



Short communication

The role of Ga in the acetylene adsorption on PdGa intermetallic

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ABSTRACT

We performed density functional calculation of the acetylene hydrogenation reaction on the PdGa(110) surface. The reaction $C_2H_2 + H_2 \rightarrow C_2H_4$ is modeled and understood in terms of chemical bonding change. The evolution of electronic structure and electron density plot also shed more light on the role of Pd, Ga and C_2H_2 during the hydrogenation reactions. This new way of looking at a particular chemical reaction includes the changes in bond order in the different reaction steps. As mentioned before the role of Ga is revealed as a part of the active site and not a single spacer.

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1. Introduction

Catalytic reactions are very important from academic, technological and economic point of view [1–3]. Catalytic activity and selectivity are the main problems to be understood [2,4–7]. For example, the selective hydrogenation of $C\equiv C$ to $C=C$ bonds is an important step in several chemical reactions including polymerization [8]. During the synthesis of polyethylene, traces of acetylene make the obtained polymer not valuable. Acetylene must be removed or reduced to ppm range [9–15]. The most effective catalysts for this process are based on intermetallic compounds (IMCs). This kind of catalyst can be constructed with preselected structural characteristics; this properties of the material permits to control the separation between the active sites and hence the activity and selectivity of the catalyst [12,16–19]. Covalent bonding in these IMCs provides long-term stability [20]. By contrast conventional Pd catalysts present limited selectivity on hydrogenation process due to the ensemble of active sites. Among these materials, one of the most promising is PdGa [11,15,20,21].

Single crystal growth of PdGa was reported for the first time by Gille et al [22]. Armbrüster et al obtained a large PdGa single crystal by the Czochralski method and they also reported the refined crystal structure of (1:1) PdGa [23]. IMC can also be formed *in-situ* due to strong metal support interaction or by reaction between differ-

ent metallic species [12]. In these cases it is not easy to determine which is the active component. The main difficulty in developing an atomistic scenario for the reactions catalyzed by complex IMCs is the insufficient knowledge of their surface properties [24–28].

The {210} surfaces can be represented by a triangle-rectangle tiling where the active centers consist of periodically distributed triangular arrangements of two Ga and one Pd atom promoting a high activity and selectivity; the possible terminations of the 3-fold surface show very different catalytic activity and selectivity. The terminations are Ga-rich, Pd-rich and a mixed Pd/Ga surfaces. The last two are catalytically active; however, the Ga-rich surfaces are inactive [26].

The PdGa(111) and $(\bar{1}\bar{1}\bar{1})$ surfaces have several terminations which can be Ga-rich or Pd-rich [24]. The most stables are PdGa:B($\bar{1}\bar{1}\bar{1}$) Pd1 and PdGa:B(111)Pd3 surfaces terminations where, one consisting of single palladium atoms (Pd1) and the second of palladium trimmers (Pd3). Using DFT calculations and experimental methods Prinz et al observe strong site isolation effects on both PdGa surfaces, which are most clearly expressed on the PdGa:B($\bar{1}\bar{1}\bar{1}$) Pd1 surface [25].

Recently, Kumar and Ghosh investigate the stability of the (100) and (110) surfaces possible terminations [28]. Several theoretical studies are made using small molecules -like CO, H_2 and atomic H- for testing catalytic behavior on PdGa intermetallic surfaces and clusters [29–35].

Krajci and Hafner found for PdGa(210), that triangular arrangements formed by two Ga atoms and one Pd atom are the more active sites for the hydrogenation of acetylene to ethylene [26].

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For the (111) and $(\bar{1}\bar{1}\bar{1})$ PdGa surfaces the calculations show that not all the possible termination are active for the hydrogenation process. The more actives ones are that which expose Pd atoms in their outermost layer. The theoretical studies show that highly corrugated surfaces with Pd atoms in the outmost layer can hydrogenate adsorbed acetylene molecules easily. But simultaneously their high reactivity with respect to both molecular and atomic hydrogen complicates dissociation and diffusion processes affecting the selectivity. The possible threefold surface terminations with isolated Pd₃ triplets and Ga atoms in one-half of the hollows between the Pd₃ triplets exhibits both higher catalytic activity and selectivity [36].

Prinz et al also found that all considered molecules are adsorbed on the topmost Pd surface atoms [37]. The different Pd atom ensembles have weak influence in the configuration adsorption of C₂H₄ and H₂, while the effect on the adsorption energy and configuration of C₂H₂ is very important [37].

Krajčí and Hafner studied the different terminations of Pd₂Ga(010) surface and found that when the number of Ga atoms increases in the surrounding of Pd active sites, the catalyst increase its selectivity [38]. They found that for the hydrogenation process the active centers are triangular configurations (formed by one Pd and two Ga atoms), while ethylene is only weakly π -bonded on top of the Pd atom [38]. For the (110) surface Bechthold et al found that break the C–C bond is unfavorable and the hydrogenation process is 2.27 eV more stable than C₂H₂+H₂ in the gas phase [39]. An interesting review of chemical reactivity on PdGa has been recently published [40].

All previous studies are mainly focused in the energy pathways for the hydrogenation process. For a better understanding of the role of Ga atom in this process an electronic and chemical bonding study could be useful.

2. Surface model and computational method

The PdGa(110) plane was represented by a super-cell. We use a seven-layer slab separated in the [110]-direction by vacuum regions in order to achieve the best compromise between computational time and accuracy for our model. In this surface, each “layer” is formed by three “sub-layers”, presenting atoms above and below. The thickness of the vacuum region was 15 Å in order to avoid the interaction of C₂H_x molecules on the surfaces. The interlayer spacing in this model is 1.745 Å. The thickness of the PdGa(110) slab should be such that it approximates to the electronic structure of 3D bulk PdGa in the innermost layer. From the two possible terminated surfaces, Pd or Ga, we analyzed only the Pd terminated because it presents better catalytic properties.

Simulations were performed using spin polarized DFT calculations implemented through the VASP code [41–43]. We used

semi-local exchange–correlation functional in the generalized gradient approximation (GGA) proposed by Perdew et al [44]. The projector augmented wave scheme was used to describe the inner cores [45]. An energy cutoff of 700 eV was used for all calculations, which converges total energy to ~ 1 meV/atom and 0.001 Å for the primitive bulk cell. We used a Monkhorst-Pack k-point mesh of $7 \times 7 \times 1$ for the Brillouin-Zone integration [46]. Optimization geometry was terminated when the energy difference was lower than 10^{-4} eV and the force on each atom was less than 0.02 eV/Å. Bader analysis is used to calculate electronic charges on atoms before and after molecule adsorption [47]. An equilibrium lattice constant of 4.899 Å is used, as we obtained with a converged mesh of $7 \times 7 \times 7$. This lattice constant agrees well with the experimental of 4.909 Å [48–50].

The transition state (TS) is obtained following three steps: First, we use nudged elastic band method to found the most probably one [51,52]; secondly, using a quasi-Newton algorithm - to make for less 0.05 eV/atom - the atomic structures are relaxed; finally, for confirmation of TS a frequency analysis is performed. Then, include the zero point energy (ZPE) into the activation energy. The adsorption energy is calculated using the following equation:

$$\Delta E = E_{Total}(C_2H_x/PdGa(110)) - E_{Total}(PdGa(110)) - E_{Total}(C_2H_x)(1)$$

Here the first term on the right-hand side is the total energy of the super cell plus one C₂H_x molecule; the second term is the total energy of the intermetallic super-cell; and the third term is the C₂H_x molecule total energy (with x=2, 3 and 4). The last one is calculated by placing C₂H_x in a 20 Å cubic box and carrying out a Γ -point calculation. The activation energy E_a is calculated following the equation:

$$E_a = E_{TS} - E_{IS} \quad (2)$$

where E_{TS} and E_{IS} are the energy of the transition state and initial state (IS), respectively.

In order to understand C₂H_x-PdGa interactions and bonding we used the concepts of Density of States (DOS) [53,54] and Bond Order (BO) as implemented in the DDEC6 method [55–57].

3. Results and discussion

3.1. Geometric and energetic considerations

Fig. 1 shows the geometric configurations for each reaction step and TS. It can be seen that when the C₂H₂ is adsorbed, the H atoms are pushed away from the surface forming an angle of approximately 121° with the C–C axis indicating a $sp \rightarrow sp^2$ hybridization; a small tilt angle with the surface is also detected (4.1°, see Fig. 1(a)). The acetylene will be hydrogenated passing by the TS1 with a C–H bond length of 1.72 Å. After this hydrogenation the C–H bond rotates around the C–C axis, while the C atom moves towards the

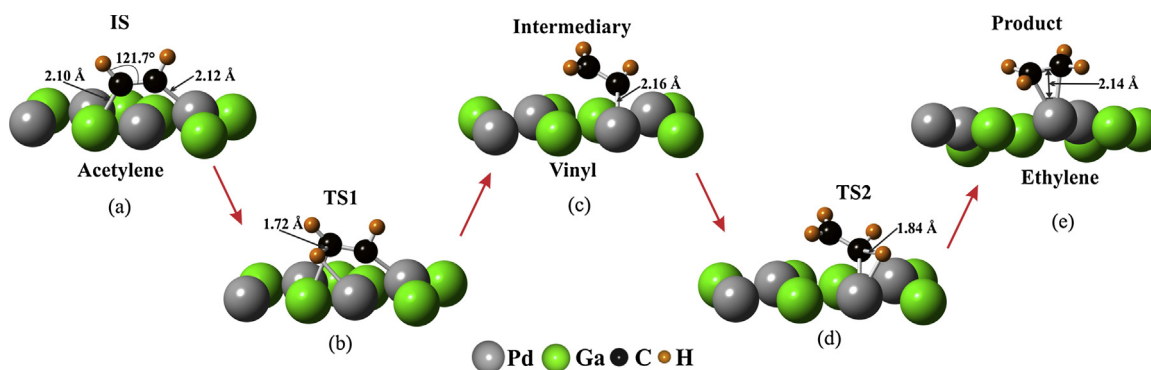


Fig. 1. Schematic view of the geometric configurations of the steps of acetylene hydrogenation (including TS).

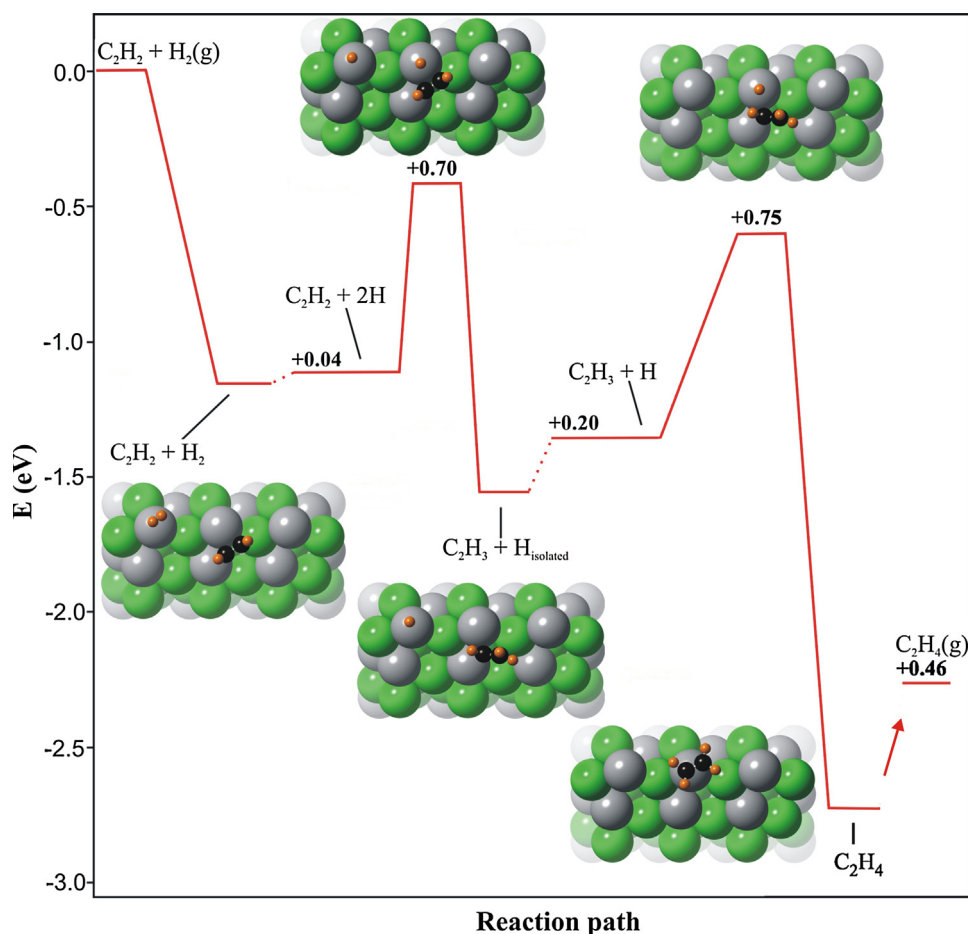


Fig. 2. Potential energy profile for the reaction steps for the hydrogenation of acetylene to ethylene. The energies are given relative to the $(C_2H_2+H_2)$ in the gas phase. The insert figures correspond to the top view of the atomistic scenario of the hydrogenation reaction steps.

Pd (see Fig. 1(c)). The vinyl will continue hydrogenation, through TS2 with a C–H bond length of 1.84 Å, to produce C_2H_4 . In this step the ethylene molecule is rotated on a plane almost parallel to the surface interacting with the Pd of the outermost layer (see Fig. 1(e)).

Regarding the energy pathway, in the PdGa intermetallic compound the (210) and the (110) surfaces are isomorphic, so we decided to follow the same reaction model as previously reported by Krajčí and Hafner [26]. Fig. 2 shows the energy profile for the acetylene hydrogenation process based on the NEB method. We can see that in the first hydrogenation step the activation barrier is 0.70 eV and the final configuration is more stable than the $C_2H_2+H_2$ co-adsorbed state. The migration barrier for the approach of a second H to the vinyl molecule is 0.20 eV. The activation barrier for the last hydrogenation is 0.75 eV and the final C_2H_4 adsorbed state is 2.73 eV more stable than the $C_2H_2(g)+H_2(g)$ with a desorption energy of only 0.46 eV -relative to $C_2H_4(g)$. The overall process is strongly exothermic (2.27 eV). For simplicity, the diffusion path of hydrogen atom are not shown explicitly, there are indicated by dashed lines in Fig. 2.

Further hydrogenation is energetically more expensive than the desorption process. Our calculated activation energy for the $C_2H_4 \rightarrow C_2H_5$ process is 0.61 eV. This result is in good agreement with that reported by Krajčí and Hafner for the PdGa(210) surface [26].

3.2. Electronic structure

Considering the total density of states (TDOS) after C_2H_2 adsorption, two narrow peaks appear at -10 and -15 eV that come from

the interaction with the acetylene molecule (see Fig. 3a and b). Also, a 3 eV stabilization for the adsorbate is found (compare the red dashed and black filled curves in Fig. 3b). After the first hydrogenation the formed vinyl (C_2H_3) do not present further stabilization (see Fig. 3d). When the second hydrogenation takes place, the ethylene peaks at the TDOS become more stabilized (it locates below -15 and -10 eV, see Fig. 3e). The intensity of the peaks decrease in the case of first and second hydrogenation steps when are compare with the C_2H_2 adsorption (see Fig. 3b, d and f). This reduction is a consequence of the changes in the C atoms hybridizations.

For a better understanding of the adsorbate interaction, we analyzed the projective DOS (PDOS) for the atoms involve in the bonding. The PDOS for Pd1 and Pd2 atoms shown two peaks below the bottom of the d band; these peaks are also present in the Ga1 projection which a much lower intensity (see Fig. 4a–c). These interactions mainly come from the C atoms projection (see Fig. 4d). When the vinyl is formed, the Ga1 atom PDOS shown a small interaction with C atom at -15 eV (see Fig. 4h). This is consistent with the distortion presented by the molecule, which push away the C2 atom from the Ga1 atom (see inserted graphic in Fig. 4f). The Pd atoms remain interacting with the non-hydrogenated carbon atom (C1) (see Figs. 4f and g). In the last step of hydrogenation the formed acetylene molecule interact mainly with the Pd1 atom, while the Pd2 atom PDOS remain almost unaffected (see Fig. 4k and l). It must be noticed that there is no direct Ga–C interaction. However, through Pd very small peaks can be detected at -10 and -15 eV (see Fig. 4m). The change in the strong Pd–Ga covalent bond is the reason for these facts. The C1 atom (from C_2H_4) PDOS show

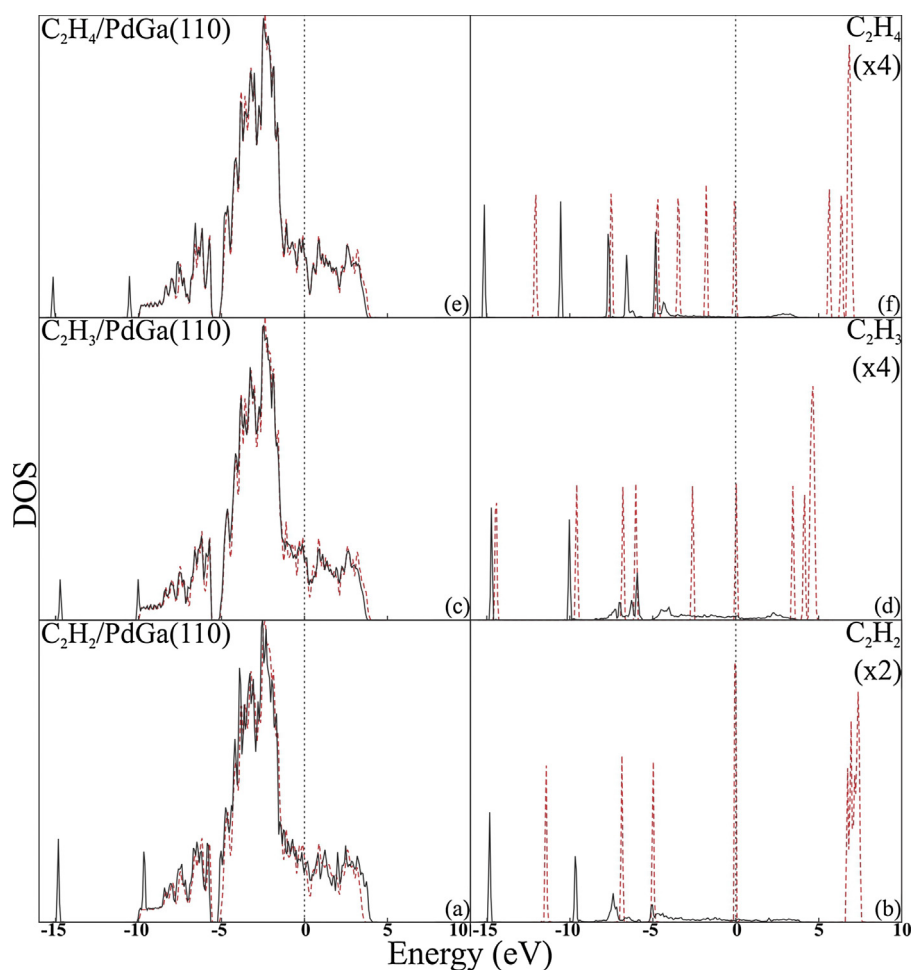


Fig. 3. TDOS curves for PdGa(110) surface and molecules before (red dashed line) and after (black filled line) adsorption. The magnifications are with respect to the PdGa TDOS curves.

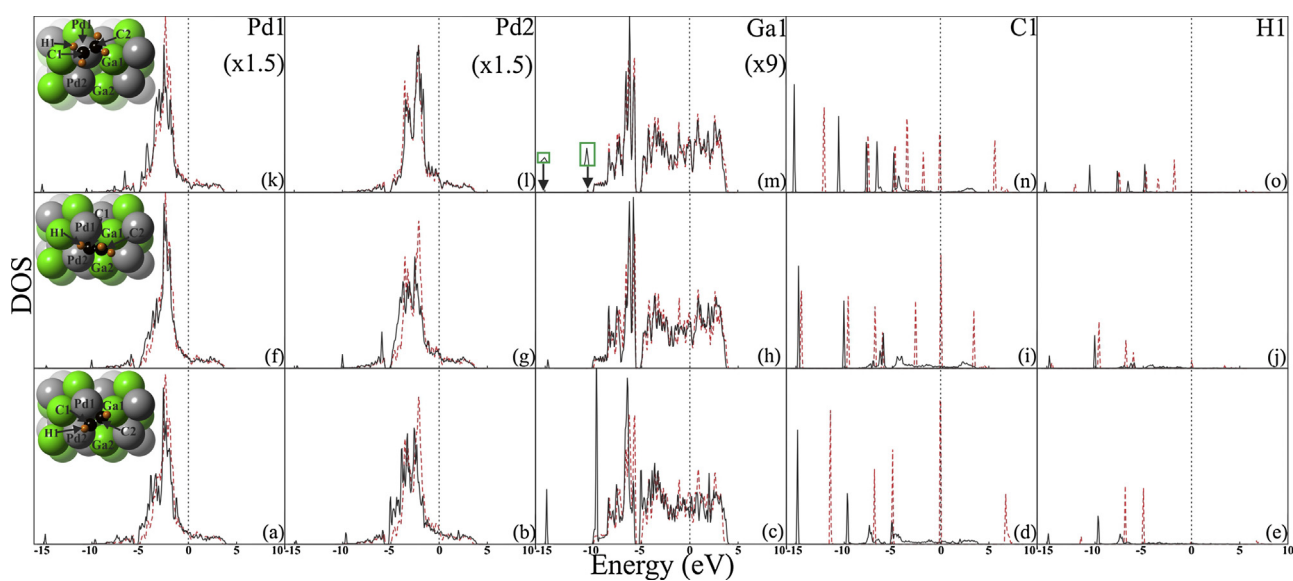


Fig. 4. PDOS curves for PdGa(110) surface before (dashed red line) and after (black filled line): C₂H₂ (a–e); C₂H₃ (f–j); and C₂H₄ (k–o) adsorption. All magnifications are with respect to the C and H PDOS curves. For a better view the peaks in Ga PDOS (m) are more magnified.

a strong stabilization when compare with the gas phase molecule (see Fig. 4n).

The shift in the electronic states towards lower energies is consistent with changes in energy with the reaction path (see Fig. 2).

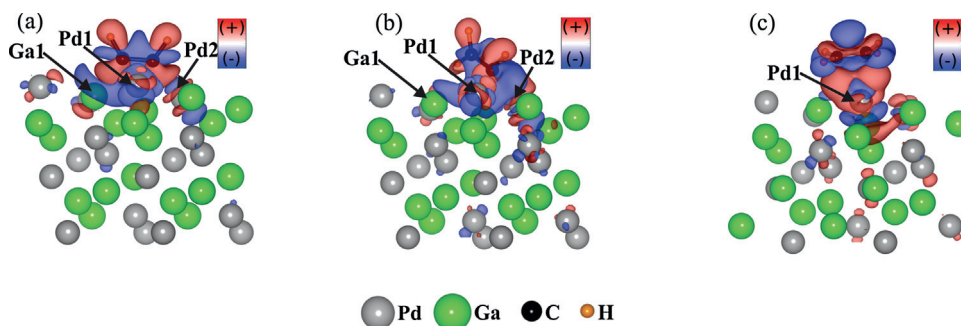


Fig. 5. Electronic charge distribution around atoms after C_2H_x adsorption. The blue (red) color indicates a negative (positive) electronic charge density.

Table 1

Bond order (BO), $\Delta BO\%$ (BO percentage change computing referring to pure system) for PdGa(110) surface after C_2H_x adsorption. The label of atoms is shown in the inserted graphics in Figs. 4.

Bond type	System										
	PdGa	C_2H_2		C_2H_3	C_2H_4	$C_2H_2/PdGa$		$C_2H_3/PdGa$		$C_2H_4/PdGa$	
	BO	BO	BO	BO	BO	$\Delta BO\%$	BO	$\Delta BO\%$	BO	$\Delta BO\%$	$\Delta BO\%$
Pd1-Pd2	0.172	-	-	-	0.147	-14.7	0.149	-13.4	0.213	+23.8	
Pd1-Ga1	0.567	-	-	-	0.263	-53.6	0.333	-41.3	0.358	-36.9	
Pd2-Ga2	0.521	-	-	-	0.429	-17.7	0.416	-20.1	0.502	-3.6	
Ga1-Ga2	0.198	-	-	-	0.132	-33.4	0.140	-29.3	0.169	-14.6	
Pd1-C1	-	-	-	-	0.364	-	0.424	-	0.378	-	
Pd1-C2	-	-	-	-	0.353	-	0.037	-	0.335	-	
Pd2-C1	-	-	-	-	0.730	-	0.739	-	0.005	-	
Ga1-C2	-	-	-	-	0.712	-	0.108	-	0.000	-	
C1-C2	-	2.934	2.431	2.157	1.925	-36.4	1.972	-18.9	1.848	-14.4	
C1-H1	-	0.880	0.921	0.892	0.851	-3.3	0.861	-6.5	0.866	-2.7	

3.3. Charge density plots

Fig. 5 shows the electron density distribution on the PdGa(110) atoms after molecule adsorption, where the blue and red colors indicate a negative and positive electronic charge density respectively. The charge density difference ($\Delta\rho$) isosurface is calculated using the following equation: $\Delta\rho = \rho(\text{molecule}/PdGa(110)) - \rho(PdGa(110)) - \rho(\text{molecule})$. Where $\rho(\text{molecule}/PdGa(110))$ is the charge density of the molecule/PdGa(110) system, $\rho(PdGa(110))$ is the charge density of the relaxed PdGa(110) surface and $\rho(\text{molecule})$ is the charge density of molecule in their final configuration for every step of the hydrogenation process.

From this figure it can be seen that the C_2H_2 molecule interact with two Pd atoms and one Ga atom. In the case of C_2H_3 the main interaction is with two Pd atoms and C_2H_4 species mainly interacts with the outmost Pd atom (Pd1). It can be seen that in the last two steps the Ga atom shown a small interaction with the formed product. This behavior is consistent with the geometric changes showed for each step during the hydrogenation process.

3.4. Chemical bonding changes

The bond order (BO) and the bond order percentage change referred to the corresponding pure system ($\Delta BO\%$), after molecule adsorption on PdGa(110) surface are summarized in Table 1. The BO analysis allows us to follow the changes during the hydrogenation process. After C_2H_2 adsorption all metal-metal BO decrease being the most affected Pd1-Ga1 bond. Pd1, Pd2 and Ga1 develop a bonding interaction with the C atoms. The C-C BO decreases while the C-H is almost unaffected. In the case of C_2H_3 the behavior is similar. Considering C_2H_4 product, Pd1-Pd2 BO increase while Pd-Ga and Ga-Ga show a less decrease in the BO that in the other step of the hydrogenation process. The C-C and C-H bonds also present a less BO decrease. This is consistent with preparation for release the hydrogenated product.

All our results support the idea presented by Krajčí and Hafner [38]. They found that when the number of Ga atoms increases in the surrounding of Pd active sites, the catalyst increase its selectivity on the different terminations of Pd₂Ga(010) surface. These authors also found that the strong molecule binding to Ga atoms, whose properties are strongly modified by the covalent bonding with the transition metal, is responsible for the activation of acetylene and vinyl for hydrogenation. While the weaker binding of ethylene on top of transition metals provides the selectivity [38]. These findings also were reported for the authors in a review of acetylene hydrogenation on PdGa surfaces [40].

4. Conclusions

In the present study we have performed theoretical calculations regarding the hydrogenation of acetylene on PdGa(110) surface. We were able to follow the changes in the electronic structure of intermediary species during hydrogenation showing the consistency for electronic stabilization and reaction path energies. The DOS and charge density plots indicates that Ga interact with the intermediates in the hydrogenation process. The electronic structure projection also reveals the charges in C atom hybridization. The BO analysis shows that metal atoms decrease their bonding for C_2H_2 and C_2H_3 cases and recover BO after C_2H_4 is formed. These finding support the idea that Ga atom cannot only be considered a simple spacer but a participant of the active site. Also show that the electronic and chemical properties of the adsorbates are strongly modified by the covalent bonding between them.

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