Effect of CO Adsorption and Coverage on Ethanol Production from Syngas

Anuradha Gundamaraju  
*Clemson University*

Ming He  
*Clemson University*

David A. Bruce  
*Clemson University*

Follow this and additional works at: [https://tigerprints.clemson.edu/grads_symposium](https://tigerprints.clemson.edu/grads_symposium)

Part of the [Biochemical and Biomolecular Engineering Commons](https://tigerprints.clemson.edu/grads_symposium)

**Recommended Citation**

Gundamaraju, Anuradha; He, Ming; and Bruce, David A., "Effect of CO Adsorption and Coverage on Ethanol Production from Syngas" (2014). *Graduate Research and Discovery Symposium (GRADS)*. 101. 
[https://tigerprints.clemson.edu/grads_symposium/101](https://tigerprints.clemson.edu/grads_symposium/101)

This Poster is brought to you for free and open access by the Research and Innovation Month at TigerPrints. It has been accepted for inclusion in Graduate Research and Discovery Symposium (GRADS) by an authorized administrator of TigerPrints. For more information, please contact kokeefe@clemson.edu.
Effect of CO Adsorption and Coverage on Ethanol Production from Syngas

Anuradha Gundamaraju, Ming He, David A. Bruce*
Chemical & Biomolecular Engineering Department, Clemson University, Clemson, SC 29634

1. Background
With the increasing interest in developing new technologies for alternative energy resources ethanol has gained prominence as it can be used both as alternative fuel and fuel additive. Most of the World's ethanol produced today comes from grains. The largest feedstocks and the ethanol broths used in ethanol production both contain high amounts of water and therefore, the energy efficiency of the process is lowered by product separation processes (azeotropic separation of water and ethanol) that are non-trivial and highly inefficient (due to the evaporation of water). An alternative route to produce ethanol, which negates the need for costly distillation processes, is via the catalytic conversion of syngas (CO and H2) generated from biomass.

2. Catalyst
In early experiments, it was shown that syngas to ethanol reactions are effectively catalyzed by supported Rhodium catalysts. However, rhodium is expensive, in relatively low abundance, and its selectivity towards ethanol is limited. To overcome these disadvantages, we propose using bimetallic catalysts that optimize the extents of CO hydrogenation and CO insertion reactions so as to favor the production of low molecular weight alcohols (including ethanol). 13 atom bimetallic clusters are used to understand the reaction mechanisms. Four major products in the reaction scheme are methanol, methane, acetone/hyde and ethanol.

3. Materials and Methods
All electronic structure optimizations were performed with ab initio quantum simulation package Jaguar 7.7 (Schroedinger, 2015), using the Density Functional Theory. Jaguar uses atomic orbital method. Basis set used is LACVQVP*†. Functional used for the calculations are B3LYP and M06. M06 is used to correct for dispersion interactions that are poorly addressed using the B3LYP functional.

4. Results and Discussion
4.1. Key observations from Microkinetic model
- A 13 atom cluster of Co7Pd6 catalyst is considered
- Concentrations of intermediate species on the surface of three sites (Co, Pd, & Co-Pd) are calculated
- Most of the reactions take place on the cobalt sites
- It was determined that the ratio of concentrations of CO/H2 on surface is 5 x 10^3
- Is there a need to include surface coverage effects
- CO prefers to adsorb only on the atop site on cobalt. As the number of CO on the surface is increased adsorption energy increases.

4.2. Surface coverage effects on the metal cluster
- CO can adsorb on metal surface binding with one (atop), two (bridge) and three (hollow) metal atoms.
- All these possibilities were considered. Number of CO molecules on the surface is calculated successively from one to six and the adsorption energies are calculated.
- B3LYP vs. M06 functional
- CO adsorption on transition metals is explained by Broyden model. According to this model, electrons are donated from CO through a bond to the metal orbitals. At the same time electronic back-donation takes place from the metal to the empty π* orbitals of the CO.
- B3LYP fails to consider the electronic effects due to the back donation of electrons.
- Geometry optimization is done using B3LYP; adsorption energy is calculated using M06 functional.

4.2.2 Coverage effects on Pd of Co7Pd6 cluster
- Number of CO on the surface is increased from 1 to 10. Initially with 1 CO on palladium, adsorption is favored on atop site. As the number of CO is increased beyond three adsorption site preference changes from bridge to atop. The adsorption energy calculated on this cluster are in good agreement with the experimental values.

4.3. Infrared spectra
- Infrared spectra can be used to determine the binding strength and the site of binding.
- Jaguar 7.7 is used to plot the IR spectra of CO. IR spectra on both cobalt and palladium correlate well with the experimental values.

4.3.1 IR Spectra for CO Adsorption on Pd Sites (Atop)

5. Conclusions
- CO prefers to adsorb molecularly on both cobalt and palladium. DFT results are consistent with experiments, with the experimental values.
- On palladium, as the number of CO molecules on the surface is increased beyond 3, adsorption site preference for CO changes from bridge to atop.
- Calculated M-C and C-O bond lengths for adsorbed CO compare favorably with literature values.
- Predicted IR spectra for adsorbed CO agree with experimental (DRIFTS) values.
- Calculated values are within 5% of the experimental values.

5. Ongoing work
- From the complex reaction network key reactions are identified and adsorption energies of intermediates are calculated with CO and syngas on the palladium side.
- Heat of reaction and activation energies are calculated for the reactions.
- Microkinetic model is developed with the coverage effects.
- Selectivity of products is compared with the previous results and also with the experimental values.

6. References

8. Acknowledgments
- Computational resources: Clemson CDT facility (Palmetto Cluster)
- Funding provided by US Department of Energy, Office of Basic Energy Sciences as part of an Energy Frontier Research Center (Center for Atomic Level Catalyst Design)