A Computational Approach for the Rational Design of Bimetallic Clusters for Ethanol Formation from Syn-gas

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1. Background

The catalytic synthesis of ethanol from syn-gas (2CO + 4H₂ → CH₃OH + H₂O) is important due to increased demand for alternative, renewable energy sources. A major challenge associated with this route is finding a low-cost catalyst that promotes the proper combination of CO dissociation and CO insertion steps, so as to yield ethanol as the primary reaction product. Bimetallic catalysts, in which one metal promotes hydrocarbon production and the other oxygenates production, may exhibit a synergistic effect that can facilitate the formation of ethanol. As such, many bimetallic combinations are possible, a fundamental theoretical investigation is essential to shed light on the complex reaction mechanism from syn-gas to ethanol. This analysis will enable a more complete computational combination screening of catalysts.

2. Materials and Methods

All electronic structure optimizations were performed using Jaguar (Schrodinger), using the unrestricted spin DFT formalism at the B3LYP/LACVP** level of theory. Reaction pathways and transition state (TS) were mapped out using climbing image nudged elastic band method (CI-NEB) coupled with the quadratic synchronous transit (QST) method implemented in Jaguar. All final transition state structures had exactly one imaginary frequency. Microkinetic models were built based on transition-state theory (TST) formalism at the B3LYP/LACVP** level of theory. Rate data was calculated from microkinetic models, considering all reaction steps and the diffusion of intermediate species. We find good agreement of reaction selectivity between model and experiments (Table 1). It is interesting to note that the C₂ oxygenate is only formed on the CoPd sites. We find a universal reaction mechanism exists on all three sites, this result suggests the atomic-level design of catalysts and novel synthesis method needed to be the mixed CoCu site or the combination of the mixed CoCu site and the Co site. This result suggests the bimetallic combinations of Co and Cu could be potential catalysts for ethanol formation reactions. To verify these assertions, BEP relationships were constructed for the four copper based catalysts. The selectivity results from individual sites were obtained from microkinetic modeling at PCO=3.33 bar, PH₂= 6.66 bar, 523K.

3.1.1 BEP relationships

A total of 37 surface reactions occurring on three distinct surface site types were included in our mechanism for ethanol formation from syn-gas, yielding more than 100 possible surface reaction steps for which to calculate rate constants. To more rapidly solve this computationally intensive problem, we judiciously employed various scaling methods.

A widely used scaling method for estimating activation energies is the Brønsted-Evans-Polanyi (BEP) relation, which linearly correlates the transition state energy of an elementary step to the reaction enthalpy of that step. Thus, a task of considerable computational cost (transition state searching) can be replaced with two moderately computations (energy minimizations of the reactant and product).

To apply the BEP relation to the Co-Pd binary cluster, the transition state energies of these steps are plotted against reaction energies, by which a linear relationship is deduced.

To conclude our microkinetic modeling study, the overall reaction mechanism chart for ethanol formation on the Co-Pd₆ cluster is presented. The reactions proceed on the Co sites of the cluster. CO insertion into the metal-carbon bonds of adsorbed methyl groups is the primary pathway to produce C₂ oxgenates. Methane is the major product (87%). Some ethanol (13%) can also form on Co sites via the diffusion of CH₂ and CH₃CO species between Co sites and CoPd sites, thus facilitating CO insertion reactions.

The surface fractional coverage of catalyst sites is altered to study the effect of catalyst composition on the overall selectivity. It is noted methane will likely be the major product on catalysts consisting of Co and Pd metals. It is also likely to have methanol production if the catalyst is very rich in a Pd phase. To promote the selectivity of C₂ oxgenates, a high surface coverage of mixed CoPd sites is required.

References


From the calculated barriers, it is suggested that the bimetallic compositions of NiPt, CoCu, FeCu, NiCu, and RuCu are promising candidates as catalysts for ethanol formation reactions. To verify these assertions, BEP relationships were constructed for the four copper based catalysts. The selectivity results from individual sites were obtained from microkinetic modeling at PCO=3.33 bar, PH₂= 6.66 bar, 523K. The Co₆Cu₄ Cluster shows characterization for ethanol formation, which suggests the bimetallic combinations of Co and Cu could be potential catalysts for this reaction. The microkinetic model on the Co₆Cu₄ cluster was extended to different metal compositions by altering surface coverage of the three reaction sites.

It is found to have significant ethanol production the majority of the catalytic surface needed to be the mixed CoCu site or the combination of the mixed CoCu sites and the Co site. This result suggests the atomic level design of catalysts and novel synthesis method is necessary to increase surface coverage of the mixed metal sites.