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Density functional theory study of the effect of subsurface H, C, and Ag on C_2H_2 hydrogenation on Pd(1 1 1)

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ABSTRACT

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. In this study, density functional theory has been used to investigate the diffusion of carbon and hydrogen into the subsurface region of Pd(1 1 1), and subsequently, to explore the effects of these subsurface species on the selective acetylene hydrogenation reaction on Pd(1 1 1). In addition, the influence of subsurface Ag on the thermodynamics and kinetics of C_2H_2 hydrogenation has been examined. We find that the presence of subsurface H lowers the barriers for each C_2H_X hydrogenation step, and could increase the overall activity of the hydrogenation reaction with a corresponding decrease in the selectivity towards ethylene. In contrast, modification with subsurface C or Ag appears to lead to heightened barriers for ethylene hydrogenation, and may increase the selectivity of the Pd(1 1 1) catalyst.

1. Introduction

The selective partial hydrogenation of C_2H_2 to C_2H_4 is critical to the manufacture of polyethylene as the presence of trace C_2H_2 in the C_2H_4 feedstock results in the poisoning of the polymerization catalyst [1]. The catalyst of choice for this system is a supported Pd catalyst, typically alloyed with Ag in order to slow coking that ultimately leads to deactivation. Improvement of both the lifetime and selectivity of this catalyst is desirable as suppression of the over-hydrogenation of C_2H_4 to C_2H_6 is also critical to the catalyst's success. The presence of Ag may also help the selectivity as the adsorption of C_2H_4 to Pd alloyed with Ag is weaker than to Pd, thereby facilitating the removal of C_2H_4 from the surface.

The hydrogenation of C_2H_2 over Pd catalysts and the role of Ag has previously been explored using density functional theory (DFT) [2–6]. Neurock and co-workers have calculated the potential energy surface for the hydrogenation of C_2H_2 and found that the barriers for each hydrogenation step range from 0.61 to 0.78 eV. However, it should be noted that the highest barrier is the hydrogenation of C_2H_3 to C_2H_4. This implies that once C_2H_4 is created, the highest barrier has already been surmounted allowing complete hydrogenation to C_2H_6 to occur as the entire sequence is thermodynamically downhill [3]. Subsequent calculations examining the effect of Ag reveal that Ag in the surface layer greatly decreases the adsorption energy of C_2H_2 as compared to C_2H_4 [2]. However, this effect is very sensitive to coverage as increasing the coverage of C_2H_2 on Pd50%Ag50%/Pd(1 1 1) from 0.25 ML to 0.33 ML results in a decrease of the adsorption energy from −1.31 eV to −0.62 eV and C_2H_4 adsorption on this surface weakens from −0.73 to −0.18 eV. Sheth et al. suggest that the presence of Ag results in an increase in C_2H_2 hydrogenation since the reactants are less strongly bound to the surface [2]. On the other hand, this does not apply to C_2H_4 whose adsorption is so weak that its lifetime on the surface is too short for reaction to ethane. In addition, Mei et al. note that while Ag generally had a small effect in reducing the hydrogenation barriers, the barrier for the hydrogenation of vinyl to ethylene was greatly reduced as a result of the change in the adsorption site for vinyl upon alloying of Pd with Ag [6]. Nørskov and co-workers examined the effect of alloying with Ag on the overall potential energy surface and observed that the primary effect of Ag was to reduce the binding energy of C_2H_2 and C_2H_4 to the surface [7,8]. Finally, DFT calculations from Gonzales et al. indicate that the presence of Ag also serves to prevent the accumulation of hydrogen in the subsurface [9].

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Khan et al. have explored the roles of surface vs. sub-surface hydrogen in the hydrogenation of C_2H_2 in their examination of model PdAg catalysts supported on planar Al_2O_3 thin films [10]. The effect of sub-surface vs. surface hydrogen was elucidated by varying the temperature of the substrate when exposing it to hydrogen. At 300 K, only surface hydrogen is present. However, when the surface is exposed to hydrogen at lower temperatures (e.g., 200 K) both surface and sub-surface hydrogen are found. Following hydrogen exposure at different temperatures, the catalyst was exposed to C_2H_2 at 90 K and a temperature programmed reaction experiment was performed. When only surface hydrogen was present, C_2H_2 was hydrogenated to C_2H_4 or decomposed to carbonaceous material. However, when sub-surface hydrogen was present, ethane was produced in addition to ethylene. When Ag is added, the reactivity of the model catalyst drops off sharply, even at a very low Ag:Pd ratio. However, it should be noted that the decrease in C_2H_6 production with increasing Ag content is faster than the decrease in C_2H_4 production with increasing Ag content, thus demonstrating the positive effect of Ag on the reaction selectivity.

Due to the well known ability of Pd to absorb hydrogen, it has long been speculated that the active phase of the catalyst is a palladium hydride phase as opposed to palladium metal. However, recent work from Schlögl's group indicates that subsurface carbon, not hydrogen, is the key to successful selective hydrogenation [11,12]. In their examination of 1-pentyne hydrogenation over Pd black catalysts at 308 K and 0.1 mbar of the alkyne, Teschner et al. observed that selectivity to the alkene drops dramatically as the hydrogen pressure is increased from 2 mbar to 8 mbar [11] (in agreement with Khan et al. [10]). *In-situ* XPS indicates the existence of a *Pd* 3*d* state at a higher binding energy (335.6 eV) than the metal (335.0 eV) when the hydrogen pressure is low (3.5 mbar). However, this high binding energy state is diminished as the hydrogen pressure increases. Teschner et al. speculate that this high binding energy state is associated with sub-surface carbon. Subsequent measurements with other alkynes indicate this is a general phenomenon. The presence of carbon in the sub-surface region has been confirmed to be theoretically favorable by Yudanov et al. [13]. Its suggested role in selective hydrogenation is to weaken the adsorption of C_2H_4 to the surface resulting in its desorption rather than its further reaction to ethane. The structure of the "PdC" phase is currently still unknown. However, neutron scattering data from Ziemecki et al. suggest that the maximum C content may be about 13% [14–16]. Calculations of stoichiometric bulk noble metal carbides suggest that such a PdC phase is metastable [17], but no experimental results exist demonstrating PdC formation even at extreme conditions [18]. Therefore, it is possible that while the formation of a PdC_x phase is desirable for catalysis, additional carbon beyond the saturation point at $x = 0.13$ would not be incorporated into the bulk under the reaction conditions and would be deposited as coke on the catalyst surface instead. Lopez and co-workers have recently examined carbide formation through adsorption of C at a Pd(1 1 1) step edge and found that the barrier for C incorporation into the bulk is ~0.8–1.0 eV [19].

In our current examination of this system, we have been focused upon the effect of subsurface H, C and Ag on the hydrogenation of C_2H_2 to form C_2H_4 and C_2H_6. The diffusion of H and C both on the surface and into the sub-surface region using density functional theory has also been examined.

2. Computational methodology

The density functional theory calculations in this work are performed using the Vienna Ab Initio Simulation Package (VASP) [20,21]. A plane-wave basis set with a cutoff energy of 400 eV and ultra-soft Vanderbilt pseudopotentials (US-PP) were employed [22]. Calculations were performed using the Perdew Wang (PW-91) form of the exchange and correlation functional [23] for thermodynamics and kinetics of C_2H_2 hydrogenation over all surfaces considered.

For the majority of the calculations, the system is modeled as a periodic 4×4 unit cell of a 5 layers thick Pd(1 1 1) slab in which the three uppermost metal layers were allowed to relax and approximately five layers of vacuum were used to separate the slabs. The Brillouin zone is sampled with a uniform $3 \times 3 \times 1$ k-point grid (Monkhorst-Pack) as determined by convergence tests [24]. In addition, some calculations were performed using a (2×2) unit cell with a $7 \times 7 \times 1$ k-point grid. In general the structures' geometries were optimized within a convergence tolerance of 10^{-3} eV. Further details of the models will be discussed below.

Reaction paths and barriers are determined using the Climbing Nudged Elastic Band (NEB) method [25]. In the NEB method a reaction coordinate relating the initial and final states are defined and a set of intermediate states are distributed along the reaction path. Each intermediate state is fully relaxed in the hyperspace perpendicular to the reaction coordinate. Vibrational frequencies were computed for the initial, transition and final states, where the substrate is frozen, but adsorbates are allowed to vibrate in any direction. If the molecule is in a true transition state it should have only one imaginary frequency associated with the bond formation/cleavage event.

3. Results and discussion

3.1. Diffusion of H and C

Before examining the influence of subsurface H and C on the hydrogenation of C_2H_2, it is prudent to assess the energetics of the adsorption and diffusion of H and C atoms both on the surface and into the subsurface of Pd(1 1 1) (listed in Table 1). Hydrogen atoms prefer to be adsorbed in the 3-fold hollow fcc site on Pd(1 1 1). As the coverage of hydrogen is increased from 0.25 ML to 1 ML, the adsorption energy of hydrogen decreases slightly from −0.52 eV to −0.48 eV per hydrogen atom (referenced to gas phase H_2). Hydrogen prefers to remain on the surface as sub-surface hydrogen (the hydrogen atoms are placed in octahedral sites in the layer immediately below the surface) is less favorable by 0.35 eV per H atom at a 1 ML coverage on Pd(1 1 1) (but still exothermic with respect to gas phase hydrogen). In agreement with previous calculations, we have found that sub-surface hydrogen prefers to be in the octahedral site as we find hydrogen in the tetrahedral site to be 0.03 eV higher in energy [3]. If the diffusion barrier of hydrogen on the surface is estimated by examining a path between neighboring lowest energy sites, hydrogen must be very mobile on the Pd(1 1 1) surface at any temperature as the barrier is only 0.15 eV. In addition, the barrier of H diffusion from the surface (fcc site) to the sub-surface (octahedral) is low (0.38 eV) as well, implying that the reverse barrier to bring hydrogen back to the surface is essentially non-existent. Sautet and co-workers. report an identical barrier and reaction enthalpy for placement of hydrogen in the sub-surface tetrahedral site [12]. In addition they note that further

Table 1
Adsorption energies for surface H and C on Pd(1 1 1) and modified Pd(1 1 1) surfaces with subsurface H, C and Ag for 0.25 ML coverage. All energies in eV.

	PdΔH	PdHΔH	$PdC_{0.25}\Delta$H	Pd/Ag/PdAg ΔH
Surface H	−0.52	−0.34	−0.41	−0.60
Subsurface H	−0.17	0.22	−0.03	0.45
Surface C	−6.71	−6.07	−6.15	−6.40
Subsurface C	−7.32	−5.48	−6.19	−5.63

penetration into the second subsurface layer requires mounting a barrier of additional 0.20 eV (or 0.58 eV total). We find that for any hydrogen coverage up to 1.0 ML, surface hydrogen is always preferred over sub-surface hydrogen. However, if the entire surface layer is covered with hydrogen, the presence of hydrogen in the first sub-surface layer is still exothermic with respect to gas phase hydrogen (−0.14 eV/per atom). This implies that once the first layer is filled, hydrogen will easily move to, and remain in, the sub-surface. Our analysis does not include the additional entropic driving force which will also favor sub-surface hydrogen (although it should be noted entropic effects will also favor hydrogen desorption as well).

The picture for C is somewhat different. Like hydrogen, carbon atoms prefer to adsorb into 3-fold hollow fcc sites on Pd(1 1 1). However, C atoms adsorb much more strongly (−4.76 eV referenced to a gas phase C atom at a 1 ML coverage) to the Pd(1 1 1) surface and diffusion of C atoms on the surface requires surmounting a barrier of 0.81 eV. Using a simple analysis by which a generic pre-exponential factor of 10^{13} s^{-1} is assumed with an Arrhenius construction of the rate, diffusion will not be rapid under C_2H_2 hydrogenation conditions (T = 350 K). In further contrast to hydrogen, carbon prefers to be in the sub-surface (also the octahedral site) by 0.76 eV per C atom as opposed to residing on the surface. Furthermore, C diffusion from the surface to the subsurface is considerably more difficult as we find a barrier of 1.25 eV. This barrier is slightly higher than that found by Lopez and co-workers although they examined a more open step configuration [19]. As the concentration of C in the sub-surface increases to 0.25 ML, the barrier to diffusion sharply increases to 1.70 eV, implying that the amount of C in the sub-surface achievable at C_2H_2 hydrogenation temperatures may reach a maximum at low concentration. Therefore, the amount of carbon present in the sub-surface (∼15%) observed by Ziemecki et al. may have been kinetically rather than thermodynamically limited. However, it is clear that the carbon concentration in the bulk will eventually reach a maximum due to thermodynamic considerations as the move of carbon from the surface to the sub-surface is thermoneutral when 0.5 ML C exists in both regions. Our calculation of stoichiometric PdC reveals that it has a positive formation energy of 2.86 eV/molecular unit (about 300 kJ/mol), indicating that its formation is unfavorable. Ziemecki et al. also found in their study of the hydrogen/carbon/palladium system that the presence of carbon prevented formation of the β-hydride phase [16], in agreement with the work of Teschner et al. [11]. To this end, we also examined the effect of carbon on the diffusion of hydrogen into the sub-surface and found that the diffusion barrier climbs to 0.47 eV when C is present in the subsurface (again in agreement with Sautet and co-workers [12]).

Finally, we should note that particle size effects may exist for the incorporation of both hydrogen and carbon into the Pd sub-surface. EXAFS measurements from McCaulley indicate that the nanosized Pd particles will incorporate less hydrogen and carbon than bulk Pd resulting in phases of $PdH_{0.44}$ and $PdC_{0.06}$ [26]. However, this estimation is made based upon the assumption that there is a direct link between the lattice parameter derived from XAFS and the amount of hydrogen or carbon incorporated. This assumption may not be valid on the nanoscale as new structures which do not form as bulk phases are possible.

3.2. C_2H_2 hydrogenation on Pd(1 1 1)

We have begun our examination of C_2H_2 hydrogenation with a calculation of the adsorption energies of all relevant species on the surface: acetylene, vinyl, ethylene, ethyl and ethane (Adsorption energies of relevant gas phase species are listed in Table 2). In agreement with the previous calculations of Sheth et al. we find that the adsorption energy of C_2H_2 on Pd(1 1 1) is −1.85 eV while

Table 2
Adsorption energies for reactive species in C_2H_2 hydrogenation over Pd(1 1 1) and modified Pd(1 1 1) surfaces with subsurface H, C and Ag for 0.25 ML coverage. All energies in eV.

	PdΔH	PdHΔH	$PdC_{0.25}$ΔH	Pd/Ag/PdAg ΔH
H_2(as 2 H)	−0.52	−0.34	−0.41	−0.60
C_2H_2	−1.85	−1.39	−1.54	−1.72
C_2H_4	−0.83	−0.67	−0.68	−0.75

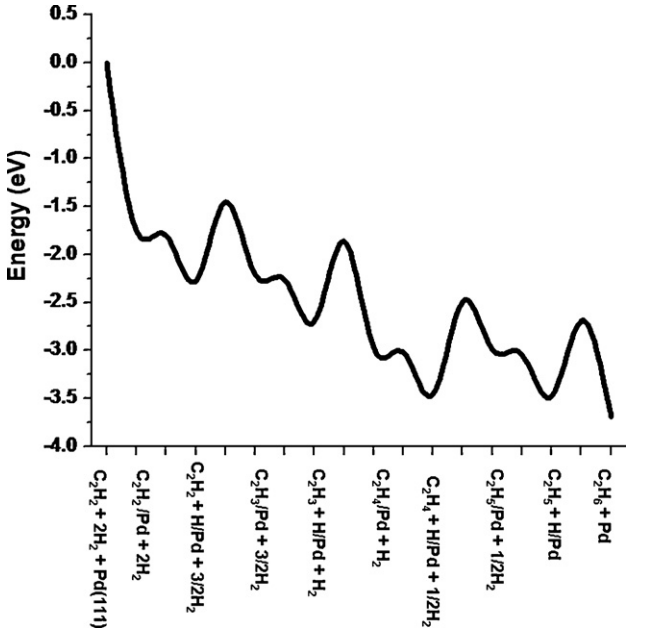

Fig. 1. Potential energy surface for the hydrogenation of C_2H_2 over Pd(1 1 1). Hydrogen dissociation is depicted with a nominal barrier of 0.05 eV for clarity (although this is found to be barrierless in all cases).

C_2H_4 adsorbs with −0.84 eV and C_2H_6 is essentially non-adsorbing (0.08 eV) [3]. In Fig. 1, the complete potential energy surface of C_2H_2 hydrogenation is depicted. First, hydrogen is adsorbed to the Pd(1 1 1) surface, followed by C_2H_2. Then in the first hydrogenation step, C_2H_2 sitting in its most favorable adsorption site (μ-bridge) is hydrogenated to form C_2H_3 (surface vinyl) as shown in Fig. 2(a–c) [27]. This reaction is essentially thermoneutral with a barrier of 0.83 eV. It should be mentioned that acetylene can isomerize to vinylidene (CCH_2) on Pd(1 1 1) and that CCH_2 is favored by 0.11 eV. Similarly vinyl can isomerize to form ethylidyne (CCH_3) on the Pd(1 1 1) surface with ethylidyne favored over vinyl by 0.37 eV. However, as Dumesic and co-workers have calculated, ethylidyne, once formed, is not a precursor to the alkene and is not easily hydrogenated [28].

The reaction proceeds with a second hydrogenation to produce the desired alkene product as shown in Fig. 1(d–f). Once again, a barrier of 0.84 eV must be overcome, but this step is slightly exothermic (−0.27 eV). In slight contrast to the previous work of Sheth et al., which found the second hydrogenation step to have the highest barrier, our calculation shows the third hydrogenation step (shown in Fig. 1(g–i)) to have the highest barrier at 0.97 eV as C_2H_4 reacts to form C_2H_5 [3]. However, this difference may be due to coverage effects. In our calculation, we are examining the reaction at a very low coverage (1/16 ML C_2H_2). Similarly, in Neurock et al.'s calculation at a C_2H_4 coverage of 0.25 ML, the barrier is found to be 0.87 eV. However, these barriers as well as the preferred adsorption site for the reactants are highly sensitive to coverage effects once surface adsorbates are close enough to interact with each other. At high C_2H_4 coverage (0.60 ML),

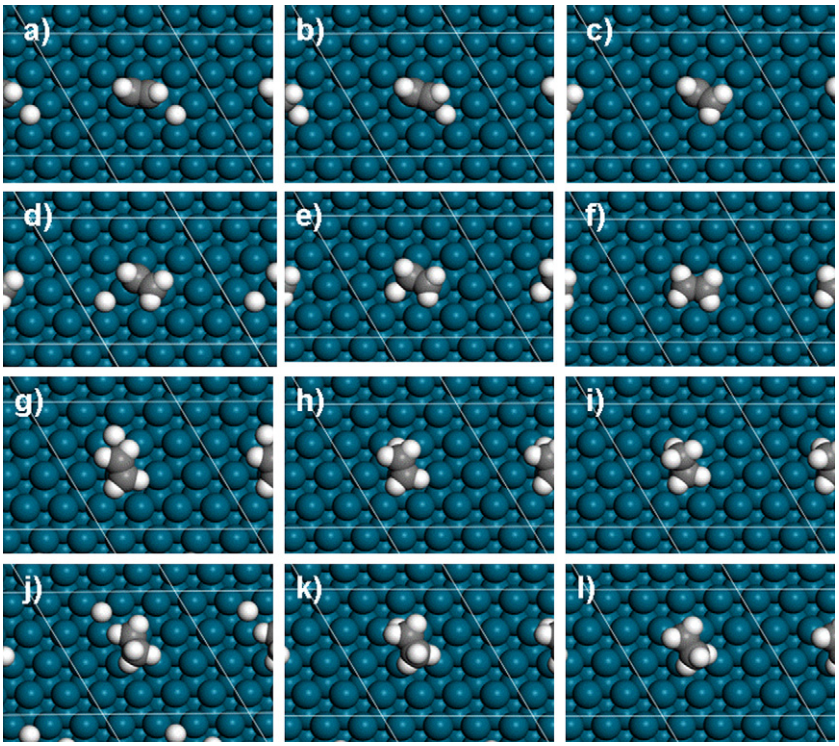

Fig. 2. Geometries for Initial States, Transition States and Final States for the reaction scheme depicted in Fig. 1. (a) Initial state C_2H_2 hydrogenation. (b) Transition state for C_2H_2 hydrogenation. (c) Final state for C_2H_2 hydrogenation. (d) Initial state C_2H_3 hydrogenation. (e) Transition state for C_2H_3 hydrogenation. (f) Final state for C_2H_3 hydrogenation. (g) Initial state C_2H_4 hydrogenation. (h) Transition state for C_2H_4 hydrogenation. (i) Final state for C_2H_4 hydrogenation. (j) Initial state C_2H_5 hydrogenation. (k) Transition state for C_2H_5 hydrogenation. (l) Final state for C_2H_6 hydrogenation.

Table 3
Reaction Enthalpies and Activation Barriers for the hydrogenation of C_2H_2 over Pd(1 1 1) and modified Pd(1 1 1) surfaces with subsurface H, C and Ag for 0.0625 ML C_2H_2 coverage. All energies in eV.

	PdΔH	E_{act}	PdHΔH	E_{act}	$PdC_{0.25}\Delta H$	E_{act}	Pd/Ag/PdAgΔH	E_{act}
$C_2H_2 \rightarrow C_2H_3$	0.07	0.83	−0.08	0.64	−0.03	0.64	0.19	0.79
$C_2H_3 \rightarrow C_2H_4$	−0.27	0.84	−0.68	0.65	−0.68	0.54	−0.34	0.93
$C_2H_4 \rightarrow C_2H_5$	0.46	0.97	0.28	0.73	0.07	0.96	0.45	1.17
$C_2H_5 \rightarrow C_2H_6$	−0.21	0.80	−0.52	0.51	−0.57	0.51	−0.21	0.68

where C_2H_4 prefers to be in the π-bonded state (both C atoms in C_2H_4 coordinated to a single Pd atom), the barrier plummets to 0.36 eV. The hydrogenation of C_2H_4 is somewhat endothermic (0.46 eV referenced to di-σ bonded C_2H_4). Finally, C_2H_5 is hydrogenated to C_2H_6 which is weakly bound as shown in Fig. 1(j–l). This step is also exothermic (−0.20 eV) and possesses a barrier of 0.80 eV. It should be mentioned that the adsorption of hydrogen is found to be a barrierless process in all cases. However, we include a nominal barrier of 0.05 eV in the potential energy surface to help guide the reader's eye. A complete summary of all barriers and reaction enthalpies is presented in Table 3 (all energies in eV).

3.3. C_2H_2 hydrogenation on PdH(1 1 1)

Our model for examining the effect of subsurface hydrogen is created by placing a hydrogen atom into every octahedral site in the first sub-surface layer. In effect, our model is similar to the Pd terminated simple cubic β-PdH(1 1 1) model which has been previously examined by King and co-workers using DFT calculations [29]. The presence of subsurface hydrogen results in a weakening of C_2H_2 adsorption to −1.39 eV and of C_2H_4 to −0.67 eV. Each hydrogenation step is more enthalpically favorable than the analogous step on Pd(1 1 1). Since the adsorption of both H and C_2H_2 are weaker on PdH(1 1 1) as compared to Pd(1 1 1), the individual reaction steps must be more exothermic (the overall reaction must have the same reaction enthalpy regardless of the surface involved). As depicted in Fig. 3, the effect on the kinetics is dramatic. The barriers for each hydrogenation step are lower than those on Pd(1 1 1). This implies that reactivity is improved by the presence of sub-surface hydrogen but that the selectivity will decrease as the barrier to C_2H_4 hydrogenation is only 0.73 eV. Interestingly, our result is somewhat in contrast to the result of Sheth et al. who found essentially no change in either the barrier or in the reaction enthalpy when a hydrogen atom is placed in the tetrahedral site at 0.25 ML coverage in the sub-surface region [3]. However, previous calculations used a much lower concentration of hydrogen in the sub-surface which is considerably less than the β-PdH which has been observed experimentally [1].

3.4. C_2H_2 hydrogenation on $PdC_{0.25}$(1 1 1)

Based upon our analysis of C diffusion into the subsurface, it was decided to model the palladium carbide phase by placing one carbon atom into every fourth octahedral site in the first subsurface layer. As indicated above, this concentration is about double the experimentally found value. We have chosen this model to provide us with relevant information regarding trends in the C_2H_2 hydrogenation reaction when compared to the Pd(1 1 1) and PdH(1 1 1) systems. Calculations performed with higher subsurface carbon

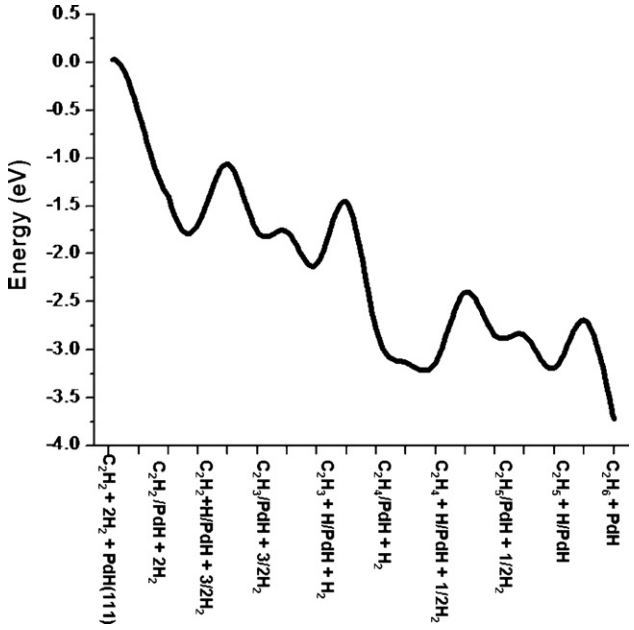

Fig. 3. Potential energy surface for the hydrogenation of C_2H_2 over Pd(1 1 1) with subsurface H.

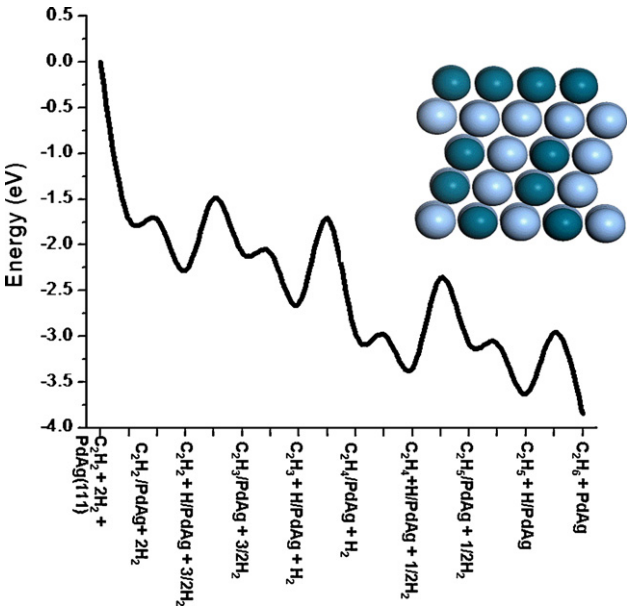

Fig. 5. Potential energy surface for the hydrogenation of C_2H_2 over Pd(1 1 1) with subsurface Ag. A depiction of the side view of the surface is shown in the upper right.

concentrations or with a PdC(1 0 0) slab, revealed that those systems were unstable and did not serve as reliable models for the catalytic surface. The adsorption of both C_2H_2 (−1.54 eV) and C_2H_4 (−0.68 eV) are weakened by the presence of C in the subsurface as has been observed by Lopez and co-workers in their model for palladium carbide [19]. The hydrogenation reactions are found to be either thermoneutral (first and third steps) or highly exothermic (second and fourth steps). As depicted in Fig. 4, however, the kinetics of C_2H_2 hydrogenation with subsurface C is in contrast with sub-surface H. For $PdC_{0.25}$ (1 1 1), just as for PdH(1 1 1), the second (0.54 eV) and the fourth (0.51 eV) barriers for hydrogenation are lower than Pd(1 1 1) to create C_2H_4 and C_2H_6 respectively. However, the highest barrier is observed for the third hydrogenation (0.96 eV) and is very similar to that of Pd(1 1 1) implying the reactivity of this catalyst may be higher than Pd(1 1 1), but may also be more selective at low temperature.

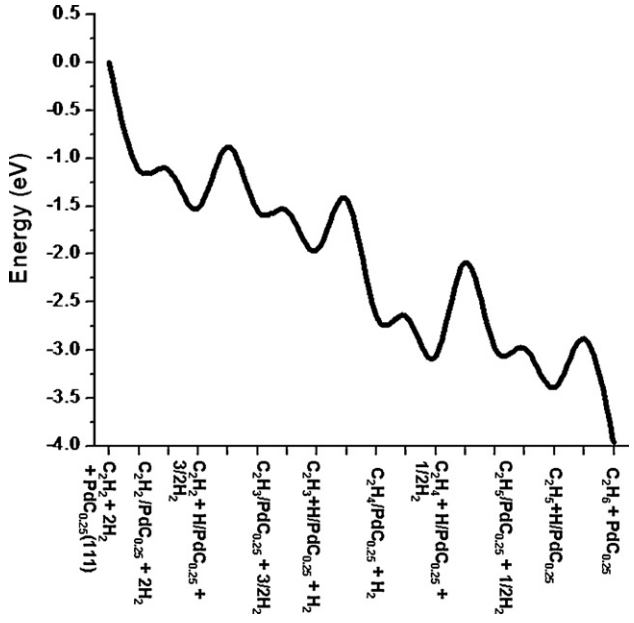

Fig. 4. Potential energy surface for the hydrogenation of C_2H_2 over Pd(1 1 1) with 0.25 ML subsurface C.

3.5. C_2H_2 hydrogenation on PdAg(1 1 1)

As the presence of Ag is well known to improve selectivity [10,30], we have also explored the effect of alloying. We have built our PdAg system as a bulk with 50% Pd and 50% Ag. We have then examined the energetics of the surface with three different models. In the first model, the top two layers have the same composition as the "bulk" (bottom 3 layers of our slab). The unit cell is now expanded by 2% to account for the fact that the lattice constant of Ag is 4% larger than Pd. In this case, we find that adsorbates such as C_2H_2 and C_2H_4 greatly prefer to associate themselves with surface Pd, in agreement with Sheth et al. [2] For example, C_2H_4 will adsorb in a di-σ configuration above two Pd atoms with a similar bond strength as to Pd(1 1 1) (−0.80 eV). However, the adsorption energy decreases to −0.08 eV if C_2H_4 is absorbed above two Ag atoms. Similarly, the C_2H_2 adsorption involves bonds to fcc sites on the surface. Therefore at least one Ag atom must participate in the bonding and the resulting adsorption energy is decreased to −1.06 eV.

The PdAg system may experience surface segregation whereby the surface is enriched in one element. Experimental studies on the surface composition under reaction conditions have not come to agreement on the favored surface termination [10,30]. Therefore, we have tried various models, beginning with a model for the PdAg alloy surface whereby a Pd monolayer sits above a 100% Ag layer (as depicted in the inset of Fig. 5). Conversely, a third surface to be considered would be the opposite, with a Ag monolayer surface above a 100% Pd second layer. Since Ag(1 1 1) has a lower surface energy than Pd(1 1 1), the Ag terminated PdAg model is lower in energy than either of the other models and would be expected in an ultra-high vacuum environment (as observed by Khan et al. [31]). However, our calculations show that the Ag terminated surface does not adsorb C_2H_2 at all and in the presence of adsorbates the Ag terminated surface is much higher in energy than the Pd terminated surface (this result was previously confirmed by Gonzalez et al. [9]). Therefore, we will not discuss the PdAg terminated or Ag terminated models further.

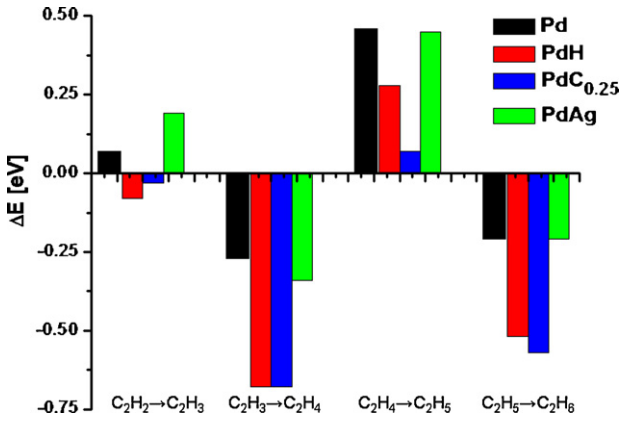

Fig. 6. Reaction enthalpies for the hydrogenation of C_2H_2 over Pd(1 1 1) and modified Pd(1 1 1) surfaces.

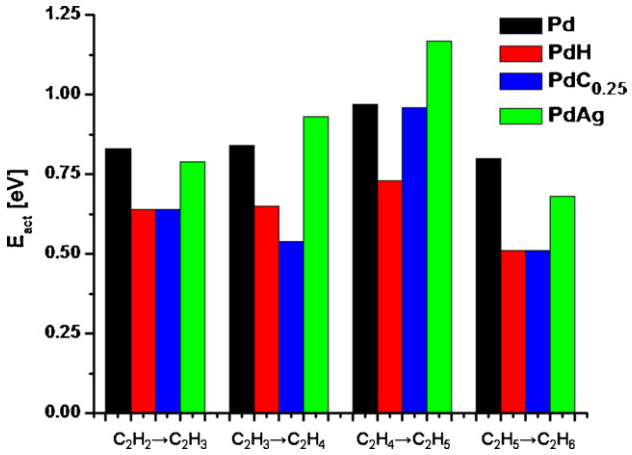

Fig. 7. Reaction enthalpies for the hydrogenation of C_2H_2 over Pd(1 1 1) and modified Pd(1 1 1) surfaces.

Another effect of the presence of Ag in the sub-surface is that both the inclusion of H and C are hindered. As shown in Table 1, both H and C have a strong preference to be associated with Pd and so the presence of Ag in the sub-surface will prevent either H or C diffusion into the bulk and therefore hinder hydride or carbide formation. Of course, we have placed Ag in the first sub-surface layer and therefore have not considered cases where Pd forms a multi-layer shell above Ag.

On the Pd terminated surface, adsorption of both C_2H_2 (−1.72 eV) and C_2H_4 (−0.75 eV) are remarkably similar to their adsorption on Pd(1 1 1). However, a view of the potential energy surface of C_2H_2 hydrogenation, shown in Fig. 5, reveals some important differences. Although the barriers for the first two hydrogenation steps are similar to Pd(1 1 1), the barrier to C_2H_4 hydrogenation has now risen to 1.17 eV which is considerably higher than on Pd(1 1 1) (0.97 eV) (which appears to be in agreement with Nørskov and co-workers [7] although their calculation takes place on a homogeneous alloy surface). This implies that with similar activity, the selectivity of this catalyst should be greatly increased. It is not entirely understood why the barrier to C_2H_4 hydrogenation is higher, but it seems to stem from the stronger bonding of H to this surface.

Nørskov and co-workers have suggested that the primary effect of Ag is to weaken the binding of C_2H_2 and C_2H_4 to the surface in an analogous manner to sub-surface C [8]. While this is true when Ag is present in the surface layer, this does not hold for cases in which Ag has segregated to the sub-surface. This fact may explain why commercial catalysts are often greatly enriched in Ag as Pd segregates to the surface under reaction conditions, a large excess of Ag is required to maintain some Ag at the surface to keep the adsorption energy of C_2H_2 and C_2H_4 low. It should also be mentioned that the presence of Ag in the subsurface also restricts C diffusion into the bulk. While we could not locate an activation barrier to diffusion from the surface to the first subsurface layer, the process is 0.77 eV uphill.

4. Conclusions

As can be seen in Fig. 6, both subsurface hydrogen and carbon contribute to weakening the adsorption of C_2H_2 and C_2H_4 on the surface and result in less exothermic hydrogenation reactions. While subsurface hydrogen leads to extremely low barriers for hydrogenation of hydrocarbons as shown in Fig. 7, the effect of the presence of sub-surface C leads to lower barriers for the hydrogenation of C_2H_2, but not C_2H_4. This suggests subsurface C should improve catalyst selectivity. Pd pseudomorphic monolayer catalysts (above a Ag layer with PdAg bulk) should also improve selectivity as the hydrogenation of C_2H_4 is more difficult over this surface as compared to Pd(1 1 1) due to the stronger adsorption of hydrogen. The presence of Ag should also prevent hydride formation and carbon diffusion into the bulk. Therefore both subsurface C and Ag should lead to improved selectivity without a simultaneous loss in activity.

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