Density Functional Theory Study of Pd and Pt Pseudomorphic Monolayer Catalysts for Water Gas Shift

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Introduction

One of the great challenges of our time is the efficient and equitable consumption of fossil fuels. One of the consequences of our need to conserve our finite petroleum resources is a transition to more efficient diesel engines and lean burning gasoline engines. Associated with the switch to these lean burning engines is an increase in NO_x production which results in a need to improve exhaust catalysts.

Surface science studies of epitaxially grown metal layers on top of a different metal single crystal have revealed that these pseudomorphic monolayers have novel adsorption properties and therefore could potentially serve as a whole new class of catalysts[1]. Specifically, the use of pseudomorphic monolayers of Pt and Pd over other transition metals have been examined for their ability to perform in both reducing and oxidizing environments. From these calculations, it is hoped that suitable candidates are identified for replacement of monometallic Pt catalysts thereby simultaneously improving performance and reducing cost. This phase of the project will summarize work done on the optimizing the catalyst for a key step in the reduction cycle, Water Gas Shift, when CO is used as a reductant.

Materials and Methods

Density functional theory based calculations were performed using the program VASP[2] with a 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[3].

Results and Discussion

In Figure 1, the volcano plot for the oxidation of NO is shown. For host metals which possess lattice constants smaller than Pd, the surface layer is in compression and the activation of oxygen is kinetically important. For systems where Pd is supported over Au or Ag and the surface is in expansion, the rate limiting step is the reaction of NO and O atoms. It should be noted that the volcano plot will shift depending upon the partial pressures and reaction temperature. Our thermodynamic analysis indicates that the surface is likely to be in a higher coverage regime under reaction conditions than that for which this volcano plot was constructed [4]. In the same way that we have examined the oxidation step in the NSR cycle, we have also examined reduction chemistry with our initial efforts focused upon the water gas shift whereby CO is used to generate hydrogen which is ultimately used for reduction of the NOx carrier. Just as in the example for NO oxidation, a volcano plot for the reaction can be constructed based upon the shift of the rate limiting step from water activation to CO oxidation. On surfaces which Pt is in expansion, hydrogen-oxygen bonds are more easily broken as compared to surfaces where Pt is in compression. Conversely, the oxidation of CO has higher barriers on surfaces where Pt is in expansion as compared to Pt supported above Ir, Rh or Ru.

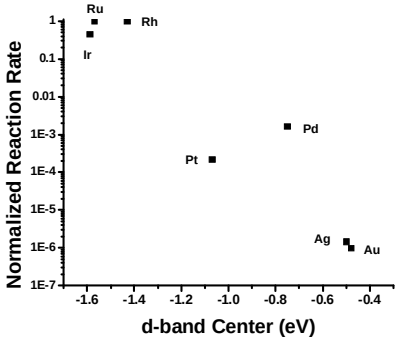

Figure 1. Volcano Plot of NO oxidation over Pd pseudomorphic monolayer catalysts. The element indicates the host metal.

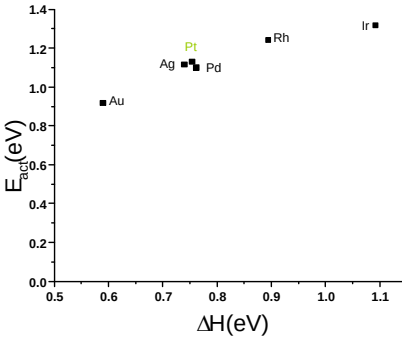

Figure 2. BEP relationship for H_2O dissociation over Pt monolayer catalysts. The element indicates the host metal.

However, in all cases water gas shift over Pt psuedomorphic monolayer catalysts was found to proceed through the carboxyl mechanism as the barriers for CO oxidation with OH were always lower than CO oxidation barriers with adsorbed O. In addition, reaction of CO with OH to form the carboxyl intermediate were always lower than H_2O dissociation barriers. Figure 2 depicts the BEP relationship for H_2O dissociation over Pt systems. New calculations will focus on the role of NCO in these systems.

Significance

The central challenge facing the development of novel NOx storage storage reduction catalysts is that the catalyst must operate under two distinct regimes. This work represents the beginning of an ambitious plan to develop two volcano describing both the oxidation and reduction chemistry in order to optimize the catalyst performance for a single material (although that may of course be an alloy).

References

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