pt/Au) and L (L = H₂O, SO₂) were modeled for 5 layers of M slab, the corresponding adsorbed L ligand(s), and a 15 Å vacuum layer to separate the interaction between the periodic models. The top two atomic layers of the formed structure were allowed to relax while others were fixed. This supercell structure contains a (3 x 3) lattice of M (111) primitive cells which was large enough to avoid an interaction between neighboring adsorbed species. All calculated parameters were the same except the Monkhorst-Pack k-points were 4x4x1.

Results/Discussion

The two reactions in the HyS cycle are:

1. $\text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$ (thermochemical, $T > 800^\circ\text{C}$)
2. $\text{SO}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq}) + \text{H}_2(\text{g})$ (electrochemical, $T = 80\text{-}120^\circ\text{C}$)

The most stable structures of the SO₂-containing Pt and Au (111) slab are shown in Figure 1. They are structurally different with M-S bond distances of 2.28 and 2.60 Å for the Pt- and Au-stabilized structures, respectively. The SO₂ molecule is further stabilized on the Pt surface with a Pt-O dative bond of 2.21 Å.

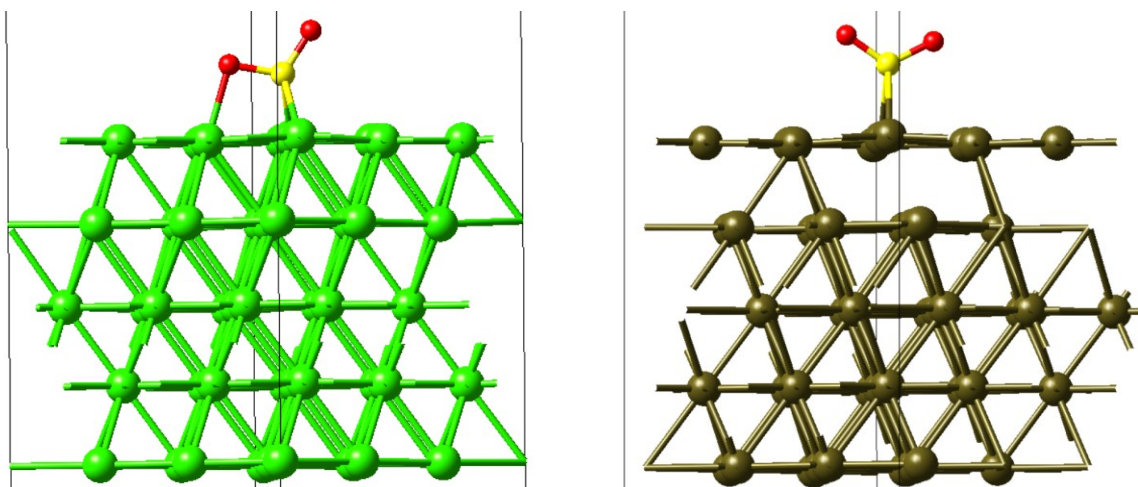


Figure 1. Stabilized structures of SO₂-Pt(111) (left) and SO₂-Au(111) (right).

The M-H₂O structures are similar with a M-O distance of 2.30 and 2.82 Å for Pt and Au, respectively. Adsorption of both SO₂ and H₂O on the metal surfaces are shown in Figure 2 with the Pt-O dative bond remaining in the case of Pt. For Pt, the M-S bond distances are 2.27 Å and dative O-H bond of 1.64 Å between SO₂ and H₂O. In the case of Au, the overall bond distances are longer with the M-S bond distances of 2.54 Å and 2.59 Å and a dative O-H bond of 1.92 Å between SO₂ and H₂O. The largest change occurs in the Au-O bond where it is significantly shortened to 2.57 Å.

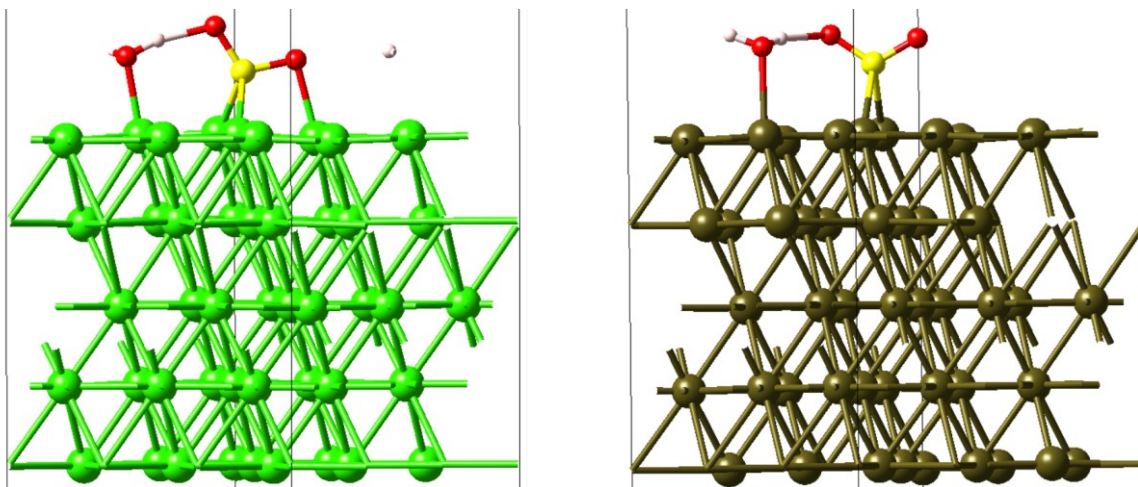


Figure 2. Stabilized structures of SO₂ and H₂O on Pt(111) (left) and Au(111) (right).

The calculated adsorption energies are found in Table 1. The interaction energies of the ligands on the metal surfaces were calculated using the following equation:

$$AE = E_{L+M} - E_L - E_M$$

where AE refers to the adsorption energy, E_{L+M} is the energy of the metal slab with the adsorbed ligand, E_L is the calculated energy of the ligand in the gas phase, and E_M is the energy of the metal slab. A lower energy for the Pt-adsorbate species suggests that the adsorbates are more stabilized by the Pt d bands. To verify this, analysis also included calculation of the densities of states for the species.

Table 1. Adsorption energy of H₂O and SO₂ on the M(111) (M = Pt, Au) surface.

Reaction	Adsorption Energy (eV)
Pt + H ₂ O → Pt-H ₂ O	-1.09
Pt + SO ₂ → Pt-SO ₂	-5.92
Pt + SO ₂ + H ₂ O → Pt-SO ₂ -H ₂ O	-5.27
Au + H ₂ O → Au-H ₂ O	-0.98
Au + SO ₂ → Au-SO ₂	-4.59
Au + SO ₂ + H ₂ O → Au-SO ₂ -H ₂ O	-4.29

The density of states for both the Pt and Au d bands are largely unaffected by the adsorbed species. Shown in Figure 3 are the partial DOS of the S p and M d bands for the structures in Figure 2 and the results show that SO_2 is more tightly bound to Pt than Au. These collective results support the postulation SO_2 is more weakly bound to Au, thereby leading to better catalytic performance compared to Pt.

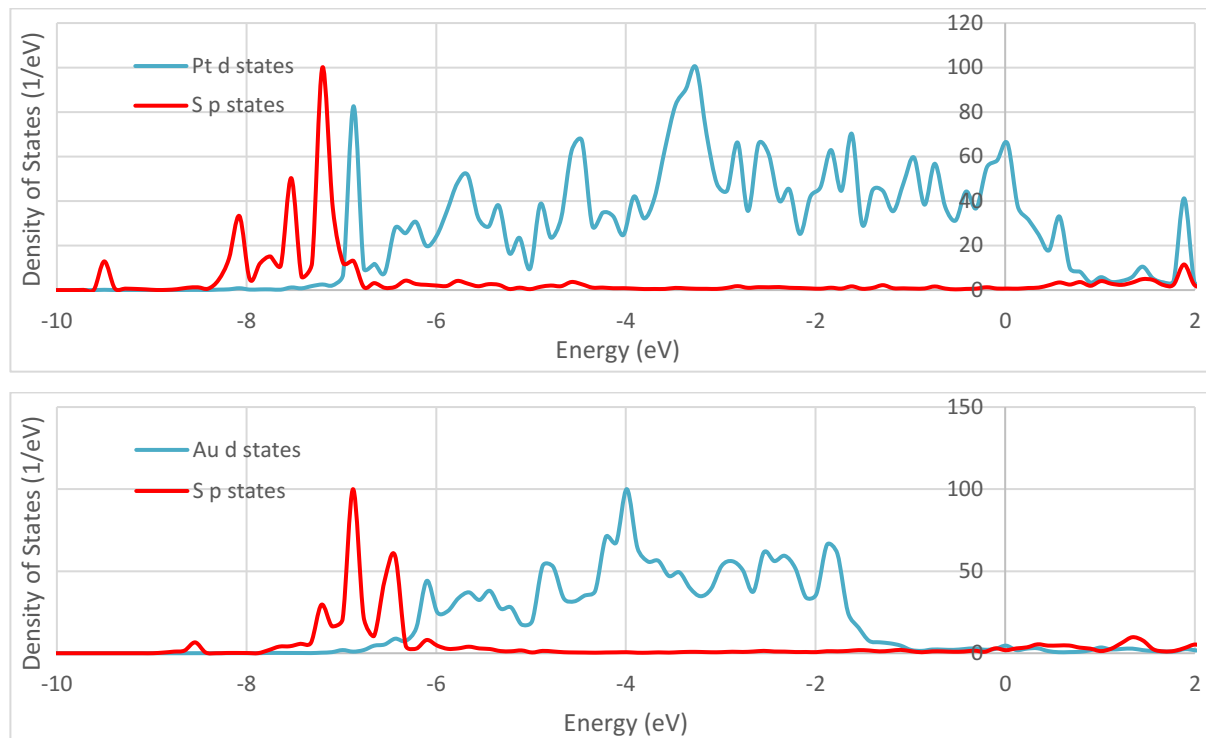


Figure 3. Normalized partial density of states for S p bands (red) with Pt (top) and Au (bottom) d bands (blue).

Based on these results, additional calculations have been begun on a Pt/Au surface models and their results are similar to the unary surfaces. Additional calculations to determine a catalytic mechanism for the first step in the electrochemical conversion were not successful when an electric field is not applied. Including an applied electric field to the models will affect the structural and electronic properties of the adsorbed species on the surface and we expect there to be a weakening effect of ligand adsorption on the surface.

FY2019 Accomplishments

- Installation of Quantum Espresso and benchmark calculations
 - Installed open source software
 - Calculated benchmark systems and showed similar performance to VASP
- Calculation of optimized adsorbate structures on Pt and Au(111) surfaces
 - Determined 8 optimized structures and analyzed their electronic properties
- Investigation of adsorption energies and catalytic activity
 - Determined the adsorption energies for SO_2 and H_2O on Pt/Au surfaces
 - Calculated several potential mechanisms and determined a path forward in these calculations
- Organization of results for publication

Future Directions

- Expand on results for publication in peer-reviewed journal
- Communicate findings to experimental collaborators at SRNL for synergy
- Apply for funding to continue calculations applying an electric field in the presence of the adsorbed species

FY 2019 Publications/Presentations

1. Publication in progress on adsorption characteristics of SO₂ and H₂O on Pt/Au (111) surfaces.

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
GGA	Generalized Gradient Approximation
HyS	Hybrid Sulfur
LDA	Local Density Approximation
PAW	Projector-augmented wave method
PBE	Perdew-Burke-Ernzerhof
VASP	Vienna ab initio Simulation Package

Intellectual Property

None

Total Number of Post-Doctoral Researchers

None

Total Number of Student Researchers

None