Graphene-Supported Metal Catalysts for Propane Dehydrogenation
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Abstract
Propane dehydrogenation (PDH) is used to produce propene, which is the primary building block for many commercial plastics. The catalyst most commonly used for this reaction is platinum. Due to rising demand for propene, an alternative catalyst is being sought due to platinum’s high cost. Alternatives might involve very small platinum particles as well as particles composed of different atoms. For this purpose, we have performed a computational study of the PDH reaction with a 4-atom platinum cluster (Pt₄) and several different 4-atom transition metal cluster (TM₄) catalysts on a graphene support. We have computed the equilibrium structures of the Pt₄ and TM₄ clusters on both single- and double-vacancy sites and have calculated the complete PDH reaction pathway for each case. This allowed us to study the effect of the graphene support on catalytic activity. We have also calculated the PDH reaction pathway for larger Ptₘ clusters, where m = 4–14, in order to study the effect of particle size on catalytic activity. These results help clarify the relationship between the PDH activation energy and the propane binding energy and overall reaction energy and may aid in the design of new potential catalysts for the PDH reaction.

Computational Methods
- Vienna Ab-Initio Simulation Package (VASP) plane wave code
- PBE density functional and PAW pseudopotentials
- 12.3 x 12.3 x 20 Å supercell
- 400 eV plane wave cutoff
- Spin-polarized calculations
- Climbing-image nudged elastic band (CI-NEB) algorithm calculates reaction pathways

Climbing-Image NEB Algorithm
- VASP implements the NEB algorithm to calculate the minimum energy path (band) between optimized reactant and product.
- NEB algorithm adds fictitious spring forces along the band between adjacent images and uses only the component of the true force perpendicular to the band.
- Each image has lowest possible energy while maintaining equal spacing to neighboring images.
- Climbing-image method forces highest image to top of band.
- Used five and eleven images to test calculation convergence at each step

Propane Dehydrogenation Reaction Path (Pt₅)

Computed Eₐ Values

<table>
<thead>
<tr>
<th>System</th>
<th>SVG Eₐ (eV)</th>
<th>DVG Eₐ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 Image NEB</td>
<td></td>
<td></td>
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<tr>
<td>Pt₅</td>
<td>0</td>
<td>0.1572</td>
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<tr>
<td>Pt₇</td>
<td>0.5303*</td>
<td>0.0804</td>
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<tr>
<td>Pt₁₄</td>
<td>0.3043</td>
<td>0.2755</td>
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<tr>
<td>11 Image NEB</td>
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<td></td>
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<tr>
<td>Pt₅</td>
<td>0*</td>
<td>0.1910</td>
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<tr>
<td>Pt₇</td>
<td>0.5701*</td>
<td>0.1211</td>
</tr>
<tr>
<td>Pt₁₄</td>
<td>0.3071</td>
<td>0.2827</td>
</tr>
</tbody>
</table>

* Results from calculations that have not converged but are within 10% of the convergence criterion.

Propane Dehydrogenation Reaction Path (Pt₅)

Endothermic reaction (catalyst required)
Multi-Step reaction (removal of two H atoms from C₃H₈)
First step is rate determining
Single vacancy graphene support stabilizes intermediate structures
Single vacancy graphene support reduces Eₐ

C₃H₈ → H₂ + C₃H₆  ΔH(calc) = 1.59 eV  (ΔH(expt) = 1.29 eV)

Conclusions
- 11 image NEB calculations are required to get a more accurate result.
- For DVG Pt clusters, Pt₇ has the lowest Eₐ.
- A SVG support gives higher Eₐ than DVG for small clusters, while for larger clusters the Eₐ values are similar.
- For SVG Pt clusters, Pt₅ has the lowest activation energy.

Acknowledgements
- Valparaiso University
- Indiana Space Grant Consortium