

Abstract Submitted  
for the MAR17 Meeting of  
The American Physical Society

**Adsorption Behavior, Thermodynamics, and Kinetics of the Methanol Decomposition Reaction on defective graphene-supported Pt13**<sup>1</sup> RAYMOND GASPER, ASHWIN RAMASUBRAMANIAM, University of Massachusetts Amherst — Defective graphene has been shown experimentally to be an excellent support for transition-metal electrocatalysts in direct methanol fuel cells. Prior computational modeling has shown that the improved catalytic activity of graphene-supported metal clusters is in part due to increased resistance to catalyst sintering and CO poisoning, but the increased reaction rate for the methanol decomposition reaction (MDR) is not yet fully explained. Using DFT, we investigate the adsorption of MDR intermediates and reaction thermodynamics on defective graphene-supported Pt13 nanoclusters with realistic, low-symmetry morphologies. We find that the support-induced shifts in Pt13 electronic structure correlate well with a rigid shift in adsorption of MDR intermediates, and that adsorption energy scaling relationships perform well on the low-symmetry surface. We investigate the reaction kinetics and thermodynamics, including testing the effectiveness of scaling relationships for predicting reaction barriers on the nanoclusters. Using these fundamental data, we perform microkinetic modeling to quantify the effect of the support on the MDR, and to understand how the support influences surface coverages, CO poisoning, and the relationships between reaction pathways.

<sup>1</sup>Funded by U.S. Department of Energy under Award Number DE-SC0010610. Computational resources were provided by National Energy Research Scientific Computing Center.

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Date submitted: 09 Nov 2016

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