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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 currently 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 prevent 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 catalyst 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 × 3 × 3 Pt atoms
- 6 × 6 × 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

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

Vacuum Phase Structures (Preliminary Data)

<table>
<thead>
<tr>
<th>Methanol</th>
<th>CH₃OH*</th>
<th>Binding site: Atop</th>
<th>Binding atom: O</th>
<th>C-O bond length: 1.39 Å</th>
<th>C-Pt bond length: 2.08 Å</th>
<th>O-C-Pt angle: 112°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxymethyl</td>
<td>CH₂OH⁺</td>
<td>Binding site: Atop</td>
<td>Binding atom: O</td>
<td>C-O bond length: 1.35 Å</td>
<td>C-Pt bond length: 1.88 Å</td>
<td>O-C-Pt angle: 125°</td>
</tr>
<tr>
<td>Hydroxymethylene</td>
<td>HOCH₂*</td>
<td>Binding site: FCC</td>
<td>Binding atom: C</td>
<td>C-O bond length: 1.34 Å</td>
<td>C-Pt bond length: 2.02 Å</td>
<td>O-C-Pt angle: 127°</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃OH⁺</td>
<td>Binding site: Atop</td>
<td>Binding atom: O</td>
<td>C-O bond length: 1.40 Å</td>
<td>O-Pt bond length: 1.99 Å</td>
<td>O-C-Pt angle: 118°</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>CH₂O⁺</td>
<td>Binding site: Atop-Bridge</td>
<td>Binding atom: C</td>
<td>C-O bond length: 1.27 Å</td>
<td>C-Pt bond length: 2.23 Å</td>
<td>O-C-Pt angle: 98°</td>
</tr>
</tbody>
</table>

Conclusions
- The thermodynamically favored decomposition pathway for methanol on a Pt(111) surface in vacuum space is: CH₃OH → CH₂OH → CH₂O → 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 H₂
- 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 catalytic materials to find alternatives for pure transition metal catalysts for use

References