Density Functional Theory Study of the Effect of Sub-Surface H, C and Ag on C_2H_2 Hydrogenation on Pd(111)

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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 C_2H_2 over Pd(111) surfaces. Sub-surface H and C both lead to a decrease in the adsorption energy of C_2H_2 (and C_2H_4) 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 C_2H_2 and H_2 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 C_2H_2 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 C_2H_4 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 pseudomorphic monolayer catalyst (above a sub-surface Ag enriched layer) over PdAg, the hydrogenation of C_2H_4 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.

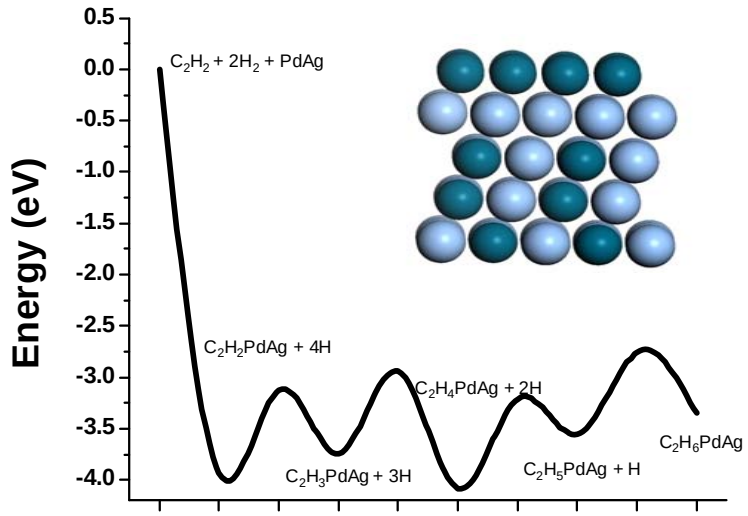

Figure 1. Hydrogenation of C_2H_2 over Pd/Ag/PdAg(111).

References

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