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2. **Title:** Ethanol from synthetic gas, an alternative route to produce an alternative fuel
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4. **Abstract:**

In the future, the availability of reliable alternative fuels will be crucial for any country to become energy independent. One such alternative is ethanol as it can be used both as a fuel and as a fuel additive. Most of the ethanol produced in the world today is derived 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 H₂) generated from biomass. Syngas is a mixture of carbon monoxide and hydrogen, which results from the reforming of natural gas, as well as the gasification of coal, biomass, and solid wastes. In theory, syngas can be readily converted to ethanol using chemical catalysts, but to-date no high efficiency, low-cost catalyst has 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 to offer the most promise for ethanol production were CoPd, CoCu, NiPt, NiIr, and FeCu.

The present study aims at developing a detailed microkinetic 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 Co$_7$Pd$_6$ catalyst. 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.

5. Citation