

Identification of ultra-low temperature water gas-shift catalysts using computational chemistry techniques

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Objectives:

The principal objective of this work is to use state-of-the-art *computational chemistry* methods for identifying novel bimetallic near surface alloy (NSA) catalysts for the ultra-low temperature Water Gas Shift (LWGS) reaction. The main target of our research is to identify NSAs that are stable in the presence of OH and O, and activate H₂O easier than Cu, which is the current industrial catalyst. Existing *collaborations with catalyst synthesis and testing* research groups at Brookhaven National Lab and UW respectively will facilitate validation of the catalysts identified with theory.

Using state-of-the-art first principles methods, based on periodic, self-consistent plane-wave Density Functional Theory (DFT) as implemented in *DACAPO* code, we will first check the stability of bimetallic NSAs in the presence of CO, O, and OH, all key surface intermediates for LWGS. We will systematically search for bimetallic combinations covering a significant portion of the late transition metals series. After having identified NSAs that will resist adsorbate-induced surface segregation, we will calculate the binding energy (BE) of CO, O, and OH on these NSAs, and compare them with the corresponding BEs on monometallic surfaces. These studies will lead to the identification of robust NSAs, which bind CO, O, and OH weaker than the monometallic Cu-based catalysts, which are currently used by industry for the low temperature WGS reaction.

In a second phase, we will perform detailed DFT calculations for the thermochemistry and kinetics of H₂O activation, which most likely is the rate-limiting step for WGS. Stable NSAs activating H₂O easier than Cu may be able to catalyze LWGS at temperatures lower than Cu does. The detailed LWGS mechanism on the most promising of these NSAs will be analyzed. The fundamental understanding of the LWGS mechanism on these new catalysts, coupled to the detailed analysis of the surface *electronic structure*, is expected to identify the key electronic properties of successful NSAs and thus guide us to designing the next generation of ultra-low Temperature WGS catalysts.

Accomplishments to date:

New start date: Sept 1 2006.

Future Work:

1. Identify NSAs stable in CO, O and OH.
2. Study Binding Energy of CO, O and OH on NSAs
3. Study H₂O activation on NSAs and WGS mechanism on selected NSAs