Effect of CO Adsorption and Coverage on Ethanol Production from Syngas

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ABSTRACT

Ethanol is an alternative fuel which can be used both as a fuel and as a fuel additive. It can be produced from biochemical or chemical processes. In the biochemical process the biomass feedstocks and fermentation broths 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). In chemical processes ethanol can be produced via the catalytic conversion of syngas (CO and H_2) generated from biomass, thereby avoiding costly distillation processes.

A high efficiency cost effective catalyst for converting syngas to ethanol is not been found. 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). These bimetallic catalysts consist of a carbon chain growth metal (catalysts to produce long chain hydrocarbons) and an alcohol forming metal (catalysts for methanol production). Of the 16 bimetallic systems initially investigated, the metal combinations that were considered promising for ethanol production were CoPd, CoCu, NiPt, NiIr, and FeCu.

The present study aims at developing a detailed micro kinetic model for ethanol production from syngas using catalysts that contain 13-atom bimetallic clusters. In order to understand the

reaction mechanism, we are using first principle methods employing Density Functional Theory (DFT) to simulate the catalyst structure, determine favorable adsorption sites, calculate adsorption energies, and find transition states for all of the reactions occurring on the bimetallic catalysts.

One of the first and important steps in the syngas to ethanol conversion process is carbon monoxide (CO) adsorption on the metal catalyst. Therefore, computational models were developed to help understand CO adsorption energetics as well as surface coverage effects on a Co7Pd6 catalyst. Key reactions for syngas to ethanol formation were identified from micro kinetic model and the influence of CO coverage on activation energies of these key reactions is determined. From these initial studies, we determined that the adsorption energies of CO on both cobalt and palladium as a function of CO surface coverage (where the number of CO species on the catalyst surface was varied from 1 to 6). Further, we calculated the infrared spectra for adsorbed CO species and key bond lengths (metal–carbonyl carbon and adsorbed CO bond lengths) using DFT. Results from the DFT simulations compared favorably with experimental values. These validated simulation results provide valuable insights into the reaction behavior of the studied bimetallic catalysts. Once the CO coverage results are obtained the rates of key reactions are calculated and compared to the previous results.

References

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