# Computational Study of Ethanol Synthesis from Biomass-derived Syngas Using Rh-based Catalysts

Shawn Kathmann[1]*, Donghai Mei[2], Roger Rousseau[2], Jim White[3], Mark Gerber[3], and Don Stevens[4]

*[1]Chemical Physics and Analysis Group, [2]Catalyst Science Group, [3]Chemical Biological & Process Group, [4]Technology Systems Analysis, Pacific Northwest National Laboratory, Richland Washington 99352 USA, *shawn.kathmann@pnl.gov*

## Introduction

The production of renewable fuels such as ethanol has received considerable attention in recent years for its use in automobiles and as a potential source of hydrogen for fuel cells. Currently, ethanol is produced primarily by fermentation of biomass-derived sugars. Gasification of biomass to syngas (CO, $CO_2$, $H_2$), followed by catalytic conversion, provides a promising alternate route to produce ethanol in large quantities. Even with the substantial amount of research focused on this catalytic conversion route, no commercial process exists due to the challenging chemical and technological barriers. Low yield and poor selectivity for ethanol production from syngas remain major hurdles using known catalysts. In order to make this catalytic conversion route commercially attractive, it is essential to develop more effective catalysts.

Synthesis gas can be catalytically converted to ethanol as well as other value-added fuels. Experimental efforts aimed at improving catalyst space-time yield and selectivity can benefit from molecular-level insights determined from computational chemistry. We developed a new simulation module to study the reaction kinetics of CO hydrogenation to ethanol over silica supported three-dimensional Rh-based nanoparticle catalysts. Given the absence of experimental kinetic parameters, we can use quantum chemistry to calculate the kinetic parameters. The resulting kinetic parameters have been incorporated into the newly developed kinetic Monte Carlo (KMC) simulations. The KMC simulations provide macroscopic kinetics such as product yields (or turnover frequencies), selectivities, conversion rates, etc. at realistic temperatures and pressures. As such, these simulated macroscopic reaction kinetics can be directly compared with experiment.

## Materials and Methods

Novel catalyst design is essential and combined experimental and theoretical/computational catalysis can provide the essential mechanisms, influence of promoters, energetics, selectivity, and activity for key reactions in the thermoconversion process. Reaction pathways calculated using quantum chemistry (using CP2K[1]) provide the reaction barriers used in the KMC simulations to fundamentally understand and control catalyst design. Furthermore, experimental characterization using X-ray Photoelectron Spectroscopy (XPS), X-ray diffraction (XRD), and Transmission Electron Microscopy (TEM) provides chemical, structural, and morphological insight, validation, and closure for the computational studies.

## Results and Discussion

Quantum chemical calculations have been performed and provide insight into catalyst design. A KMC module has been developed and the results are in agreement with experiment. 230 elementary reactions were included in the KMC module including the results of 80 quantum chemical calculations. XPS results indicate late transition metals get reduced to metal in processed Rh-based catalysts. Prior to processing the catalysts are oxidized. TEM and XRD are consistent with conclusions from XPS and show the validity of our computational model.

## Significance

Computational catalysis design can improve conversion efficiencies and optimize commercial synthesis processes by providing a fundamental scientific foundation to catalysis design. Further investigation of doping with other promoters is highly recommended as well as exploring other non-precious metal/promoter combinations. Quantum chemistry provides a powerful toolkit to interpret existing data for ethanol/mixed-alcohol production and generate correlations toward optimal catalyst synthesis and design. Future studies will lead to a better understanding of synthesis, preparation, and actual use of catalysts. Additionally, incorporation of "*in situ*" measurements will help to better understand the operational state of the catalyst.

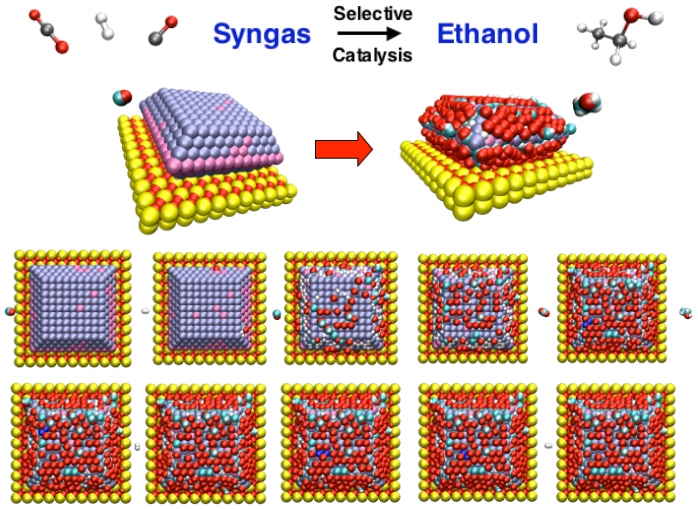


**Figure 1.** (upper) Reaction of Syngas over Rh-based catalyst to produce ethanol. (lower) Kinetic Monte Carlo simulation (using quantum chemical data) of transient kinetics over Rh-based catalytic particle on silica support.

**Acknowledgement:** This work was supported by the DOE/EERE Biomass Program. This research was performed in part using the Molecular Science Computing Facility in the Environmental Molecular Sciences Laboratory located at PNNL. Battelle operates PNNL for DOE.

## References

1. http://cp2k.berlios.de/