Density Functional Theory Study of the Effect of Sub-Surface H, C and Ag on C₂H₂ Hydrogenation on Pd(111)

Pavithra Tirrupathi¹, Randall Meyer¹*, Ally Chan² and Simon Bare²
¹University of Illinois at Chicago, Chicago, IL 60607 (USA)
²UOP LLC - Honeywell Company, Des Plaines, IL 60017-5017 (USA)
*rjm@uic.edu

Introduction
The selective hydrogenation of acetylene in the presence of ethylene over Pd catalysts (generally modified with silver) is of critical importance to prevent deactivation of polyethylene polymerization catalysts[1]. Due to the large concentrations of both hydrogen and hydrocarbons, it is not surprising that the presence of both surface hydrogen and surface carbon as well as subsurface hydrogen and subsurface carbon have been detected in the working catalyst[2]. We have used density functional theory to explore the effect of subsurface species upon the selective hydrogenation reaction on Pd(111) using various models for palladium hydride and palladium carbide. In addition, we have explored the diffusion of both carbon and hydrogen into the subsurface region. Finally we have examined the influence of Ag in the subsurface on the thermodynamics of the surface reactions.

Materials and Methods
Density functional theory based calculations were performed using the program VASP[3] 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[4].

Results and Discussion
We have examined the influence of subsurface H, C, and Ag on the hydrogenation of C₂H₂ over Pd(111) surfaces. Sub-surface H and C both lead to a decrease in the adsorption energy of C₂H₂ and C₂H₄ to the Pd(111) surface. Sub-surface H leads to a lowering of the hydrogenation barriers and should therefore lead to an increase in reactivity and a loss of selectivity. Furthermore, the barrier of H diffusion from the surface to the sub-surface is very low (0.38 eV), whereas C diffusion is considerably more difficult (1.25 eV). As the concentration of C in the sub-surface increases, the barrier to diffusion sharply increase, implying that the amount of C in the sub-surface should reach a maximum at low concentration.

As the presence of Ag is well known to improve selectivity, we have also explored the effect of alloying. In Figure 1, it is clear that the adsorption of C₂H₂ and H₂ are highly exothermic on the pseudomorphic monolayer of Pd over Ag above the PdAg bulk alloy. This implies that the surface reaction is essentially thermoneutral (given a finite hydrogen reservoir) as opposed to on Pd(111) where the initial adsorption event is considerably less exothermic. Given that BEP relationships are likely to apply to the C₂H₂ hydrogenation across various surfaces, this implies that the hydrogenation barriers should be higher on this surface leading to a loss in activity. However, selectivity should be improved as the hydrogenation of C₂H₄ switches from an exothermic reaction to an endothermic one.

Significance
Due to the switch from an exothermic reaction to an endothermic reaction on the Pd pseudomorphous monolayer catalyst (above a sub-surface Ag enriched layer) over PdAg, the hydrogenation of C₂H₂ is more difficult over this surface as compared to Pd(111). Our work therefore provides new insight into the role of Ag in this catalyst and how Ag should lead to improved selectivity with a simultaneous loss in activity.

Figure 1. Hydrogenation of C₂H₂ over Pd/Ag/PdAg(111).

References