



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

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## 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

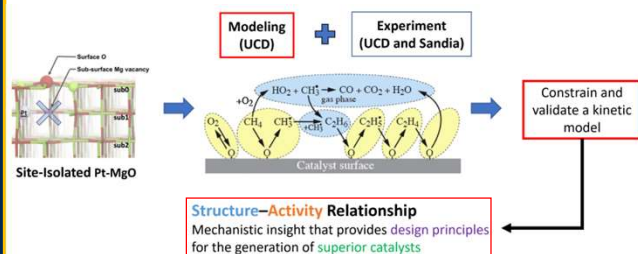


Fig 1. Project overview. Utilization of site-isolated catalysts within an integrated experiment-theory approach to generate and validate kinetic models for coupled gas and surface phase reactions. (Karakaya et al., Int. J. Chem. Kinet., 2016)

## 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)

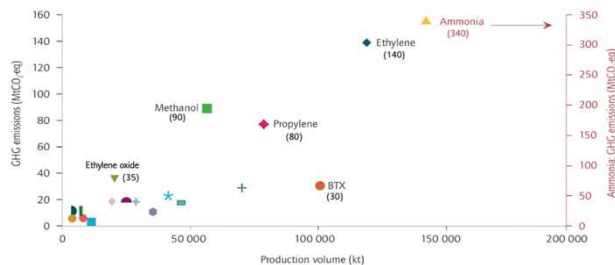
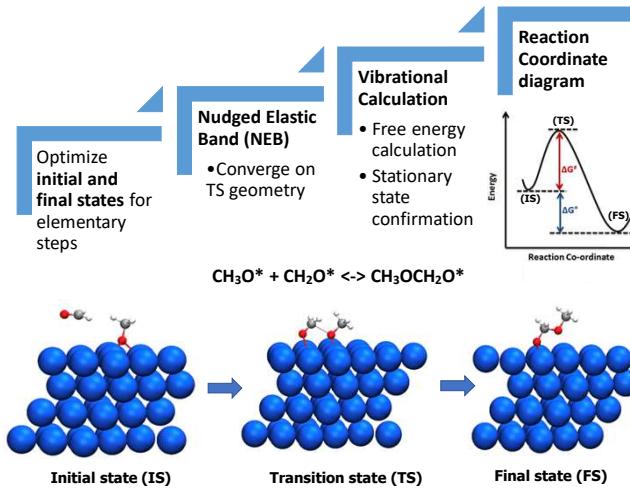


Fig 2. Carbon footprint associated with top 18 commodity chemicals

## Methods: DFT Reaction Modeling

- DFT enables calculation of energetics of elementary reaction steps



## Methods: RMG-MKM, Stagnation flow

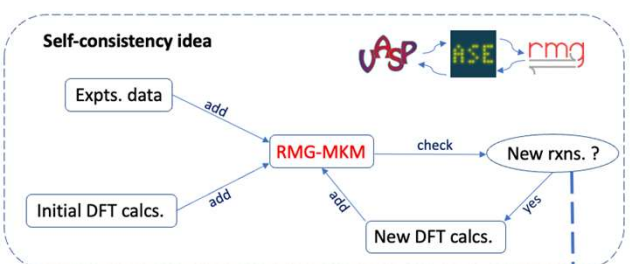
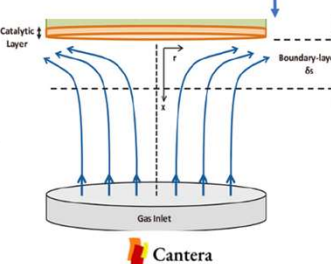


Fig 3. Use of RMG-MKM for generation of a kinetic model for future use in stagnation flow modeling. (Karakaya et al., Catal., 2018)

- 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

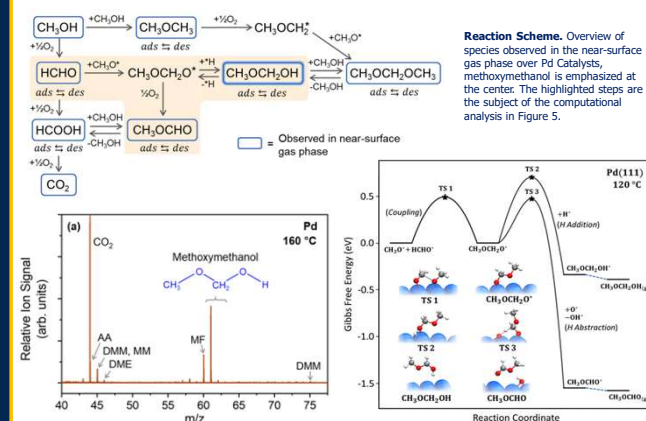


Figure 4. Near-surface molecular beam mass spectrometry results associated with methanol oxidation over polycrystalline Pd.

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

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