

Density Functional Theory Study of Pd-based Pseudomorphic Monolayer Alloy Catalysts for NO_x Storage Reduction Applications

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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 the oxidation reaction while introducing the analysis of the more complicated reduction chemistry.

Materials and Methods

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

As a starting point, the oxidation of NO to NO₂ was examined for a variety of potential candidate catalysts. Figure 1 shows the relationship between reaction enthalpy and the reaction barrier for Pt pseudomorphic monolayer catalysts for this reaction. It is important to recognize that the stable surfaces in the oxidizing environment may in fact be surface oxides. Using an approach popularized by Scheffler et al.[4] known as *ab initio* thermodynamics, one can analyze the temperatures and partial pressures under which a given surface phase (for both oxygen and NO) will be stable. Furthermore, core-shell systems like Pt/Cu may be reversed in the presence of oxygen such that a surface oxide of copper forms above a Pt core depending upon the temperature and partial pressure of oxygen. Indeed we have found that oxygen in general is a stronger segregator than NO and that some of our systems are in fact thermodynamically unstable. However, the kinetics of metal atom diffusion from the surface to the subsurface (and vice versa) is currently still under examination.

New results will more thoroughly examine the reduction chemistry which is significantly more complex than the oxidation chemistry. Work has begun with the use of H₂ as the reductant.

Significance

The central challenge facing the development of novel NO_x 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).

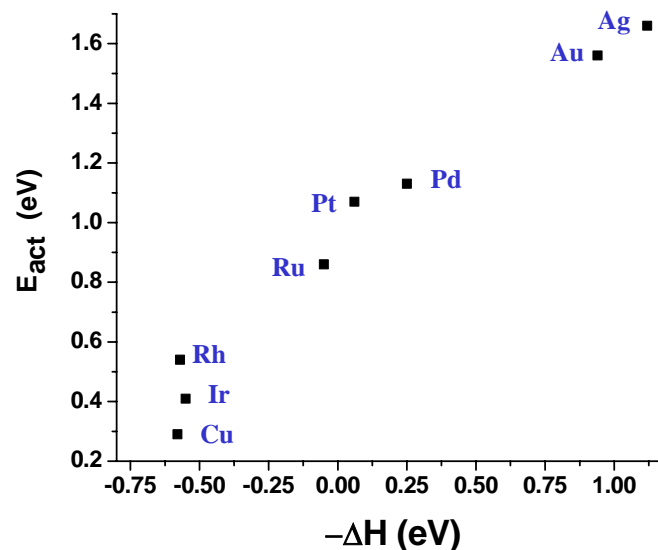


Figure 1. Bronsted Evans Polanyi relationship for NO oxidation with atomic oxygen comparing various substrates for Pt pseudomorphic monolayer catalysts

References

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