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

Graphene-Supported Pt Clusters
- No clear trend between $E_a$ and $\Delta E$
- $E_a$ depends on cluster size and is a minimum for Pt$_8$
- 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 $\Delta E$ exists for both Ni and Pt, contrary to BEP principle

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