Propane Dehydrogenation Using Transition Metal Cluster Catalysts

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Abstract

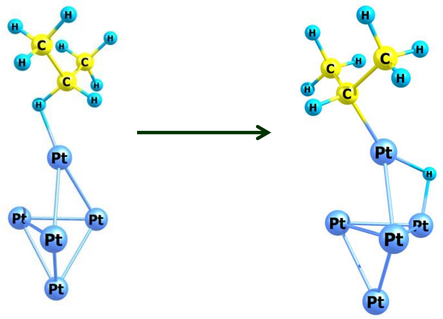
Our research seeks to determine the propane dehydrogenation (PDH) reaction pathways using various transition-metal cluster catalysts. We are studying the first step of the reaction, in which a C-H bond is broken. This has been previously shown to be the rate-limiting step of the PDH reaction. We are calculating the PDH activation energy (E_a) using the Vienna Ab-Initio Simulation Package (VASP) in conjunction with the nudged elastic band algorithm. Thus far, we have studied Pt, Ta, and Ni clusters ranging in size from 2-10 atoms. Our goal is to better understand the dependence of E_a on metal type and cluster size.

Computational Procedure

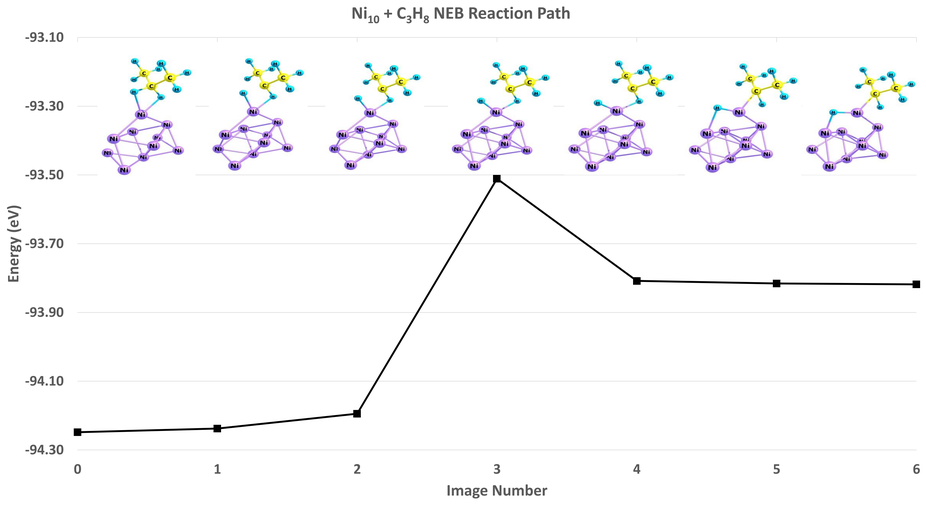
- Use Vienna Ab-Initio Simulation Package (VASP) which implements density functional theory (DFT) to optimize the reactant and product structures
- Use the nudged elastic band (NEB) algorithm to calculate reaction pathways for the first step of PDH reaction: C-H bond cleavage
- Calculate E_a for each TM by subtracting the initial energy from the transition state energy

NEB Algorithm

- VASP implements DFT and the NEB algorithm to calculate minimum energy path between known reactants and products
- The NEB algorithm functions by adding spring forces along the band between images and by projecting out the component of the force due to the potential perpendicular to the band
- We use a total of 7 images (5 intermediate structures) to model the reaction path

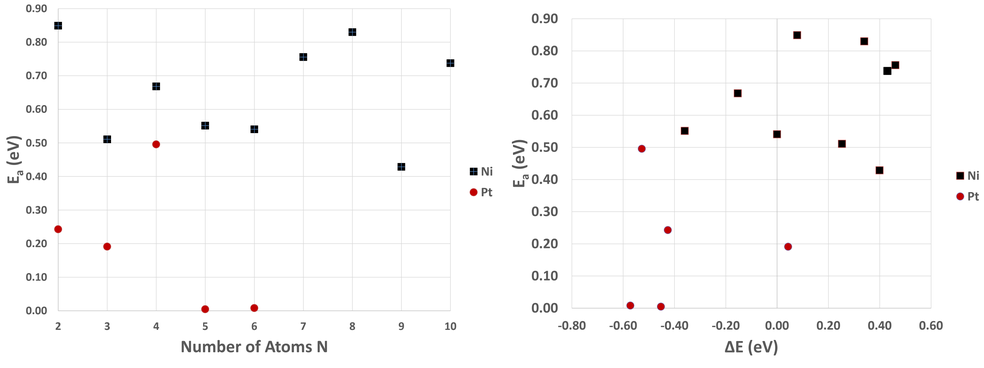


NEB Calculation Procedure



- Each structure was initially optimized as an isolated TM cluster, then a propane molecule was added to begin NEB calculation
- Each NEB calculation maps the energetic pathway of the first step of the PDH reaction (C-H bond cleavage)
- Our goal: calculate E_a and investigate correlations with reaction energies and TM characteristics

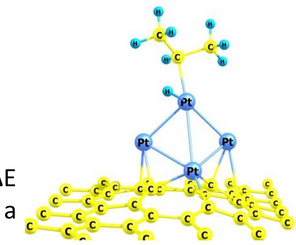
Dependence of E_a on Cluster Size and ΔE



- E_a varies according to cluster size, but not in a linear fashion
- No linear relation between E_a and ΔE; Bell-Evans-Polanyi (BEP) principle does not hold for these results

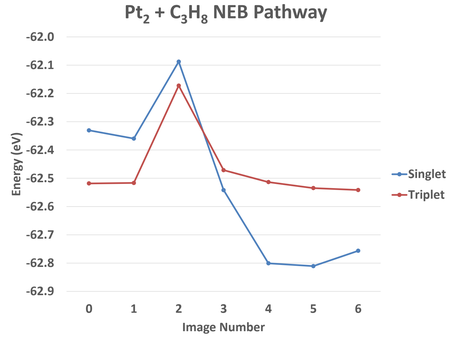
Graphene-Supported Pt Clusters

Cluster	ΔE (eV)	E_a (eV)	Pt-Pt (Å)
Pt	0.15	0.75	--
Pt_2	-0.06	0.51	2.362
Pt_3	-0.95	0.46	2.503, 2.587
Pt_4	-0.16	0.08	2.580, 2.642, 2.773
Pt_6	-0.34	0.45	2.491, 2.606, 2.660



- No clear trend between E_a and ΔE
- E_a depends on cluster size and is a minimum for Pt_4
- Local geometry of interacting Pt atom may influence catalytic activity

Spin State Crossing



- Spin state crossing occurs in some structures
- Position at which the crossing occurs is currently unknown

Conclusions

- E_a is dependent on spin state, metal type, and size of cluster
- Spin state crossing occurs for some clusters
- No clear dependence of E_a on ΔE exists for both Ni and Pt, contrary to BEP principle

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