ABSTRACT

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Title: Density Functional Theory Analysis of Conversion of Light Hydrocarbons into Fuels and Chemicals

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The recent surge in shale gas production led to increases in alkane resources across the United States. One promising approach to convert the alkanes to higher value products is through dehydrogenation and oligomerization processes. This conversion to alkenes, if done in small modular units near the shale wells further aids in the ease of transportation and distribution of the final products. However, having highly selective processes is a major hindrance to improve the economic feasibility of the modular processes. Theoretical studies are of great significance to analyze detailed reaction mechanisms and identify the reaction pathways that leads to unselective product formations. These studies further enable the search for selective catalysts for any given chemistry based on descriptor analysis and aids in making the modular processes realizable. Therefore, in this work Density Function Theory and Ab-initio Molecular Dynamics methods are used in conjunction with microkinetic modeling analyses to investigate the complex reaction networks involved in the shale gas conversion. Specifically, the work focuses on propane dehydrogenation (PDH) on alloy surfaces along with ethylene oligomerization on zeolite catalysts.

A major part of thesis is focused on finding selective and stable alloy catalysts for PDH chemistry. The initial work focused on understanding the selectivity, activity, and stability differences between 1:1 intermetallic alloys (PdIn) and the pure metal surfaces. This combined experimental and computational study shed light on the important role of step surfaces in understanding the activity trends across alloys. Through a detailed microkinetic and simplified rate expression analysis, a novel selectivity descriptor in terms of effective barriers for propane C-H bond breaking and propyne C-C bond breaking was derived for propylene formation. This newly proposed descriptor showed greater fidelity for predicting the trends in experimental selectivities for a small set of Pd alloys than the previously proposed selectivity descriptors.

Building upon these insights, a high throughput screening framework using graph-theory algorithms and python-based databasing has been developed to identify trends across a larger set of alloy combinations. The framework helped us identify a novel set of alloys that have not been explored until now for this chemistry. These alloy combinations were then experimentally tested and shown to have high selectivities for propylene formation and along with stabilities close to benchmark Pt-Sn catalysts. Detailed transition state analysis on terraces shows that the undesired C-C bond breaking pathways involves larger surface atom ensembles (4-5 atoms) while the C-H bond breaking involves smaller surface atom ensembles (1-2 atoms). This led to the conclusion that the site-isolation of active metal atoms is important to increase the selectivities for propylene formation. More importantly the combination of detailed mechanistic and screening studies using graph-theory methods shows a generalized framework towards finding new catalysts spaces for complex chemistries.

The work on ethylene oligomerization on the other hand is focused on understanding the role of mobility of active Ni species in the zeolites towards isomerization and deactivation reaction mechanisms. For this specific project, we have used state-of-the-art AIMD methods, including potential of mean force calculations, for accurate estimation of free energies for the reaction intermediates and transition states. The thermodynamic and kinetic analyses show that the reaction pathways involving mobile intermediates have the highest rates towards butene formations even under pressures lower than 1 bar. Further the isomerization step is found to be feasible on Ni-ethyl complex in agreement with experiments. Finally, the mobile complexes are shown to dimerize through alkyl bridged complexes and the generated complex has higher barriers for C-C bond formation than the isolated complex indicating that these are likely pathways for catalyst deactivation. This mechanistic understanding paves the way for fine-tuning the reaction conditions as well as ways in which the active site can be speciated inside the zeolitic frameworks to increase the selectivity towards 1-butene and reduce deactivation.