

## V.G.9 Computational Design of Graphene-Nanoparticle Catalysts

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### Program Scope

This program supports the mission of the Office of Basic Energy Sciences Catalysis Science Program through the development of a systematic computational approach for the rational design of nanoscale transition-metal catalysts supported on graphene, a two-dimensional sheet of carbon atoms arranged in a honeycomb lattice. The use of graphene, as compared to traditional carbon supports, has been experimentally shown to enhance significantly the catalytic activity of metal nanoclusters in fuel cell electrodes. However, there is no clear mechanistic understanding of the role played by graphene supports in improving catalyst performance. This program is concerned with development and implementation of computational models to understand and predict electronic interactions between transition-metal nanoclusters and graphene supports, taking into account practical complexities that arise from statistical variations in cluster size and morphology, quantum size effects at the nanoscale, and the presence of physical and chemical defects in graphene. Model transition metal/graphene catalysts are employed for statistical sampling of selected reactions pathways, in particular, the technologically important methanol decomposition reaction, to probe the influence of substrate-cluster interactions on reaction thermodynamics and kinetics. The fundamental understanding gained from these studies seeks to guide the rational design of superior, graphene-supported, transition-metal nanocatalysts with potential applications in energy conversion pathways for alternative fuels.

### FY 2016 Highlights

Theoretical studies by our group have pursued advances along two interrelated fronts, namely (1) the implementation and application of Genetic Algorithms to predict ground-state morphologies and electronic structures of graphene-supported Pt nanoclusters and (2) studies of reaction thermodynamics of the methanol decomposition reaction on graphene-supported Pt nanoclusters.

### Genetic Algorithms for Structural Optimization of Supported Nanoclusters

Graphene-supported Pt nanoclusters were recently found to be promising electrocatalysts for fuel-cell applications due to their enhanced activity and tolerance to CO poisoning, as well as their long-term stability toward sintering. However, structure-function relationships that underpin the improved performance of these catalysts are still not well understood. We developed a combined approach that uses empirical potential simulations and density functional theory (DFT) calculations to investigate structure-function relationships of small  $Pt_N$  ( $N=2-80$ ) clusters on model graphene supports. A bond-order empirical potential was employed within a Genetic Algorithm to go beyond local optimizations for obtaining minimum energy structures of  $Pt_N$  clusters on pristine as well as defective graphene supports. Point defects in graphene were found to strongly anchor Pt clusters and also appreciably affect the morphologies of small clusters, which were characterized via various structural metrics such as the radius of gyration, average bond length, and average coordination number. A key finding from the structural analysis is that the fraction of potentially active surface sites in supported clusters is maximized for stable Pt clusters in the size range of 20–30 atoms, which provides a useful design criterion for optimal utilization of the precious metal. Through selected ab initio studies, we found a consistent trend for charge transfer from small Pt clusters to defective graphene supports resulting in the lowering of the cluster  $d$ -band center, which has implications for the overall activity and poisoning of the catalyst. The combination of a robust empirical potential-based Genetic Algorithm for structural optimization with ab initio calculations opens up avenues for systematic studies of supported catalyst clusters at much larger system sizes than are accessible to purely ab initio approaches. Our ongoing work aims at extending this computational framework to alloy clusters, notably, the Pt-Ru system, which is among the most efficient catalysts for direct methanol fuel cells.

### Thermodynamics of Methanol Decomposition on Graphene-Supported $Pt_{13}$ Nanoclusters

Defective graphene has been shown experimentally to be an excellent support for transition-metal electrocatalysts in direct methanol fuel cells. Computational modeling reveals that the improved catalytic activity of graphene-supported metal clusters is in part due to increased resistance to catalyst sintering and to CO poisoning, but the increased reaction rate for the methanol decomposition reaction (MDR) is not yet fully explained. Using DFT, we investigated the adsorption and reaction thermodynamics of MDR intermediates on defective graphene-supported  $Pt_{13}$  nanoclusters with realistic, low-symmetry morphologies. We found that the support-

induced shifts in catalyst electronic structure correlate well with an overall change in adsorption behavior of MDR intermediates and that the reaction thermodynamics are modified in a way that suggests the potential of greater catalytic activity. We also found that adsorption energy predictors established for traditional heterogeneous catalysis studies of MDR on macroscopic crystalline facets are equally valid on catalyst nanoclusters (supported or otherwise) with irregular, low-symmetry surface morphologies. Our studies provide theoretical insights into experimental observations of enhanced catalytic activity of graphene-supported Pt nanoclusters for MDR and suggest promising avenues for further tuning of catalytic activity through engineering of catalyst–support interactions. Ongoing research pursues *ab initio* calculation of reaction barriers with the aim of establishing robust predictors for the MDR kinetics and applying these in microkinetic models.