

Investigation of CO Hydrogenation Mechanisms using Co Carbonyl Catalysts

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Introduction

The rapid depletion of oil necessitates the discovery and development of new ways to make other potential energy sources viable. One such process is the Fischer-Tropsch catalytic process to take syn-gas, a mixture of CO and hydrogen produced from coal, to make higher molecular weight hydrocarbons of greater value such as those used for diesel fuels. Unfortunately, Fischer-Tropsch catalysis is a complex process whose mechanisms and surface intermediates are not well understood. Therefore, as a first step to develop improved Fischer-Tropsch catalysts with a high selectivity to particular products, we have chosen to examine a homogeneous analog, $\text{HCo}(\text{CO})_4$. If we can precisely identify the reaction pathways for the homogeneous catalyst and understand what factors influence the catalyst's selectivity, then we can ultimately use this knowledge to aid in the design of new heterogeneous catalysts.

Materials and Methods

Density functional theory based calculations were performed using the program VASP[1] with plane wave basis set and ultrasoft pseudopotentials with periodic supercells. Transition state calculations for the evaluation of kinetics used the climbing nudged elastic band method as described by Jonsson and coworkers[2].

Results and Discussion

Previous NMR results from Rathke and Klingler [3] led to a proposal for a reaction pathway which has now been confirmed by our calculations. We have calculated the energies of all stable intermediates in the reaction cycle as proposed by Klingler and Rathke allowing for the creation of a potential energy surface as depicted in Figure 1. Two different product pathways are possible based upon the insertion of CO leading to either ethylene glycol and methanol or methyl formate and methanol. Previous calculations in the literature have indicated much higher energy paths for these reactions than have been observed experimentally. However, our own examination of this system has revealed significantly better agreement with experiment as shown in Table 1 for several key reaction steps.

Reaction (energies expressed in kcal/mol)	Ziegler et al [4]	Bursten et al [5]	Current Work (VASP)	Experimental
Co-Co dissociation	35.4	29.9	21.9	19.7
Decarbonylation	45	26	32.9	26
$\text{Co}_2(\text{CO})_8$ hydrogenation	6.5		0.1	4.7
CO hydrogenation			37	40.7

New results will more thoroughly examine the influence of ligands such as triethylphosphine (replacing carbonyl groups) upon the product selectivity. In addition we have begun to examine the production of ethanol by the homologation of methanol, another homogenous catalytic process of great importance given the recent increase in demand for ethanol based fuels.

Significance

It appears we have positively identified the transition state in the reaction cycle of methanol production: $(\text{CO})_3\text{H}_2\text{CoCOH}$. The results also indicate that $(\text{CO})_4\text{CoCOH}$ should be an observable intermediate, giving guidance to new NMR experiments to be performed by Klingler and Rathke. Finally, we can also use our calculations to explain product distributions based on the relative reaction enthalpies.

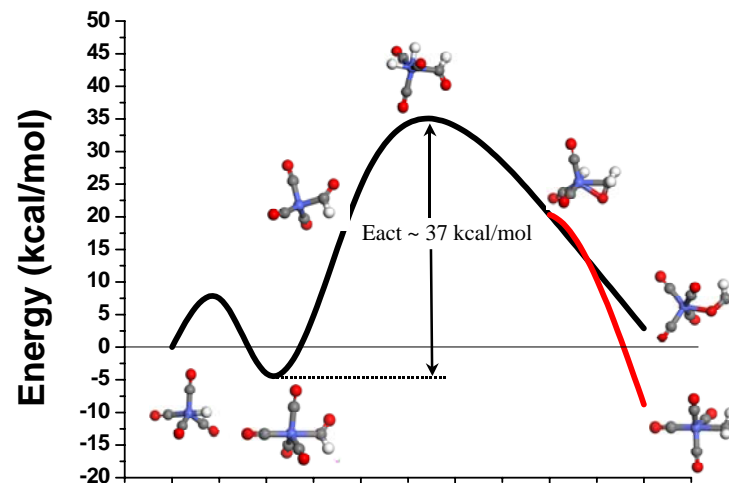


Figure 1. A view of the potential energy surface for CO hydrogenation. The black line indicates the energy of intermediates leading to methyl formate and methanol production. The red line indicates an alternative path leading to the formation of methanol and ethylene glycol.

References

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