Spring 2015

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/chembio_grs

Part of the Chemical Engineering Commons

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

Concern over ever decreasing oil supplies, increasing levels of pollution and energy independence have been the primary driving forces behind significant efforts focused on the development of new technologies capable of increasing the production of alternative fuels. To-date, ethanol and to a lesser extent biodiesel have been the only alternative fuels or fuel additives to gain widespread use and be synthesized on a commercial scale. Currently, most of the World's ethanol is produced from renewable biomass. The biomass feedstocks and fermentation broths used in ethanol production contain high amounts of water, and therefore, the energy efficiency of the process is lessened due to product separation processes (azeotropic separation of water and ethanol) that are non-trivial and energy intensive (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 H_2) generated from biomass.

$$m\ CO + n\ H_2 \rightarrow C_2H_5OH + other\ products$$

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 mechanism. Four major products in the reaction scheme are methanol, methane, acetaldehyde and ethanol.

Syngas Products
- hydrocarbons
- oxygenates
- ethanol
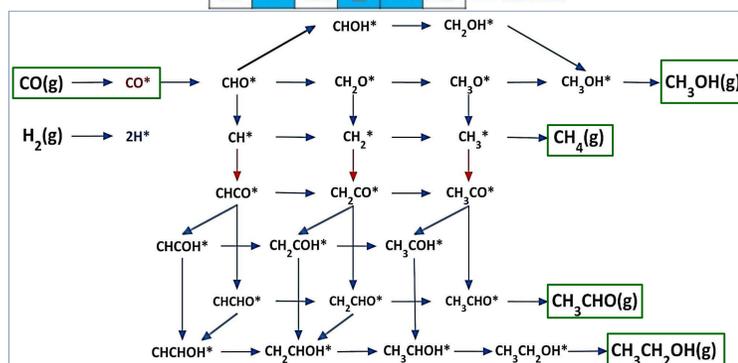
3. Materials and Methods

All electronic structure optimizations were performed with ab initio quantum simulation package Jaguar 7.7 (Schrodinger, 2010), using the Density Functional Theory. Jaguar uses atomic orbital method. Basis set used is LACVP**. Functionals used for the calculations are B3LYP and M06. M06 is used to correct for dispersion interactions that are poorly addressed using the B3LYP functional.
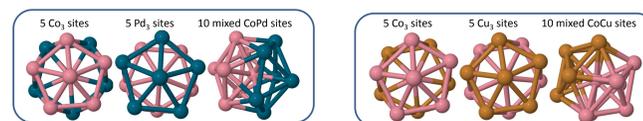
4. B3LYP vs. M06 functional

- CO adsorption on transition metals is explained by the Blyholder model. According to this model, electrons are donated from CO through a σ bond to the metal orbitals. At the same time, electronic back-donation takes place from the metal to the empty 2π* orbitals of the CO.
- B3LYP fails to consider the electronic effects due to the back donation of electrons.
- M06 is a new functional used to correct the dispersion interactions which are poorly addressed by B3LYP functional.
- Geometry optimization is done using B3LYP, while the adsorption energy is calculated using M06 functional.

σ bonding   π bonding

Metal Surface
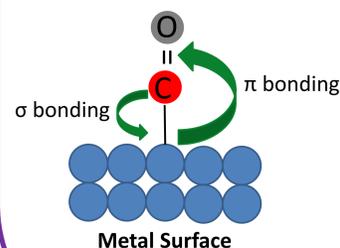
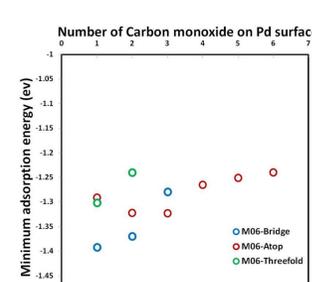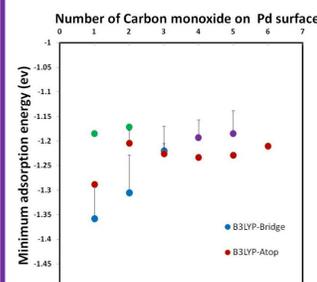## 5. Results and Discussion

5.1. Key observations from Microkinetic model

- Concentrations of intermediate species on the surface of three sites (Co_3, Pd_3/Cu_3, & Co-Pd/Co-Cu) are calculated
- Most of the reactions take place on the cobalt sites
- It was determined that the ratio of concentrations of CO/H on surface is 5×10^4
- Is there a need to include surface coverage effects ?

{ Cluster Optimizations }
{ Adsorption ΔE_{ads} }
{ Reaction E. ΔH }   BEP   DFT
{ Activation E. Ea }
{ Rate Constant k }   Microkinetic model
Selectivity

5 Co₃ sites   5 Pd₃ sites   10 mixed CoPd sites
5 Co₃ sites   5 Cu₃ sites   10 mixed CoCu sites

5.2. CO Coverage effects on Co_7Pd_6 and Co_7Cu_6 cluster

Number of CO on the surface is increased from 1 to 10. Initially with 1 CO on palladium, adsorption is favored on bridge site. As the number of CO is increased beyond three adsorption site preference changes from bridge to atop. The adsorption energies calculated on this cluster are in good agreement with the experimental values.
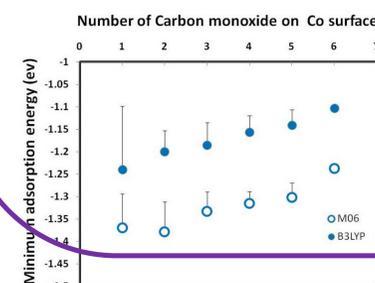
Number of Carbon monoxide on Pd surface
- B3LYP-Bridge
- B3LYP-Atop

Number of Carbon monoxide on Pd surface
- M06-Bridge
- M06-Atop
- M06-Threefold

CO Adsorption on Pd (eV)	
Experimental	Theoretical
-1.3	-2.09 (VASP PW91)
	-1.68 (VASP RPBE)

Bond lengths between carbon-oxygen and Palladium- carbon are also calculated and compared to the experimental values. From the tables it can be noted that B3LYP over estimates the C-O length and underestimated the Pd-C length.

Bond length C-O in Å			
	Experimental	M06	B3LYP
Atop		1.1471	1.1501
Bridge	1.15	1.1581	1.1626
Hcp		1.1688	1.1758

Bond length Pd-C in Å			
	Experimental	M06	B3LYP
Atop		2.146	
Bridge	1.96		2.2989
Hcp		2.1622	2.1088

4.2.3 Coverage effects on Co of Co7Pd6 cluster

CO prefers to bind only on the atop site on cobalt. As the number of CO on the surface is increased adsorption energy increases.

Number of Carbon monoxide on Co surface
- M06
- B3LYP

Bond length	Experimental	M06	B3LYP
M-C in Å	1.78±0.06	1.8527	1.8467
M-O in Å	1.17±0.06	1.1509	1.1508

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
- As the surface coverage of CO is increasing , the IR vibrational frequency shifts to a higher value, which also correlates with experimental observations

	IR FREQUENCY (cm-1)		
	Atop(Pd)	Bridge(Pd)	Atop(Co)
Experimental	2049-2061	1909-1994	2010-2070
M06 (Corrected)*	2015-2065	1920-2000	2040-2100
% error	less than 2.5%	less than 5%	less than 5%

* Correction factor for M06 = 0.9638

IR SPECTRA FOR CO ADSORPTION ON Pd SITES (ATOP)   # of CO

Intensity

Frequency (cm⁻¹)
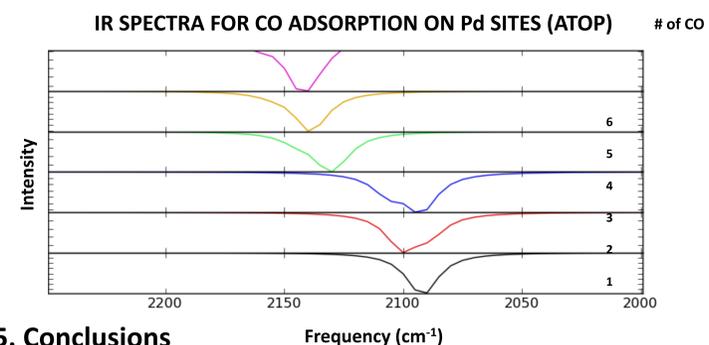
5. Conclusions

- CO prefers to adsorb molecularly on both cobalt and palladium. DFT results are consistent with experiments.
- 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.

6. Ongoing work

- Key reactions are identified and adsorption energies of intermediates are calculated with CO covering the palladium side of the cluster.
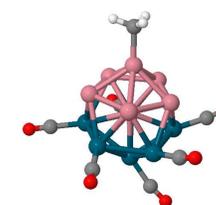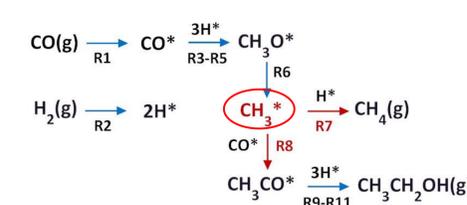
7. References

[1] Subramani, V. et al (2008)
[2] Gaur, S. et al. (2012)
[3] Spivey, J. J. et al. (2007)
[4] YongMan, C. et al (2009)
[5] Mayank, G. et al. (2011)
[6] Guochang, C. et al.(2011)

8. Acknowledgments