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Effect of CO Adsorption and Coverage on Ethanol Production from Syngas

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1. Background

With the growing 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 Worlds ethanol produced today comes from Biomass. The biomass feedstocks and fermentation broths used in ethanol production both contain high amounts of water and therefore, the energy efficiency of the process is lessened 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 H_2) generated from biomass.

$$m\ CO + n\ H_2 \rightarrow C_2H_5OH + \text{other products}$$

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.

Cr	Mn	Fe	Co	Ni	Cu
Mo	Tc	Ru	Rh	Pd	Ag
W	Re	Os	Ir	Pt	Au

Syngas Products
- hydrocarbons (red)
- oxygenates (blue)
- ethanol (yellow)
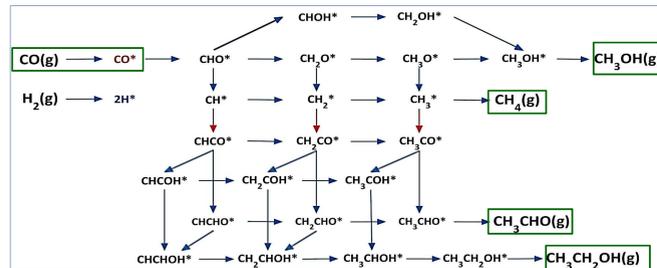
3. Materials and Methods

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.
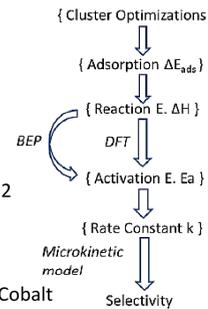
4. Results and Discussion

4.1. Key observations from Microkinetic model

- 13 atom cluster of Co_7Pd_6 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 5×10^4
- 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

❖ **Pink**: Cobalt
❖ **Blue**: Palladium
❖ **Red**: Oxygen
❖ **Grey**: Carbon

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 three possibilities were considered. Number of CO molecules on the surface is increased systematically from one to six and the adsorption energies are Calculated.

Atop   Bridge   Threefold
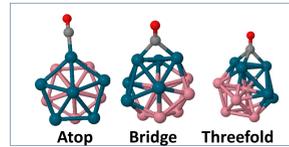
4.2.1 B3LYP vs. M06 functional
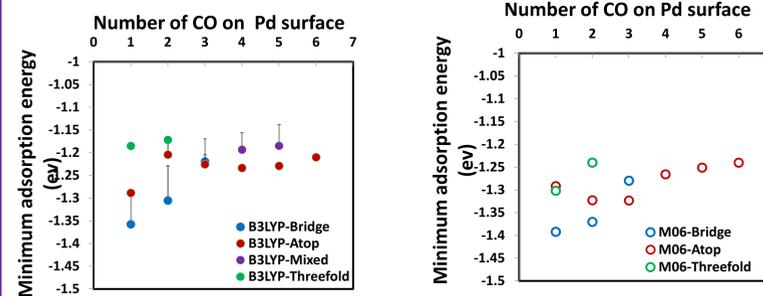

σ bonding   π bonding
Metal Surface
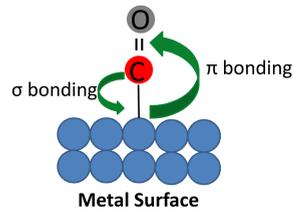
- Co adsorption on transition metals is explained by Blyholder model. According to this model electrons are donated from CO through a σ bond to the metal orbitals. At the same time electronic back-donation takes place from the metal to the empty $2\pi^*$ orbitals of the CO
- B3LYP fails to consider the 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. adsorption energy is calculated using M06 functional

4.2.2 Coverage effects on Pd of Co_7Pd_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 CO on Pd surface
- B3LYP-Bridge
- B3LYP-Atop
- B3LYP-Mixed
- B3LYP-Threefold

Number of CO on Pd surface
- M06-Bridge
- M06-Atop
- M06-Threefold

Experimental value for adsorption energy of CO on palladium is -1.3 ev.

	Bond length C-O in Å				Bond length Pd-C in Å		
	Experimental	M06	B3LYP		Experimental	M06	B3LYP
Atop		1.1471	1.1501	Atop		1.9402	1.9146
Bridge	1.15	1.1581	1.1626	Bridge	2.004	2.1103	2.0989
Hcp		1.1688	1.1758	Hcp		2.1622	2.1088

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.

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.

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

	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	< 2.5%	< 5%	< 5%

* Correction factor for M06 = 0.9638

**IR SPECTRA FOR CO ADSORPTION ON Pd SITES (ATOP)**
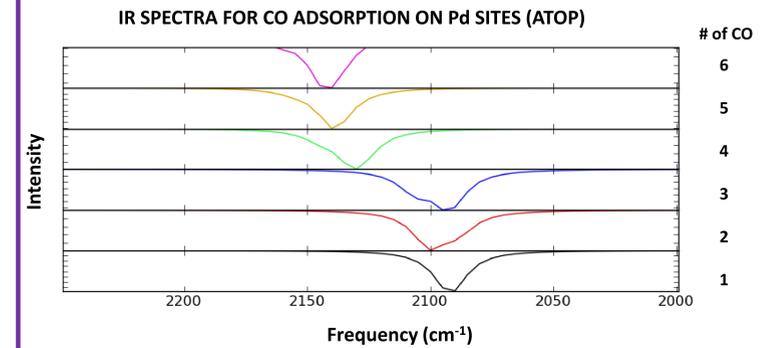
- As the surface coverage of CO is increasing ,the IR vibrational frequency shifts to a higher value, which also correlates with experimental observations

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

- From the complex reaction network key reactions are identified and adsorption energies of intermediates are calculated with CO covered 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
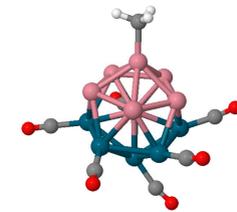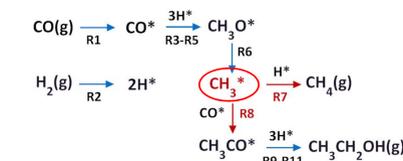
7. References

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

8. Acknowledgments