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Sub-Nanometer Catalyst Clusters for Propane Dehydrogenation

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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 (Pt_4) and several different 4-atom transition metal cluster (TM_4) catalysts on a graphene support. We have computed the equilibrium structures of the Pt_4 and TM_4 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 Pt_x clusters, where x = 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.

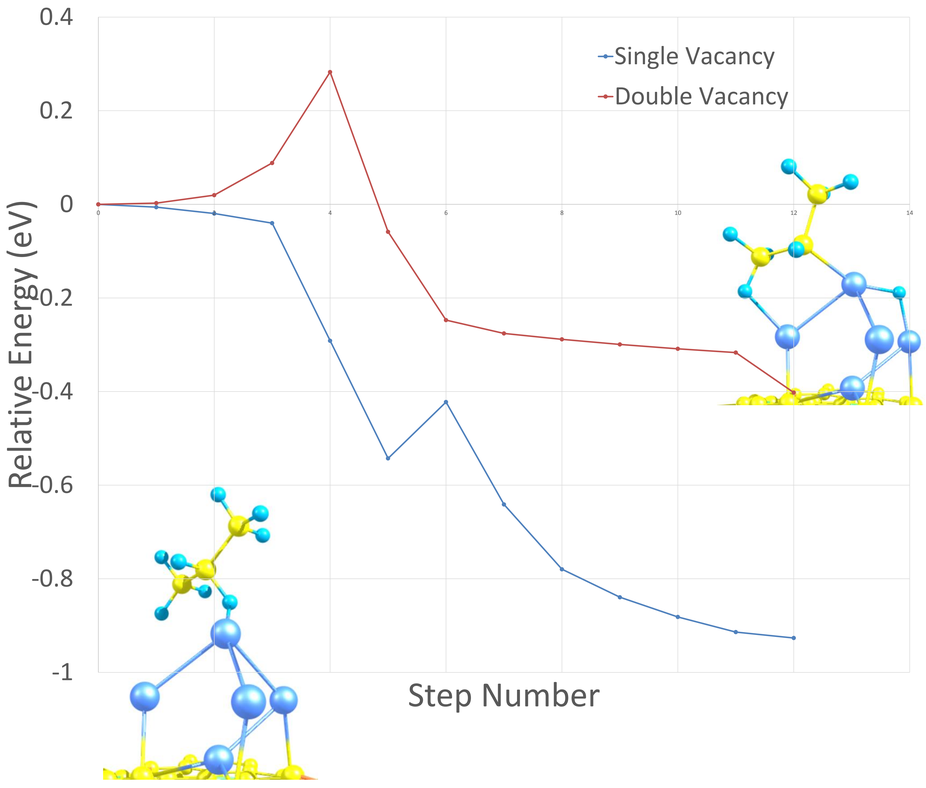
Computational Methods

- 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

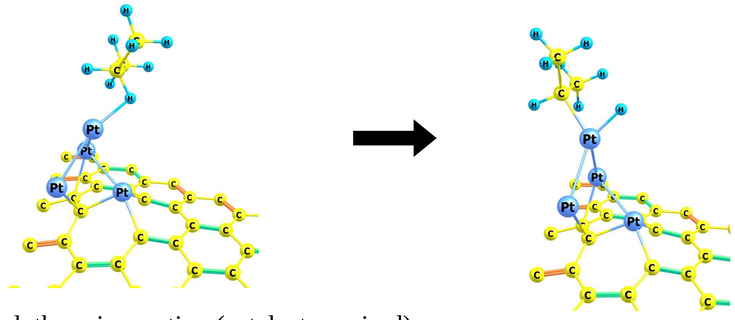
Climbing-Image NEB Algorithm

- 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 (Pt_5)



Pt_4 On Single Vacancy Graphene Support



- Endothermic reaction (catalyst required)
- Multi-Step reaction (removal of two H atoms from C_3H_8)
- First step is rate determining
- Single vacancy graphene support stabilizes intermediate structures
- Single vacancy graphene support reduces E_a

$$C_3H_8 \longrightarrow H_2 + C_3H_6 \quad \Delta H_{calc} = 1.59 \text{ eV} \quad (\Delta H_{expt} = 1.29 \text{ eV})$$

Computed E_a Values

System	SVG E_a (eV)	DVG E_a (eV)
5 Image NEB		
Pt_5	0	0.1572
Pt_7	0.5303*	0.0804
Pt_{14}	0.3043	0.2755
11 Image NEB		
Pt_5	0*	0.1910
Pt_7	0.5701*	0.1211
Pt_{14}	0.3071	0.2827

PDH activation energies for single (SVG) and double vacancy graphene (DVG) systems, with varying platinum cluster size. Results for both 5 and 11 image NEB calculations are shown.

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

Conclusions

- 11 image NEB calculations are required to get a more accurate result.
- For DVG Pt clusters, Pt_7 has the lowest E_a.
- A SVG support gives higher E_a than DVG for small clusters, while for larger clusters the E_a values are similar.
- For SVG Pt clusters, Pt_5 has the lowest activation energy.

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