Developing an integrated experiment-theory approach to provide new insights into heterogeneous catalysis using atomically dispersed materials

Trevor Price, Sudheesh Kumar Ethirajan, Saurabh Sivakumar, Ambarish Kulkarni, Coleman Kronawitter (University of California Davis)

Contact Information: tdprice@ucdavis.edu, arkulkarni@ucdavis.edu

Introduction

This is a DOE-funded project that aims to develop an integrated experiment-theory approach to provide new insights into heterogeneous catalysis using atomically dispersed materials as model catalysts. This project leverages the following advances in Gas Phase Chemical Physics and Catalysis Science:

1. Application of techniques from the field of combustion science to the interrogation of the near-surface gas phase above catalyst surfaces under operating conditions
2. Comprehensively characterized site-isolated supported TM-MgO (TM = Pt, Ir, Pd, Rh)
3. First-principles-based microkinetic models for the interpretation of experimental results at an atomistic level

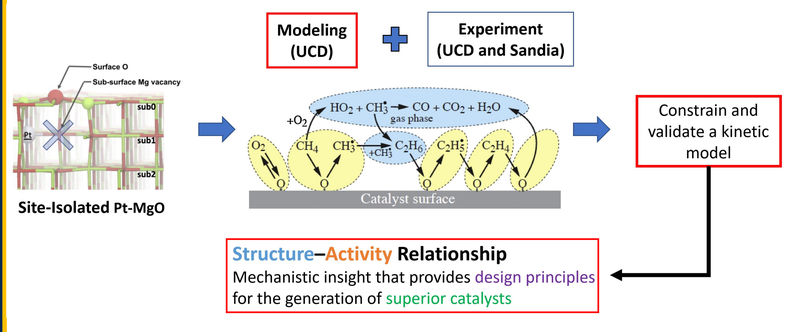


Fig 1. Project overview. Utilization of site-isolated catalysts within an integrated experiment-theory approach to generate and validate kinetic models for coupled gas and surface phase reactions. (Karakaya et al., Int. J. Chem. Kinet., 2016)

Motivation

- Decarbonization of the chemical manufacturing industry
- Oxidative coupling of methane is an example of a complex reaction network of coupled gas and surface phase reactions
- Characterization of near-surface gas phase enables new mechanistic insight for the development of catalyst design principles (structure-activity relationships)

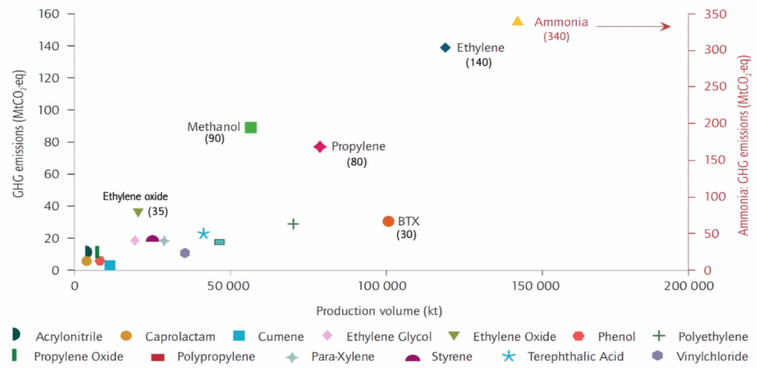
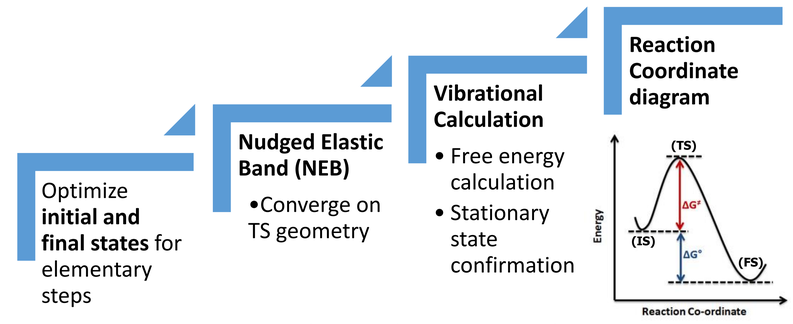


Fig 2. Carbon footprint associated with top 18 commodity chemicals

Methods: DFT Reaction Modeling

- DFT enables calculation of energetics of elementary reaction steps



Methods: RMG-MKM, Stagnation flow

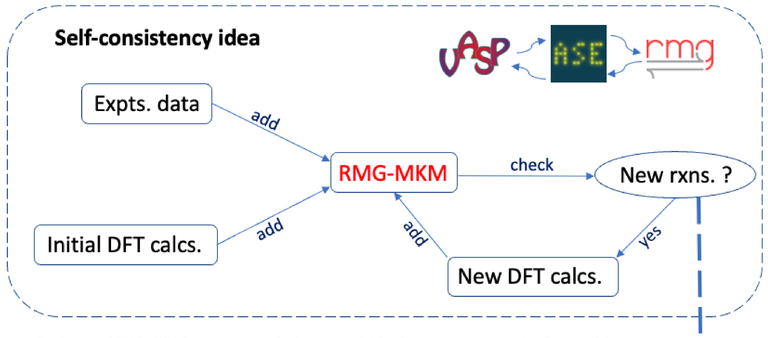
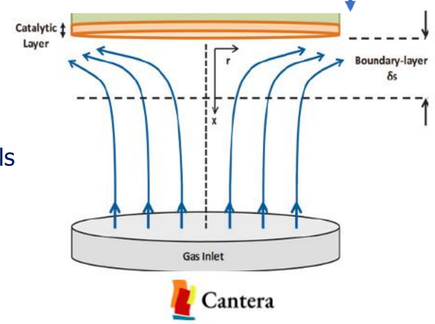


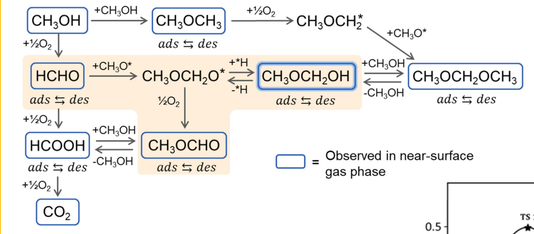
Fig 3. Use of RMG-MKM for generation of a kinetic model for future use in stagnation flow modeling. (Karakaya et al., Catal, 2018)

- Thermodynamic and Kinetic databases of RMG are updated upon DFT calculated reaction barriers and vibrational frequencies
- Converged microkinetic models are simulated in Cantera with a Stagnation flow reactor and the results are compared with the experimental data obtained at Sandia for validation



Results / Discussion

Partial oxidation of methanol over a palladium catalyst.
1. Near-surface measurement enabled detection of methoxymethanol
2. DFT-derived reaction coordinate proposed potential formation pathway



Reaction Scheme. Overview of species observed in the near-surface gas phase over Pd Catalysts, methoxymethanol is emphasized at the center. The highlighted steps are the subject of the computational analysis in Figure 5.

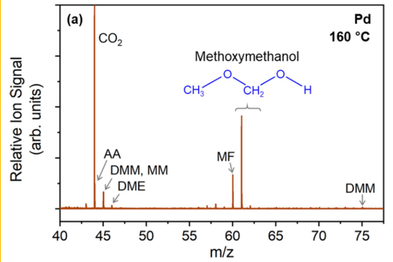


Figure 4. Near-surface molecular beam mass spectrometry results associated with methanol oxidation over polycrystalline Pd.

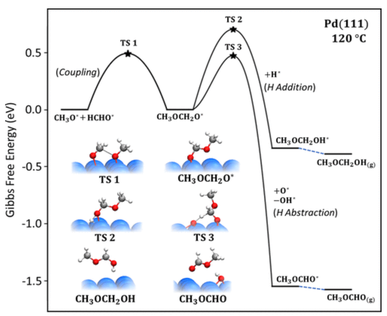


Figure 5. DFT-calculated Gibbs free energy change over the reaction coordinate for formation of methoxymethanol and methyl formate.

Challenges / Future Directions

Challenges
- Large reaction networks
  - Computationally demanding
- Unknown catalytic activity of TM-MgO family of catalysts

Future Directions
- Need MKM to enable a detailed study of the reaction network
- Automated reaction exploration
- Implementation of self-consistent DFT-MKM framework
- Machine learning enhanced enumeration of the reaction network to obtain kinetic data and transition states

Acknowledgements

The authors acknowledge Sandia's Campus Executive LDRD program for support to conduct research with the Combustion Research Facility. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE's National Nuclear Security Administration under contract DENA0003525.
We also acknowledge the U.S. Department of Energy (DOE), Office of Basic Energy Sciences (BES), Division of Chemical Sciences, Geosciences and Biosciences (CSGB), Grant DE-SC0020320.