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# Heterogeneous Catalysis of Aqueous Phase Reforming of Glycerol with first principle calculations and molecular dynamics simulations

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## Motivation

- Biomass research is recently receiving increasing attention because of the probable waste-to-energy application
  - Glycerol, methanol and other sugar alcohols can be readily obtained from biomass
- Liquid-phase heterogeneous catalysis can be practically applied to produce hydrogen from biomass
  - Current materials are made out of noble metals, and the cost of these materials prevents its extensive application
  - Surface coverage can complicate the surface chemistry
  - Solvation effects from water molecules close to the reacting surface make it difficult to observe the chemistry
- Using first principle calculations with Density Functional Theory (DFT) to investigate the surface chemistry
- Using molecular dynamics method to incorporate the aqueous background as well as the perturbation/stabilization brought by the background
- Screen catalyst materials for alternative compositions other than pure precious metals

## Objective

- Get a better understanding in mechanisms of the dehydrogenation steps of sugar compounds (methanol and glycerol) in vacuum space and in aqueous phase.
- Use Density Functional Theory (DFT) to model adsorption of all possible reacting species, and determine the most thermodynamically favored reaction path
- Analyze effects of various solvation models, binding sites, and adsorbate coverages on binding/reaction energies.
- Compare the calculated results with real experimental data in order to garner a molecular-level hypothesis about how the catalysts function. Then, we can devise the new catalyst substitute

## Systems of Interest

- Metal surface consists of a pure Pt (111) slab, with periodical unit cell of  $3 \times 3 \times 3$  Pt atoms
  - $6 \times 6 \times 3$  slab can give more free space for large and complex intermediates, but computational cost rises significantly
- First principle calculations are conducted for the adsorbates while immobilizing the water molecules
- Molecular Dynamics (MD) method is for equilibrating the water molecules while keeping the adsorbates fixed at the surface

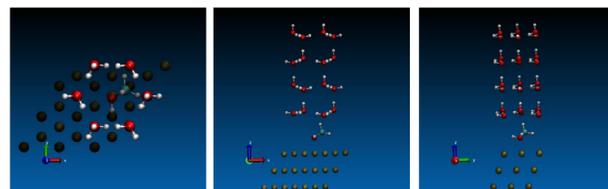


Figure 1: repeating unit for methanol adsorption at the interface of Pt(111) and water

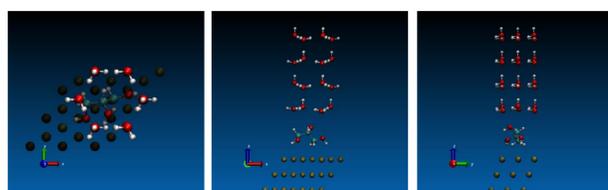


Figure 2: repeating unit for glycerol adsorption at the interface of Pt(111) and water

## Simulation Settings in Detail

- DFT simulations were conducted using the *Vienna Ab-initio Simulation Package (VASP)* implementation of plane-wave DFT

VASP Computational Parameters	
Cut-off Energy	400 eV
Electronic Iteration Tolerance	$1 \times 10^{-6}$ eV
Geometric Iteration Tolerance	0.03 eV/Å
Pseudopotential	Projector Augmented Wave (PAW) <sup>[1]</sup>
Exchange-Correlation Functional	Perdew-Burke-Ernzerhof (PBE) <sup>[2]</sup>
K-points	$7 \times 7 \times 1$
Dispersion Force Correction	DFT-D2 (Grimme) <sup>[3]</sup>

Table 1: Parameters used in VASP calculations

- Molecular Dynamics (MD) simulations were conducted using the *Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)*

LAMMPS Computational Parameters	
Time Step	1 fs
Simulation Time	5 ns (2 ns equilibration, 3 ns production)
Platinum Potential	UFF
Water Potential	TIP3P
Adsorbate Potential	OPLS-AA
Ensemble	NVT with Nosé-Hoover Thermostat
Interactions	LJ + C with Lorentz-Berthelot Mixing

Table 2: Parameters used in LAMMPS calculations

- K-points mesh size was determined to be  $7 \times 7 \times 1$  for current systems
  - $11 \times 11 \times 1$  K-points mesh size hits the limit of feasible running time
  - $7 \times 7 \times 1$  K-points mesh size can give reliable results at lower cost
  - Larger systems (with unit cell of  $6 \times 6 \times 3$  Pt atoms) requires few K-points, whereas the increase of plane waves arise the calculation expense

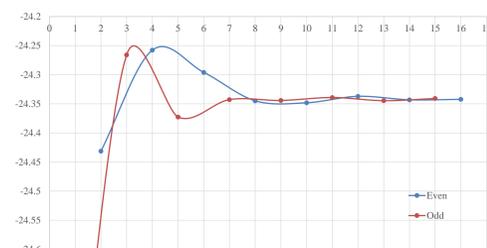


Figure 3: Free energy of bulk Pt (111) vs various K-Points mesh sizes

## Methanol Decomposition in Vacuum

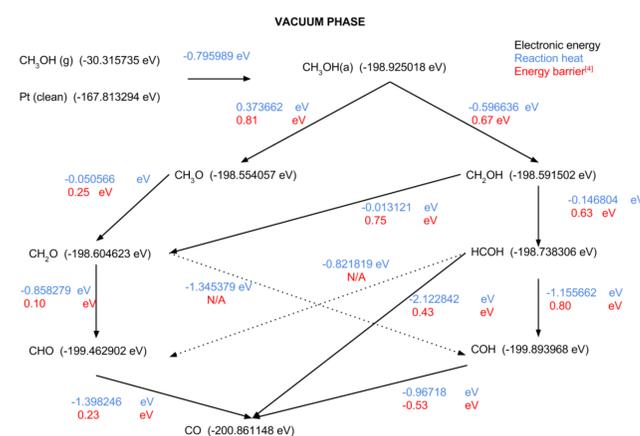
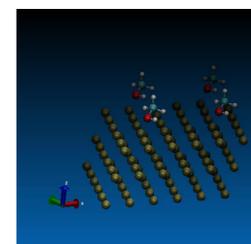


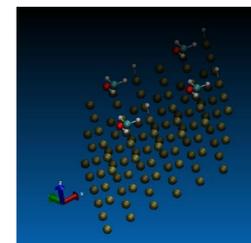
Figure 4: Methanol break-down in vacuum phase via competitive pathways

## Vacuum Phase Structures (Preliminary Data)

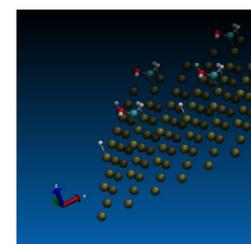
- Methanol
- $\text{CH}_3\text{OH}^*$
- Binding site: Atop
- Binding atom: O
- C-O bond length: 1.45 Å
- O-Pt bond length: 2.26 Å
- C-O-Pt angle: 117°



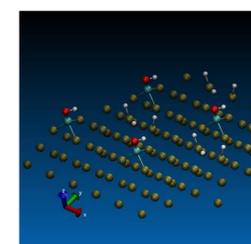
- Hydroxymethyl
- $\text{CH}_2\text{OH}^* + \text{H}^*$
- Binding site: Atop
- Binding atom: C
- C-O bond length: 1.39 Å
- C-Pt bond length: 2.08 Å
- O-C-Pt angle: 112°



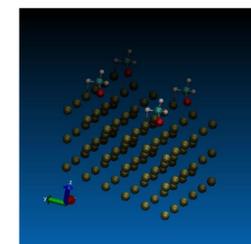
- Hydroxymethylidyne
- $\text{COH}^* + 2\text{H}^*$
- Binding site: Atop
- Binding atom: C
- C-O bond length: 1.35 Å
- C-Pt bond length: 1.88 Å
- O-C-Pt angle: 125°



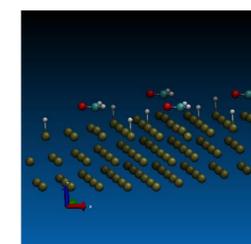
- Hydroxymethylidyne
- $\text{COH}^* + 3\text{H}^*$
- Binding site: FCC
- Binding atom: C
- C-O bond length: 1.34 Å
- C-Pt bond length: 2.02 Å
- O-C-Pt angle: 127°



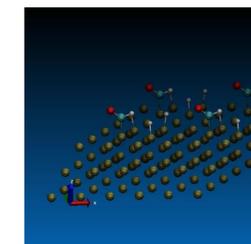
- Methoxy
- $\text{CH}_3\text{O}^* + \text{H}^*$
- Binding site: Atop
- Binding atom: O
- C-O bond length: 1.40 Å
- O-Pt bond length: 1.99 Å
- C-O-Pt angle: 118°



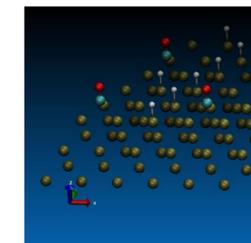
- Formaldehyde
- $\text{CH}_2\text{O}^* + 2\text{H}^*$
- Binding site: Atop-Bridge-Atop
- Binding atom: C
- C-O bond length: 1.27 Å
- C-Pt bond length: 2.23 Å
- O-C-Pt angle: 98°



- Formyl
- $\text{CHO}^* + 3\text{H}^*$
- Binding site: Atop
- Binding atom: C
- C-O bond length: 1.21 Å
- C-Pt bond length: 1.98 Å
- O-C-Pt angle: 126°



- Carbon monoxide
- $\text{CO}^* + 4\text{H}^*$
- Binding site: FCC
- Binding atom: C
- C-O bond length: 1.20 Å
- C-Pt bond length: 2.11 Å
- O-C-Pt angle: 180°



## Conclusions

- The thermodynamically favored decomposition pathway for methanol on a Pt(111) surface in vacuum space is:
 
$$\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{O} \rightarrow \text{CHO} \rightarrow \text{CO}$$
- The scission of O-H bond at the initial step is least likely to occur while it is expected under water environment the step will be facilitated
- Dissociated hydrogen is explicitly included in these systems, alternatively the contribution of the total free energy from dissociated hydrogen can be compensated implicitly

## Future Work

- Investigate the effects brought by water in sugar alcohol reforming
- Complete a map of reaction paths for glycerol decomposition to CO and H<sub>2</sub>
- Incorporate force field study of adsorbate placement and surface coverages
- Create a well-defined potential surface (PES) to better understanding the reaction kinetics
- Determine the entropic contribution to reaction energies
- Screen potential catalyst materials to find alternatives for pure transition metal catalysts for use

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