

The adsorption and reaction pathway of dehydrogenated ethylene on Ni(111): a theoretical study

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Abstract. Acetylene is an important intermediate product of ethylene decomposition on transition metals. The adsorption of acetylene on the Ni(111) surface is investigated by theoretical calculation, as well as its migration pathway from the aligned bridge site, the favourite adsorption site for ethylene, to the cross-bridge site. Acetylene is preferably adsorbed in the cross-bridge site on Ni(111). The C–C bond length of C₂H₂ is stretched by 20% compared with that of the gas phase, which is in good agreement with the previous SEM PhD results, and the corresponding bond order is much less than that of the gas phase. After studying several reaction pathways of C₂H₂ on Ni(111), we find that acetylene, as the product of dehydrogenated ethylene, will migrate from the aligned bridge site to the cross-bridge site with a very small energy barrier, 0.02 eV. The favourite pathway of the migration is a translation to the nearest cross-bridge site, with a rotation through 30° simultaneously.

1. Introduction

The nature of adsorbate–substrate interactions is one of the primary objectives of theoretical studies of surface structure, particularly of adsorbed molecules on surfaces. Understanding where and how C–H, C–C and H–H bonds are broken, as well as migrations of reaction products on transition metal surfaces, has been the goal of numerous hydrocarbon catalysis and surface science studies. This has been intensively investigated for the interaction of ethylene and a metal surface in recent years [1–10], because ethylene is an important material in industrial manufacturing.

The general picture emerging is that ethylene adsorbs molecularly at low temperature and decomposes between 200 and 230 K, while acetylene adsorbs molecularly and starts to decompose to CH and CH₂ only above 300 K [1, 8–10]. This indicates that dehydrogenation, i.e. C₂H₄ → C₂H₂ + 2H, is an important reaction pathway of the decomposition of C₂H₄ on Ni(111). Moreover the reaction product C₂H₂ can be adsorbed on Ni(111) as a molecule in a large temperature range, between 230 and 300 K. Furthermore, previous SEM PhD (scanned energy mode photoelectron diffraction) experimental work has shown that ethylene adsorbed at low temperature (120 K) lies with its C–C axis parallel to the surface and on an aligned bridge site (see figure 1) [7]. Heating this surface leads to dehydrogenation of the adsorbed ethylene to adsorbed acetylene, and the acetylene occupies a cross-bridge site (see figure 1) with the C atoms directly above inequivalent hollow sites on the surface, but there is no

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knowledge of how the acetylene, the important intermediate reaction product, migrates to the cross-bridge from the aligned bridge, which is the most favourable site for ethylene. The process of acetylene migration to the cross-bridge from the aligned bridge site is a short-timescale behaviour, which cannot be detected by experiment directly at present. As pointed out by Bao *et al* in [7], an incisive quantum chemistry calculation might be expected to resolve this issue.

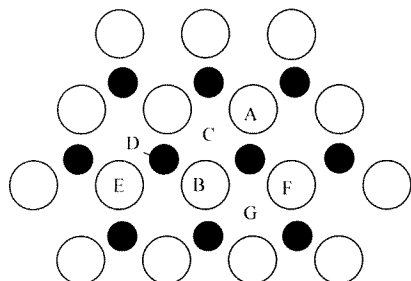


Figure 1. The Ni_{26} cluster model. Shaded circles are for the second layer, the others for the first layer. T1 site: C_2H_2 atop B with two carbon atoms located one between E and B and one between F and B. T2 site: C_2H_2 atop B with two carbon atoms located one between D and B and one between G and B. Aligned bridge site: two carbon atoms lie approximately atop Ni atoms A and B. Cross-bridge site: two carbon atoms directly above inequivalent hollow sites C and D. Here C and G indicate fcc hollow sites, while D indicates an hcp hollow site.

It is difficult to simulate the actual procedure of $\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2 + 2\text{H}$, including dehydrogenation and migration of C_2H_4 . It is assumed that no migration exists before the dehydrogenation, which presumably occurs by a concerted loss of the two H atoms. Here we study the migration of acetylene from an aligned bridge site to a cross-bridge site using the discrete variational X_α method (DV X_α) to obtain detailed knowledge about it. First, in order to make comparisons with previous experiment results, we study the adsorption of acetylene on Ni(111). We also find that the cross-bridge site is the preferred site for acetylene adsorption and the corresponding C–H and C–C bond lengths are in good agreement with previous SEM PhD results. In addition, the bond orders of acetylene in different cases are analysed. Finally, several possible geometrical pathways are studied to determine the real reaction pathway. It is found that acetylene is not stable in the aligned bridge site, and it will migrate to the cross-bridge site with a very small energy barrier, 0.02 eV. Furthermore, changes of the geometrical structure of acetylene in the procedure of migration are also discussed.

2. Model and method

Here we use the $\text{Ni}_{26}\text{-C}_2\text{H}_2$ cluster to simulate the C_2H_2 adsorption and migration on the Ni(111) surface (figure 1). The lattice parameter of the Ni crystal structure is chosen as 3.52 Å in our model. The distance between atoms is 2.49 Å, and the distance between layers is 2.03 Å.

The DV X_α method is used in the process of our theoretical study. The molecular wave functions and eigenvalues were determined using the self-consistent charge (SCC) approximation to the potential. In the present procedure, the C 1s–2s and Ni 1s–3p core orbitals have not been varied, that is to say, the 'frozen-core' approximation has been used. More details of this method have been given in [11, 12]. The DV X_α method has been used

in many systems, and is reliable for hydrocarbons [13, 14]. Here we find C–C and C–H bond lengths of the free C_2H_2 molecule are overestimated by 0.08 Å and 0.07 Å by the DV X_α method, respectively.

Table 1. Optimal geometrical parameters of acetylene adsorbed on Ni(111). AB, aligned bridge site; CB, cross-bridge site.

	C–C bond (Å)	C–H bond (Å)	C–Ni(111) distance (Å)	C–C–H angle (°)	Adsorption energy (eV)
Theor. (T1)	1.38	1.17	1.69	142	2.94
Theor. (T2)	1.39	1.17	1.67	143	3.29
Theor. (AB)	1.40	1.17	1.69	126	4.59
Theor. (CB)	1.48	1.18	1.27	120	6.18
Exp. (CB)	1.44	—	1.36	—	—

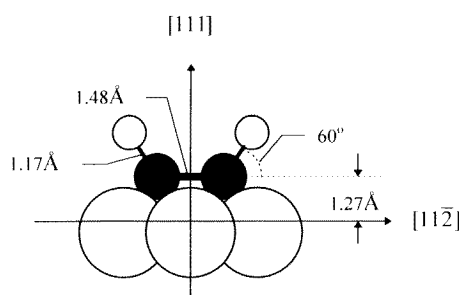


Figure 2. The local adsorption geometry (side view) for acetylene on Ni(111) at the cross-bridge site.

3. Results and discussion

3.1. Adsorption of C_2H_2 on Ni(111)

First, we study the adsorption of acetylene on Ni(111) using the DV X_α method so that we can develop insight into the migration of C_2H_2 on Ni(111). We calculate the binding energies of acetylene at the aligned bridge site, the cross-bridge site and two atop sites (see figure 1). In our calculations, we optimized 12 coordinates of the four atoms of acetylene at all four possible adsorption sites. The results show that acetylene adsorbs easily on the Ni(111) surface, and the favourite adsorption site is the cross-bridge site. The results of the optimized geometry and adsorption energies are shown in table 1. In particular, the geometric structure of C_2H_2 in the cross-bridge site is indicated in figure 2. It turns out that the adsorbed acetylene has an elongated C–C bond, 1.48 Å, which is stretched by 20% compared with the calculated C–C bond length in the gas-phase molecule, 1.29 Å. All the calculated geometry configurations are in good agreement with previous experimental results [7]. The C–C–H angle is strongly distorted to 120°, i.e. the C–H bond is bent upwards by as much as 60°, which is consistent with *ab initio* calculation results [15].

The calculated bond orders of the C–C for the aligned bridge site and the cross-bridge site are shown in table 2. In comparison with the C–C bond order of gas phase, 1.91, the

Table 2. The bond orders of C–C and C–H of C₂H₂ adsorbed on Ni(111). AB, aligned bridge site; CB, cross-bridge site.

Bond order	C–C	C–H
Free	1.91	0.84
AB	1.24	0.82
CB	1.07	0.84

corresponding bond order at the favourite adsorption site decreases greatly to 1.07, while the C–H bond order decreases slightly. The changes of bond order are consistent with the stretching of bond length. Furthermore, the C–C bond order in the cross-bridge site is noticeably less than that of the aligned bridge site. In the case of the adsorbed acetylene it is tempting to suggest that the bond extension is related to the geometrical site in which the C–C distance is commensurate with the separation of the two symmetric surface sites. The distance between the nearest Ni atoms is 2.49 Å, while that of the fcc hollow site and the nearest hcp hollow site is 1.44 Å, so the cross-bridge site is commensurate with the C–C bond length of adsorbed acetylene, while the two C atoms of adsorbed C₂H₂ are one on the fcc and one on the hcp hollow site.

3.2. Reaction pathway study

Since C₂H₄ → C₂H₂ + 2H is an important process of the decomposition of adsorbed ethylene on Ni(111) and little knowledge has been gained about how C₂H₂ migrates to the cross-bridge site after dehydrogenation of C₂H₄, we focus on studying the migration pathways of C₂H₂ from the aligned bridge site, the favourite adsorption site for C₂H₄, to the cross-bridge site, the preferred site for C₂H₂ adsorption. There are two obvious possible mechanisms based on our theoretical results and previous experimental results [7], which are shown in figure 3. One possibility (a) is a simple rotation by 90°, accompanied by a reduction in the molecule–substrate spacing of 0.42 Å, a small discrepancy with the previous experiment results, 0.5 Å. The second mechanism (b) involves a coupled 30° azimuthal rotation and a translation, again accompanied by a reduction in the molecule–substrate spacing. Mechanism a is simple, while b is more complicated, because mechanism b couples rotation and translation. In the case of a, we study the special pathway as path 1 of the following. In the case of b, three possible pathways are discussed as paths 2–4 as follows. We will discuss two simple pathways first. One is that C₂H₂ rotates around its centre by 30° first, then translates to the destination. The other pathway is that C₂H₂ translates from the centre of A and B to the centre of C and D (A–D as in figure 1) first, then it rotates around the centre of C and D by 30° (path 3). In order to find a more favourable pathway, we let the C₂H₂ rotate as it translates in path 4. In the following parts of this section, we will discuss these possible migration pathways separately.

3.2.1. Path 1. First we study mechanism a, the simplest mechanism, which only relates to rotation. As we have done with the adsorption of C₂H₂, we also optimized 12 coordinates of four atoms in the following migration pathway studies. The changes of total energy related to the increase of rotation angle are shown in figure 4(a). It turns out that there is an energy barrier of 0.20 eV at the beginning of the rotation, after 25°. After C₂H₂ ‘climbs over’ the barrier, the two C atoms can easily migrate one to the hcp and one to the fcc hollow site. In the process of rotation, we find the C–C bond length increases from 1.40 Å to 1.48 Å

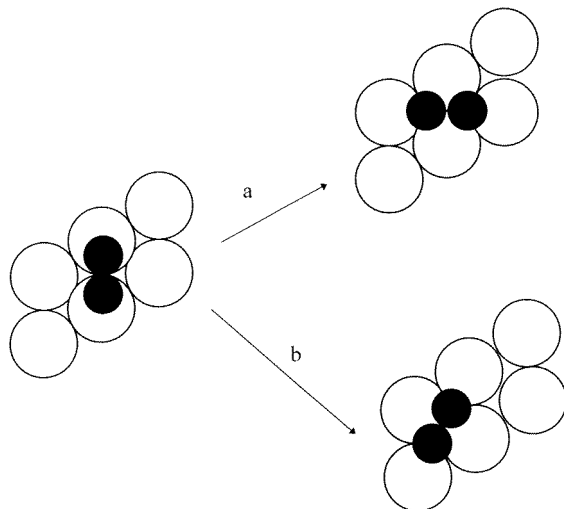


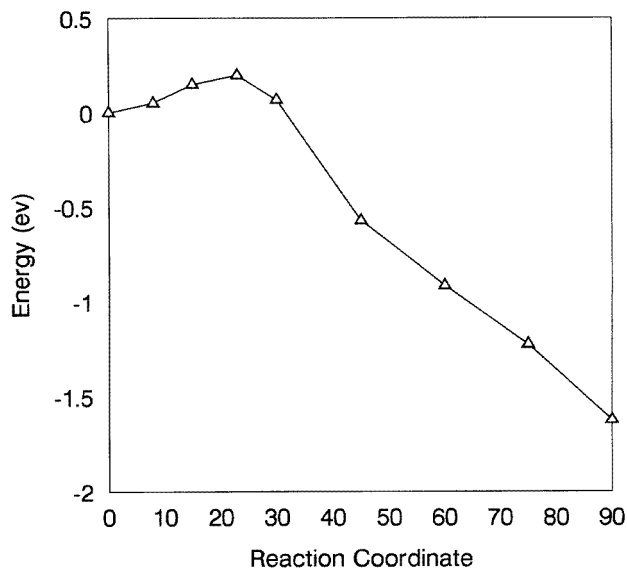
Figure 3. Two mechanisms of C_2H_2 migration on Ni(111) from the aligned bridge site to the cross-bridge site.

steadily, while the C–H bond length does not change obviously, and the molecule–substrate spacing reduces slowly too from 1.69 to 1.27 Å. However changes of the angle of the C–H bond bent upwards appear to be a little complex. It reduces from 53 to 47° at a rotation of 30°, then increases to 65° at a rotation of 60°. Finally, it approaches around 60°.

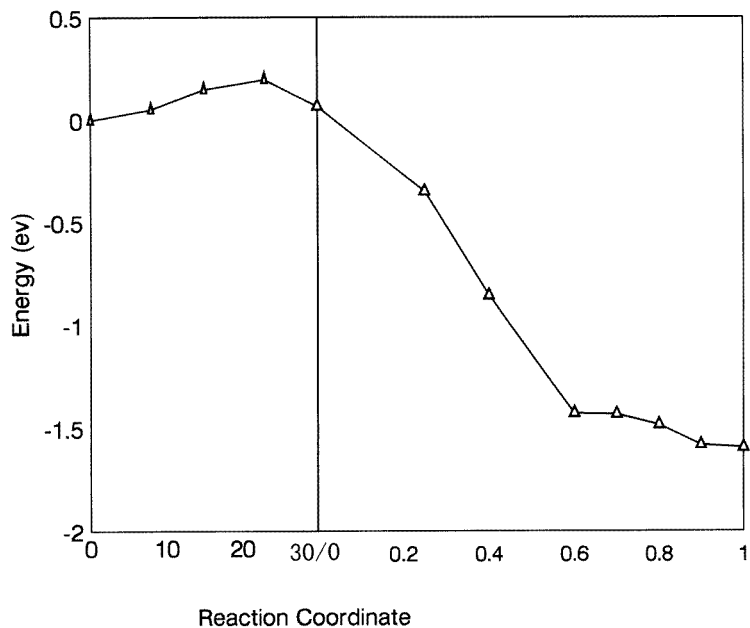
3.2.2. Path 2. Now we begin to study the more complicated mechanism, b. To simplify the mechanism, we first let the C_2H_2 molecule rotate to the centre of the aligned bridge through 30°, then translate to the centre of the cross-bridge. The distance between the aligned bridge centre and the cross-bridge centre, i.e. the total distance of translation, is about 1.24 Å. Figure 4(b) gives the total energy of the corresponding reaction coordinate. The reaction coordinate of the first part is the degree of rotation, while the second part is the ratio of distance translated to the total translation distance. Although there is no energy barrier in the translation, there is still an energy barrier of 0.20 eV, because the rotation part of this path is equivalent to path 1. In the process of translation, the C–C bond length still increases steadily, while the molecule–substrate spacing reduces. The angle of the C–H bond bent upwards increases from 47 to 60° continuously in the translation.

3.2.3. Path 3. Figure 4(c) gives another simple migration pathway of mechanism b. Here, C_2H_2 translates to the destination first, then rotates by 30°. The energy barrier is noticeably reduced to 0.04 eV at the beginning of the pathway as shown in figure 4(c), but there arises an energy barrier of 0.16 eV at the last section of the translation. The molecule–substrate spacing reduces as for the above paths. The angle of the C–H bond bent upwards hardly increases until the rotation begins.

3.2.4. Path 4. Although the energy barrier at the beginning of path 3 is very small, the barrier in the last section of the translation does not seem reasonable. There must be a more favourable pathway for the C_2H_2 migration from the aligned bridge site to the cross-bridge



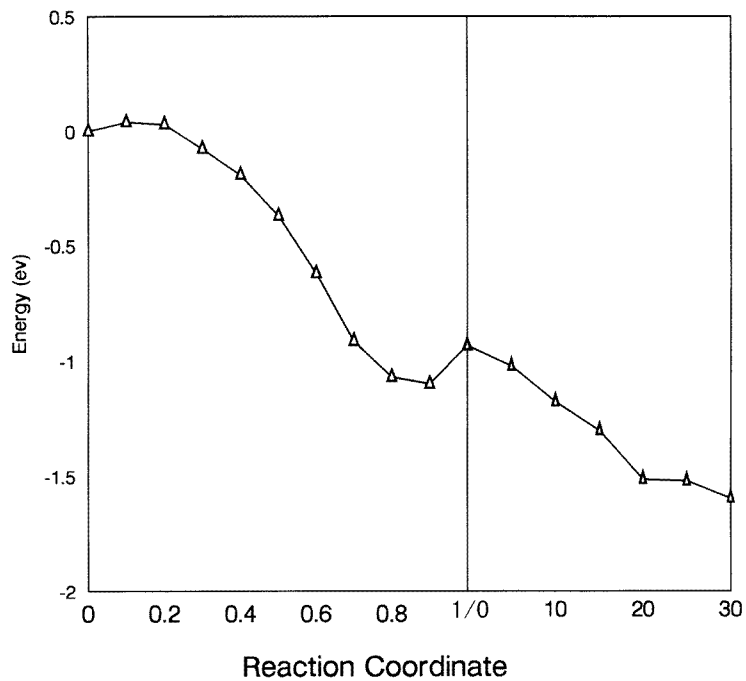
(a)



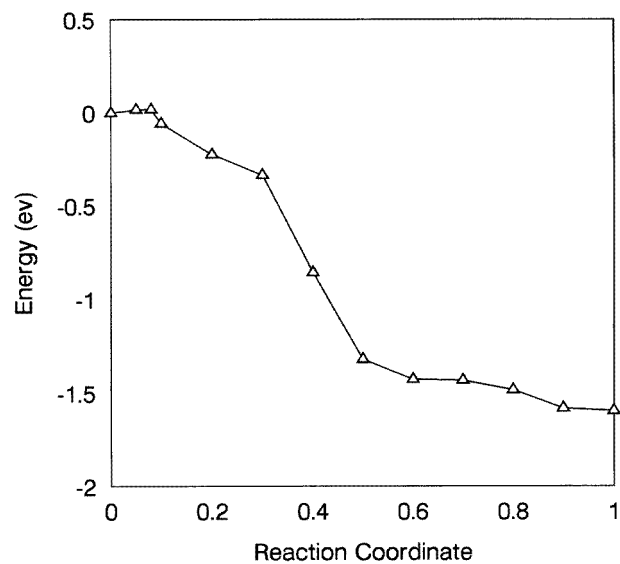
(b)

Figure 4. The total energy of the $\text{Ni}_{26}\text{-C}_2\text{H}_2$ cluster versus the reaction coordinate for (a) path 1, (b) path 2, (c) path 3, and (d) path 4. Here the total energy of C_2H_2 in the aligned bridge site is chosen to be zero.

site. To find out the favourite pathway, we take the angle of rotation as a new coordinate to be optimized with the 12 coordinates of the four atoms when C_2H_2 migrates from the aligned bridge site to the cross-bridge site. The changes of total energy in the whole process are shown in figure 4(d). Here, no rotation degree appears in the reaction coordinate. The



(c)



(d)

Figure 4. (Continued)

relationship between the rotation angles and the reaction coordinate of translation is shown in figure 5. The energy barrier is as small as 0.02 eV at the beginning, and no new barrier arises in the whole procedure. From figure 5, we learn that the rotation takes place in a

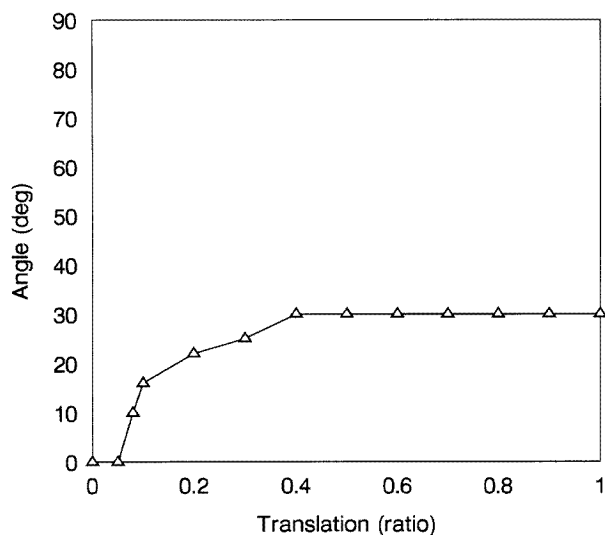


Figure 5. The relationship between the rotation angles and translation coordinate of path 4. Here the translation coordinate is the ratio of distance translated to the total translation distance, 1.24 Å.

small region of translation coordinate, 0.05–0.40, i.e. within a translation of 0.43 Å. The molecule–substrate spacing reduces slowly through the whole procedure, while the angle of the C–H bond bent upwards does not increase until C₂H₂ translates to the coordinate of 0.75, by 0.93 Å.

4. Summary

Acetylene is an important medial reaction product of ethylene decomposition on transition metals. In order to develop a deeper insight into our previous SEM PhD experiment work, the adsorption of acetylene on the Ni(111) surface, as well as the migration pathway of acetylene from the aligned bridge site to the cross-bridge site, has been investigated by theoretical calculations. A summary of the important results is as follows.

(i) On the Ni(111) surface, the favourite acetylene adsorption site is calculated to be the cross-bridge site, which is consistent with previous experiment results, and the calculated geometric configuration is in good agreement with previous studies too. Furthermore, the difference of the acetylene geometric configuration in different adsorption sites seems reasonable with the analysis of corresponding C–C and C–H bond orders.

(ii) Acetylene is not stable in the favourite adsorption site of ethylene, the aligned bridge site, and will migrate to the cross-bridge site with a very small energy barrier, 0.02 eV. The corresponding pathway is translation to the nearest cross-bridge site by 1.24 Å, with a rotation by 30° simultaneously.

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