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THEORETICAL STUDY ON THE CATALYTIC ACTIVITY OF PALLADIUM FOR THE HYDROGENATION OF ACETYLENE

H. NAKATSUJI, M. HADA * and T. YONEZAWA

Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 606, Japan

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The catalytic activity of palladium for the hydrogenation reaction of acetylene is studied by the ab initio quantum chemical method with the use of the cluster model. Based on our previous theoretical result that the hydrogen molecule is easily adsorbed dissociatively on the Pd_2 fragment, we investigate the reactivity of this absorbed hydrogen for acetylene in two modes of the reaction, namely the Eley–Rideal (ER) mode and the Langmuir–Hinshelwood (LH) mode. Full catalytic reaction cycles are studied for both modes. From the study of the ER mode, it is shown that these hydrogens are almost as reactive as free atomic hydrogens in spite of the existence of the Pd–H bonds binding these hydrogens on the surface. The barrier of the reaction is calculated to be 32 kcal/mol. The electronic origin of the catalytic activity of palladium is shown to be the electron correlation and the participation of the dangling bond of the palladium surface. The nature of the reaction is clarified by analyzing the force and electron density along the reaction process. From the study of the LH mode, which is more realistic as a model of the catalytic reaction than the ER mode, it is shown that the two-step mechanism involving vinyl radical as a surface reaction intermediate is more preferable than the one-step simultaneous mechanism. The barriers of these catalytic cycles of the reactions are calculated to be 7 and 28 kcal/mol, respectively. The mechanism of the catalytic selectivity that acetylene is selectively converted to ethylene (not to ethane) in the ethylene–acetylene mixture is clarified.

1. Introduction

Catalytic processes on a metal surface constitute one of the most attractive unknown fields in chemistry. It is important for catalyst design to have an insight on the electronic processes occurring in the reactions on a catalytic surface. In quantum-chemical calculations, we often adopt the localized cluster model. Since the effective interaction radii of reactants are of the order of a few ångströms, the reactants can interact only with a few surface atoms. Taking such atoms out of the surface, we consider the reaction on the "surface" of the cluster as a model for the catalytic reactions on a real surface.

* Present address: Production Engineering Research Laboratory, Hitachi, Ltd., Totsuka-ku, Yokohama 244, Japan.

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Palladium shows a unique affinity to hydrogen [1]. It dissociatively adsorbs the hydrogen molecule [2]. It is a good solid "solvent" of hydrogen and acts as a molecular sieve for hydrogen. Further, it is a good catalyst for hydrogenation reactions [3,4]. For example, it converts acetylene included as impurities in ethylene gas into ethylene. We report here a theoretical study on the catalytic activity of palladium for the hydrogenation reaction of acetylene. This reaction consists of two steps: First a hydrogen molecule is chemisorbed on a palladium surface and subsequently this hydrogen attacks acetylene which is coadsorbed on the surface. Experimentally, it is known that the first step, namely the dissociative adsorption of the hydrogen molecule, is a necessary step for the occurrence of the second hydrogenation reaction step [5].

Previously, we have theoretically studied the chemisorption of a hydrogen molecule on palladium using the cluster model [6–8]. A single Pd atom in the ground $^1S(d^{10})$ state shows an affinity to the H_2 molecule, but does not act to cleave the H–H bond. The excited $^{1,3}D(d^9s^1)$ states of palladium are all repulsive for hydrogen. The Pd_2 fragment, on the other hand, shows an activity for molecular and dissociative adsorptions of the hydrogen molecule [7,8]. There seems to be a smooth equilibrium between these two forms at a distance of about 1.5 Å from the Pd_2 "surface". The dissociative form is more stable than the molecular form by a few kcal/mol. The electronic mechanism of this catalytic activity is explained with the use of the orbital correlation diagram. The 4d and in the second place the 5s AO's of palladium, which constitute the so-called "dangling" bond of the surface, play a crucial role. In addition, electron correlation is shown to be essential for explaining the dissociative adsorption even qualitatively. The Pd–Pd bond is not weakened in this catalytic process, a fact important from a viewpoint of stability of the catalytic surface. We have observed the redistribution of the electron density which supports this mechanism. The mechanism of the catalytic activity of palladium is different from the mechanisms proposed for a nickel surface [9–11] and for a calcium surface [11].

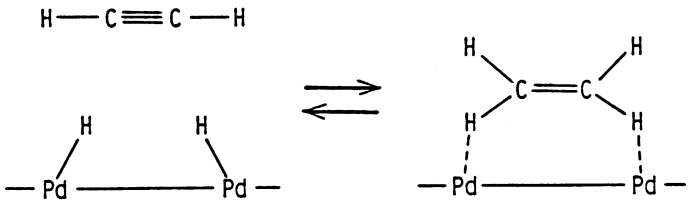
As we have thus obtained the dissociatively absorbed hydrogens on the Pd_2 fragment on a purely theoretical ground, we investigate here the activity of this system for the hydrogenation reaction. We have chosen acetylene as a reactant because the catalytic reaction

$$C_2H_2 + H_2 \rightarrow C_2H_4 \qquad (1)$$

is useful in chemical industry to convert acetylene included as impurities in ethylene gas [1,4]. Palladium is a good catalyst for this reaction and shows the selectivity which is practically very important [4]. Namely, as far as acetylene exists in the mixture, it is hydrogenated selectively to ethylene, and ethane is not formed, even though palladium is a better catalyst for the hydrogenation of ethylene than of acetylene. Another reason we have chosen this reaction is that it is typically a symmetry-forbidden reaction [12,13]. Without the ex-

istence of the catalyst the barrier is too high for a smooth reaction to occur. Then, the actual occurrence of this reaction on a palladium surface must be due to the catalytic activity of the palladium. We are interested to know the electronic origin of this catalytic activity.

We consider here two modes of the reaction. One is that acetylene in the gas phase or in a van der Waals layer of catalyst reacts with the hydrogen molecule dissociatively adsorbed on palladium, namely,



(2)

This pathway is called the Eley–Rideal (ER) mode [1]. This mode is suitable for investigating the reactivity of the hydrogens dissociatively adsorbed on Pd_2. Experimentally this mode is not necessarily realistic, since acetylene is more easily adsorbed on palladium than hydrogen [1]. However, Bond and Wells [4b] proposed this mode for the hydrogenation of ethylene when an excess of H_2 molecules exists. Further, this reaction mode would become realistic when a molecular beam experiment is undertaken. It would give valuable information on the reactivity of the hydrogens adsorbed on a metal cluster.

Another mode we investigate is the surface reaction in which hydrogen dissociatively adsorbed on palladium attacks acetylene also adsorbed on the surface. This mode is called Langmuir–Hinshelwood (LH) mode [1,14]. This mode is experimentally natural [1], but theoretically more difficult to study than the ER mode, because we have to clarify the mode of acetylene adsorption and then the interaction mechanism between acetylene and hydrogen both on a palladium surface. The experimental and theoretical knowledge we have now is not sufficient to settle these aspects of the reaction. We will describe later how we assume the reaction pathway of the LH mode. In the following sections, we describe the calculational method and give the results for the ER mode and then for the LH mode. A preliminary result of this study has been reported elsewhere [15].

2. Calculational method

The energy and the electronic structure of the reaction system are calculated by an ab initio method including electron correlations. The gaussian

basis is the (3s3p3d)/[3s2p2d] set for Pd and the Kr core is replaced by a relativistic effective core potential [16]. For hydrogen we use the (4s)/[2s] set [17], and for carbon the 4-31G set [18]. In the calculation of the ER mode, we further add the derivatives of the basis set for carbons and hydrogens, so that the Hellmann–Feynman theorem is approximately satisfied for the forces acting on these nuclei [19].

The calculations are carried out by the CAS (complete active space)-MC-SCF method [20] with the addition of a small modification [21]. In the CAS-MC-SCF calculation of the Pd_2–H_2–C_2H_2 system used for the ER mode, we select 50 orbitals from the Hartree–Fock (HF) MO's and perform SCF calculations within these 50 orbitals [21]. Among them, there are 9 doubly occupied inactive orbitals, 12 complete active orbitals, and 29 secondary SCF orbitals. The configurations are generated by distributing 18 electrons among these 12 active orbitals. For the Pd_3–H_2–C_2H_2 system employed for the LH mode, SCF calculations are made within 61 orbitals selected from the HF orbitals. They are classified into 20 doubly occupied inactive orbitals, 6 active orbitals, and 35 secondary orbitals. For the Pd_2–H–C_2H_2 system used also for the LH mode, the SCF calculation is performed within 66 orbitals selected from the HF MO's. The numbers of orbitals are 15 for doubly occupied inactive orbitals, 6 for active orbitals, and 45 for secondary orbitals. The complete set of configurations is generated by distributing 6 and 5 electrons among these 6 active orbitals of the Pd_3–H_2–C_2H_2 and Pd_2–H–C_2H_2 systems, respectively. By virtue of this algorithm [21], we have been able to apply the CAS-MC-SCF method even to these computationally large systems. The calculations are carried out using the modified version of the GAMESS program [22].

3. Eley–Rideal mode

3.1. Force along the reaction

The assumed pathway of the ER mode is shown in fig. 1. Table 1 gives the coordinates of the reaction path. Acetylene attacks from side-on orientation the two hydrogen atoms dissociatively adsorbed on the Pd_2 fragment. The geometry is assumed to change gradually as a function of R, shown in fig. 1. At $R = 2.0$ Å, we use the geometry of free acetylene and the optimum geometry of the Pd_2–H_2 system calculated previously [8] by the SAC method [23]. The Pd–Pd length is fixed to 2.7511 Å, the distance observed for fcc crystal structure [24]. At $R = 0$ we use the geometry of ethylene. The dependence of the geometrical parameters on R is assumed to be the same as that of the H–H distance in the molecular adsorption step of the hydrogen molecule on Pd_2 [8].

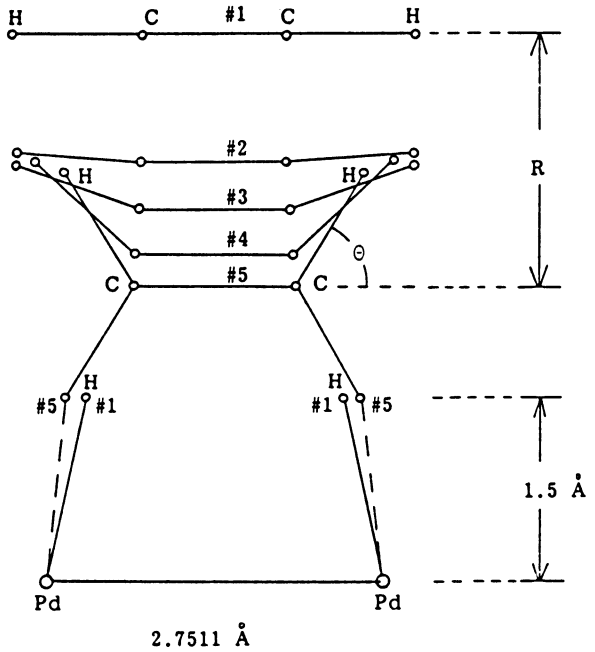


Fig. 1. Assumed reaction pathway for the Eley–Rideal mode of the hydrogenation reaction of acetylene on Pd_2.

The forces acting on the carbons and hydrogens of the system during the reaction are shown in fig. 2. This force is calculated by using the Hellmann–Feynman theorem,

$$F_A = Z_A\left(\int \left(r_{A1}/r_{A1}^3\right)\rho(r_1)\,\mathrm{d}r_1 - \sum_{B\,(\neq A)} Z_B R_{AB}/R_{AB}^3\right). \tag{3}$$

Table 1
Definition of the reaction coordinate of the Eley–Rideal mode shown in fig. 1

No.	R [a] (Å)	r_{CC} (Å)	r_{CH} [b] (Å)	r_{HH} [c] (Å)	θ [d] (deg)	$r_{Pd_2\text{-}C_2}$ [e] (Å)
1	2.0	1.1826	1.0575	2.100	0.00	4.4150
2	1.0	1.1876	1.0582	2.113	2.22	3.4162
3	0.6	1.2272	1.0640	2.215	19.58	3.0166
4	0.3	1.2769	1.0711	2.339	40.82	2.7169
5	0.0	1.3178	1.0770	2.443	58.51	2.4172

[a] See fig. 1 for definition.
[b] The C–H bond of acetylene, originally.
[c] The H–H distance of the dissociatively adsorbed hydrogen, originally.
[d] See fig. 1 for definition.
[e] The distance between the centers of the C–C bond and of the Pd–Pd bond.

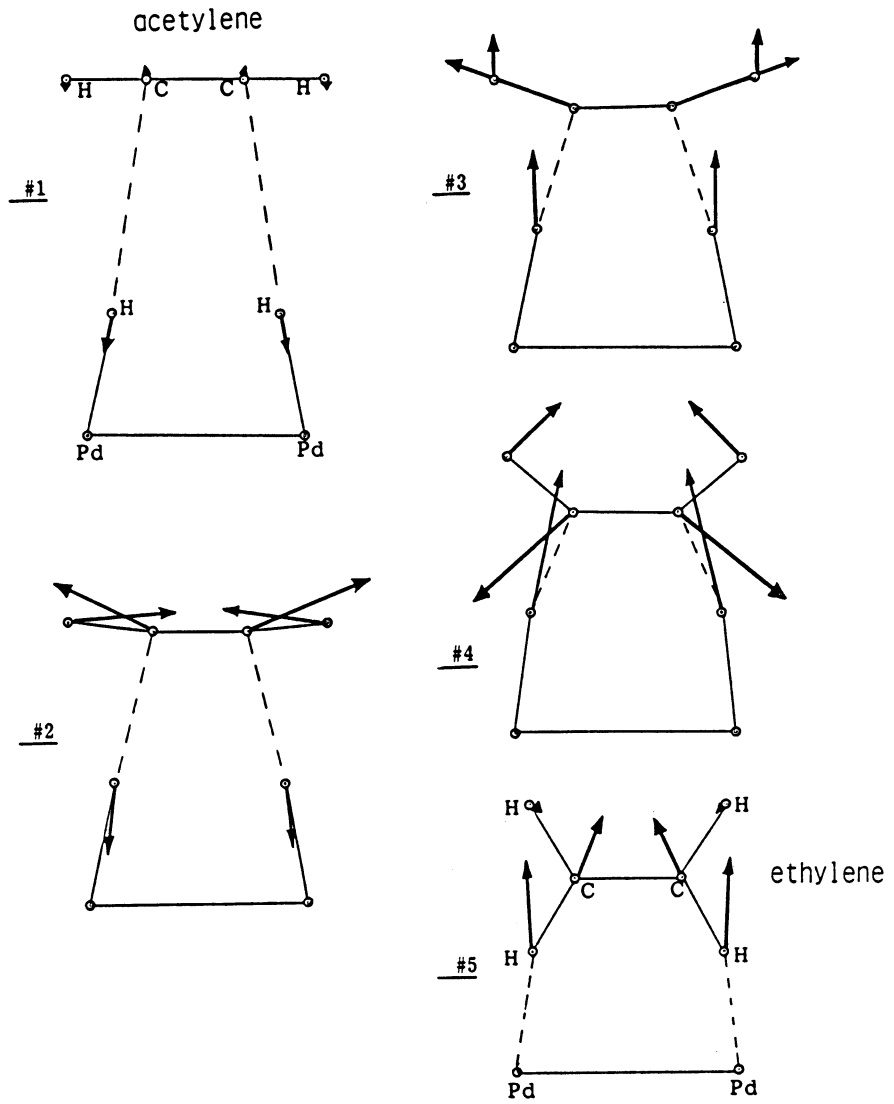


Fig. 2. Force acting on carbons and hydrogens during the Eley–Rideal mode of the reaction.

In the beginning of the reaction, the system is repulsive, demonstrating the existence of a potential barrier. This is seen for the positions 1 and 2 of fig. 2. The hydrogens adsorbed on Pd_2 and acetylene are mutually repulsive. In the form 3, the forces acting on the carbons are still repulsive, but the forces acting on the hydrogens on Pd_2 are attractive and the terminal hydrogens of acetylene feel the bending force. In the form 4, all of the forces acting on the

hydrogens and carbons work to accelerate the reaction. In the forms 2–4 the force on carbon works to elongate the C–C distance. In the form 5, ethylene is formed and the force works to separate the product from the Pd_2 fragment. Therefore, the product ethylene is released automatically from the catalytic "surface" of Pd_2. The active site of Pd_2 thus generated again absorbs H_2 and recycles the catalytic reaction. We should note that although ethylene is attractive to palladium when its π-orbitals attack palladium [25], it is repulsive in the form 5 shown in fig. 2.

3.2. *Energetics of the Eley–Rideal mode*

The potential energy curve of the system along the reaction coordinate is shown in fig. 3. It also shows the potential curves for the same reaction without Pd_2. The curve starting from the level $C_2H_2 + H_2$ (2.1 Å) is the

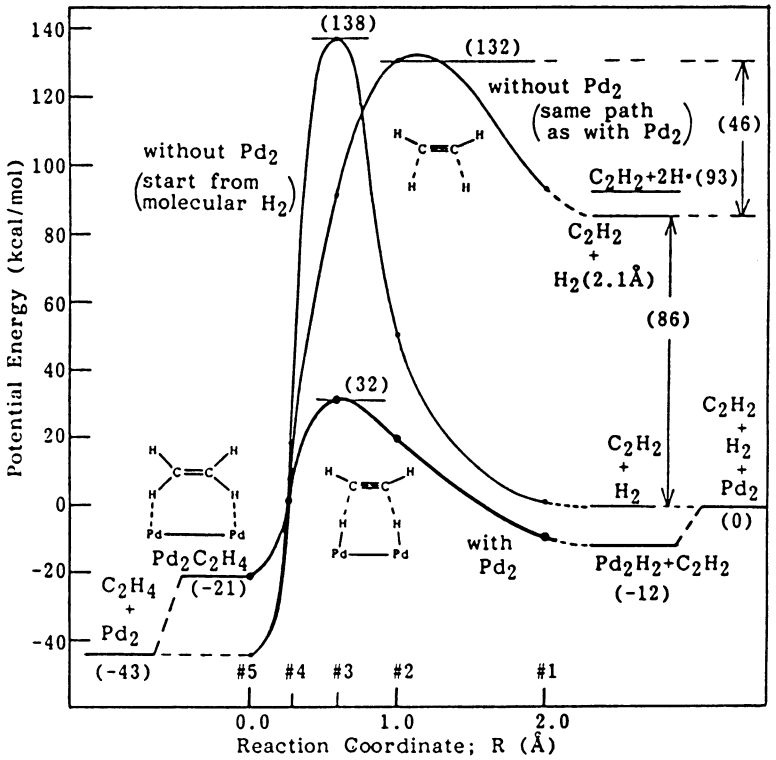


Fig. 3. Potential energy curves for the hydrogenation reaction of acetylene with and without Pd_2. For the reaction without Pd_2, the steep curve on the left-hand side corresponds to the path starting from C_2H_2 and molecular hydrogen, and the curve on the right-hand side corresponds to the same pathway as that in fig. 1 except for the non-existence of the Pd_2. The number in the parentheses shows relative energies in kcal/mol obtained by the CAS-MC-SCF method.

potential curve of the system which is essentially the same as that shown in fig. 1 except for the non-existence of the Pd_2 fragment. For the reaction without Pd_2 starting from C_2H_2 and molecular hydrogen ($R_{HH} = 0.74$ Å), another sharp curve is obtained. The dependence of the H–H distance on R is assumed to be the same as that used in defining the reaction coordinate shown in fig. 1.

The barrier of the reaction with Pd_2 present is about 32 kcal/mol with respect to the free system. When ethylene is formed on Pd_2, it is repelled automatically from the surface, since there, C_2H_4 and Pd_2 are coplanar so that the system is more unstable than the free system by 22 kcal/mol. This is also pointed out in the form 5 of fig. 2. The Pd_2 fragment thus generated again adsorbs H_2 and enters again into the reaction cycle. This is the catalytic cycle of the hydrogenation reaction in the Eley–Rideal mode involving Pd_2 as a catalyst. The barrier of the reaction in this cycle, 32 kcal/mol, is much smaller than that of the same reaction without Pd_2. When we start from C_2H_2 and molecular hydrogen, the barrier is as large as 138 kcal/mol, due to the symmetry-forbidden nature of the reaction. When we start from C_2H_2 and two almost atomic hydrogens with a H–H distance of 2.1 Å, the H–H distance of the dissociatively adsorbed hydrogen on Pd_2, the barrier is about 46 kcal/mol, but to elongate H_2 to 2.1 Å, about 86 kcal/mol is necessary so that the sum is 132 kcal/mol. Thus, the existence of Pd_2 is essential to reduce the barrier of the reaction. This is an important role of the catalyst.

It is interesting to compare the barriers of the reactions starting from $C_2H_2 + H_2$ (2.1 Å) with and without Pd_2. It is 46 kcal/mol without Pd_2 as shown above, but it is 44 kcal/mol even with Pd_2. The slopes of the two curves up to the transition states are also similar. This result implies two facts. First, the most important step, energetically, in this catalytic process is the dissociative adsorption of the H_2 molecule on the Pd_2 surface. Since this process occurs essentially without barrier [7,8], we see that the catalytic activity of Pd_2 reduces the barrier of this step by more than 86 kcal/mol. The electronic mechanism of this catalytic activity has been clarified previously [8]. Second, the hydrogen dissociatively absorbed on Pd_2 is essentially as reactive as free atomic hydrogen, in spite of the existence of the Pd–H bonds in the Pd_2–H_2 system. (Note that without Pd_2, the H_2 molecule separated by 2.1 Å is essentially two free atomic hydrogens.) This is indeed surprising and shows the catalytic activity of Pd_2 in the second hydrogenation step. If the hydrogens were tightly bound by Pd_2, a much larger energy barrier would have been resulted in the hydrogenation reaction step.

3.3. Origin of the catalytic activity

Now, what is the origin of the catalytic activity of Pd_2 in the hydrogenation reaction step? Fig. 4 displays the orbital correlation diagram of this system in

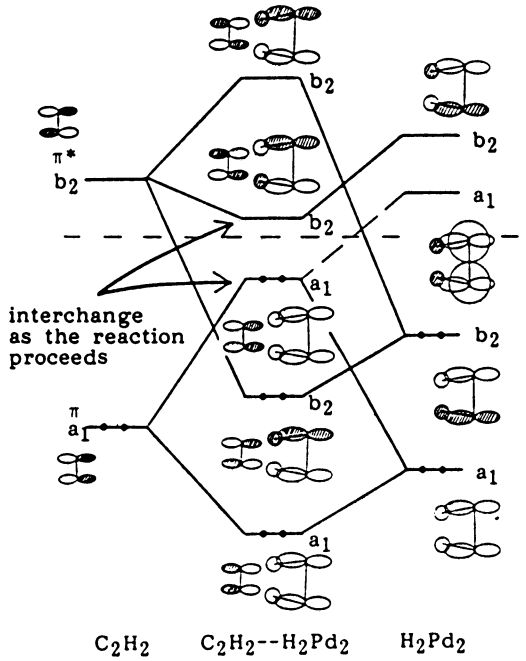


Fig. 4. Orbital correlation diagram for the earlier stage of the reaction, $C_2H_2 + H_2\text{-}Pd_2 \rightarrow C_2H_4\text{-}Pd_2$.

an earlier stage of the reaction. It is based on the analysis of the natural orbitals of the CAS-MC-SCF method. The left-hand side shows the π and π^* MO's of acetylene. The right-hand side shows the active MO's of the Pd_2–H_2 system. They were shown in the previous paper [8] to be the principal MO's of the Pd_2–H_2 system. Here again, the existence of the b_2 MO in the occupied space of the Pd_2–H_2 system is very important. This MO is antibonding between two H's so that it can interact with the π^* MO of acetylene to form new C–H bonds. However, this interaction alone does not explain the reactivity of the H_2 molecule adsorbed on Pd_2. Another factor is the existence of the second b_2 MO in the unoccupied space of the Pd_2–H_2 system. This MO is very important to describe the electron correlation of the system. In fact, its occupation number is 0.14 even in the free Pd_2–H_2 system. In these b_2 MO's the dominant palladium orbitals are d_δ AO's, which constitute the "dangling" bond of a palladium surface. As the interaction increases, the second a_1 MO of the interacting system becomes more and more unstable. This is the origin of the existence of the barrier. The spacing between the occupied a_1 and the unoccupied b_2 MO's becomes closer and closer and the electron correlation involving these two orbitals increases and works to reduce the activation barrier. At the transition state, the order of the occupation numbers of these

two MO's is inverted, and then the reaction proceeds further. Without the electron correlation, the HF potential curve is discontinuous at the transition state and the barrier height is calculated to be 63 kcal/mol, about twice as large as that calculated with electron correlation included.

We thus conclude that the participation of the dangling bond on the palladium surface and the electron correlation are the two major factors of the catalytic activity of palladium. This is so for both the dissociative adsorption step of the hydrogen molecule [8] and the hydrogenation reaction step on the palladium surface.

The origin of the energy barrier in the hydrogenation reaction step is, in the HF picture, the inversion of the a_1 and b_1 MO's between occupied and unoccupied spaces. This barrier is essentially due to the symmetry-forbidden character of the approach [12]. Therefore, to reduce the barrier of the reaction, a non-symmetric approach would be more favorable than the present approach. In such approach, we expect the barrier to be reduced to about one half, i.e., 16 kcal/mol, of that of the present simultaneous hydrogenation pathway.

3.4. Electron density and analysis of the force

The force acting on the system during the reaction shown in fig. 2 is connected with the electron density of the system $\rho(\boldsymbol{r})$ by eq. (3). The force of the reaction reflects the behavior of the electron density along the reaction coordinate [26]. In fig. 5, we have shown the contour maps of the electron density difference along the reaction path. The electron density difference is defined by

$$\Delta\rho = \rho(Pd_2\text{–}H_2\text{–}C_2H_2) - \rho(Pd_2) - \sum_A \rho(A), \tag{4}$$

where A runs over all hydrogens and carbons [27]. The forms 1–5 correspond to the coordinates given in fig. 1 and table 1. The form 0 corresponds to the non-interacting intial system, $C_2H_2 + Pd_2\text{–}H_2$, and the form 6 to the non-interacting final system, $C_2H_4 + Pd_2$.

The electron density of the system at the form 1 is essentially a simple superposition of the densities of the non-interacting C_2H_2 and $Pd_2\text{–}H_2$. The electron density of the dissociatively adsorbed hydrogens are polarized towards palladium. The electron density of the form 2 is essentially the same as that of the form 1. The π-bond density of acetylene extends upwards, showing repulsive interaction between the two systems. In the form 3, which is close to the transition state as seen from fig. 3, the polarization of the electron density around the hydrogens on Pd_2 is very much relaxed. This means a weakening of the Pd–H bond and a sign of the formation of the new C–H bonds [28]. The extension of the C–C π bond of acetylene also diminishes. On going from

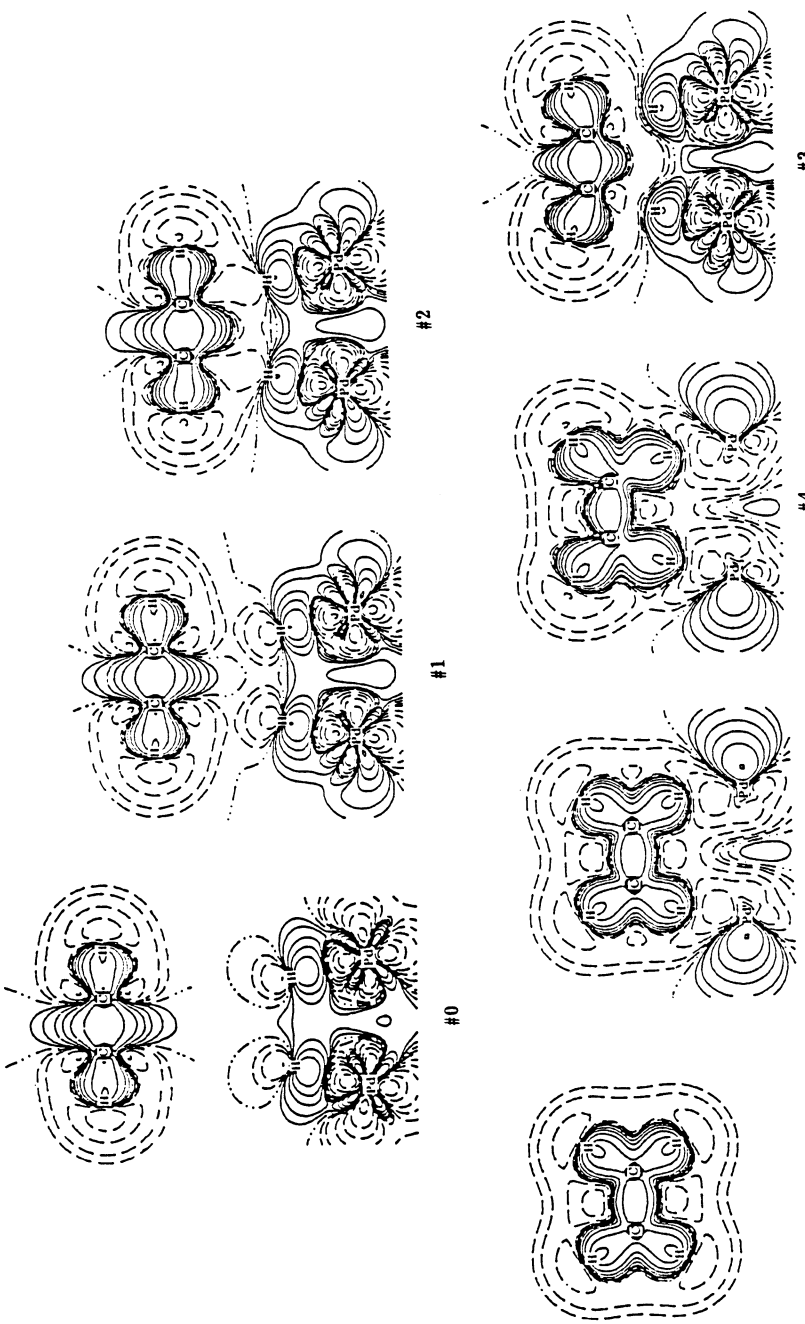


Fig. 5. Contour maps of the electron density difference of the Pd_2–H_2–C_2H_2 system. The density difference is defined by eq. (4) of the text. The geometries for the positions 1–5 are given in table 1 and fig. 1. The positions 0 and 6 correspond to the initial system $C_2H_2 + Pd_2H_2$ and the final system $C_2H_4 + Pd_2$, respectively.

3 to 4, a drastic change occurs in the electron density. The hydrogens originally on Pd_2 are completely separated out from the palladium system and form new C–H bonds in ethylene. The electron density around these hydrogens is polarized towards the carbons and a large overlap density is seen between the carbons and hydrogens. The density profile is essentially similar to that of ethylene shown in 6. The electron density in the Pd_2 region also changes largely. The Pd–H bond is essentially broken and the density becomes similar to that of the free Pd_2. An increase of electron density in the two outer sides of Pd_2 indicates a weakening of this Pd–Pd bond and a strengthening of the neighboring Pd–Pd bond of the surface. In the form 5, the electron density is essentially the same as that of the free molecules, C_2H_4 and Pd_2 shown in 6.

During the reaction, the electron density around the hydrogen initially absorbed on Pd_2 shows an interesting behavior. It is strongly polarized towards palladium in the beginning of the reaction (1 and 2), the polarization diminishes at the transition state (3), and finally (4 and 5) it is polarized towards the carbons of ethylene; the C–H bonds are formed and the Pd–H bonds disappear. This behavior of the electron density is typically electron-cloud preceding, a general behavior of electron density [26], in the course of the hydrogenation reaction. The Pd–Pd bond seems to be weakened slightly when ethylene is formed. It is mainly due to the interchange of the a_1 and b_2 orbitals as shown in fig. 4.

The behavior of the electron density is the source of the driving force of the reaction [26]. We analyze the force acting on the hydrogens initially adsorbed on Pd_2 in terms of the regional roles of the electron density. We partition the force acting on these hydrogens as

$$\boldsymbol{F}(\text{total}) = \boldsymbol{F}(\text{H–C}) + \boldsymbol{F}(\text{H–Pd}) + \boldsymbol{F}(\text{AD}) + \boldsymbol{F}(\text{Pd}_2) + \boldsymbol{F}(\text{C}_2\text{H}_2). \tag{5}$$

The total force is given by eq. (3), and each element is defined by

$$\boldsymbol{F}(\text{H–C}) = \boldsymbol{F}^{\text{EC}}_{\text{H–C}} = 2Z_{\text{C}} \sum_{r}^{\text{on C}} \sum_{s}^{\text{on H}} P_{rs}\langle \chi_r | (f_{\text{H}})_0 | \chi_s \rangle,$$

$$\boldsymbol{F}(\text{H–Pd}) = \boldsymbol{F}^{\text{EC}}_{\text{H–Pd}} + \boldsymbol{F}^{\text{EC}}_{\text{H–Pd}'} = 2Z_{\text{Pd}} \sum_{r}^{\text{on Pd, Pd}'} \sum_{s}^{\text{on H}} P_{rs}\langle \chi_r | (f_{\text{H}})_0 | \chi_s \rangle,$$

$$\boldsymbol{F}(\text{AD}) = \boldsymbol{F}^{\text{AD}} = \sum_{r,s}^{\text{on H}} P_{rs}\langle \chi_r | f_{\text{H}} | \chi_s \rangle,$$

$$\boldsymbol{F}(\text{Pd}_2) = \boldsymbol{F}^{\text{EGC}}_{\text{Pd}} + \boldsymbol{F}^{\text{EGC}}_{\text{Pd}'} + \boldsymbol{F}^{\text{EGC}}_{\text{H}} + \boldsymbol{F}^{\text{EGC}}_{\text{H}'},$$

$$\boldsymbol{F}(\text{C}_2\text{H}_2) = \boldsymbol{F}^{\text{EGC}}_{\text{C}_2\text{H}_2}, \tag{6}$$

where the net exchange force integral is defined by [29]

$$\langle \chi_{r\text{C}} | (f_{\text{H}})_0 | \chi_{s\text{H}} \rangle = \langle \chi_{r\text{C}} | f_{\text{H}} | \chi_{s\text{H}} \rangle - \tfrac{1}{2} S_{r\text{C},s\text{H}} \langle \chi_{r\text{C}} | f_{\text{H}} | \chi_{r\text{C}} \rangle. \tag{7}$$

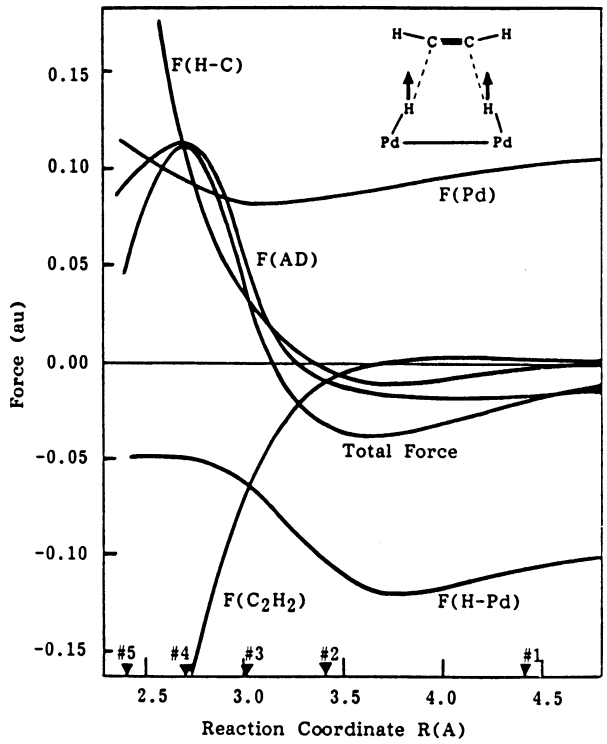


Fig. 6. Force acting on the hydrogen initially adsorbed on Pd_2 of the Pd_2–H_2–C_2H_2 system. The definition of the force component is given by eq. (6) of the text. The value is positive when it points upwards towards acetylene.

The definitions of atomic dipole force F^{AD}, exchange force F^{EC}, and extended gross-charge force F^{EGC} were given by Nakatsuji [23b,28,29]. The force F(H–C) represents the force acting on H due to the electron density in the overlap region of H and C. The force F(H–Pd) has a similar meaning. The force F(AD) represents the force acting on H due to the polarization of the atomic density surrounding it. $F(Pd_2)$ and $F(C_2–H_2)$ represent the force due to the gross charge of the Pd_2 and C_2H_2, respectively.

Fig. 6 shows the force curves along the reaction coordinate defined in fig. 1. We see that the trend of the total force is determined by the elements, F(AD), F(H–Pd), and F(H–C). F(AD) is due to the polarization of the electron density near the proton under consideration. It is polarized towards Pd's in the initial stage and towards carbons in the final stage. The polarization disappears between the forms 2 and 3. Thus, the polarization of the electron density near the hydrogens is an important source of the reaction. The F(H–Pd) force is towards Pd_2 and is large in the initial stage, but becomes rapidly weak near

the geometry 3. There, the F(H–C) force rapidly increases, suggesting a transfer of the electron cloud from the H–Pd region to the H–C region. This corresponds well to the change in the electron density shown in fig. 5. The force $F(Pd_2)$ is almost constant throughout the reaction. This suggests that the electronic structure of the Pd_2 fragment does not change much throughout the reaction. This analysis supports the general guiding principle of the electron density discussed in detail previously [26].

4. Langmuir–Hinshelwood mode

4.1. Assumed pathway of the Langmuir–Hinshelwood mode

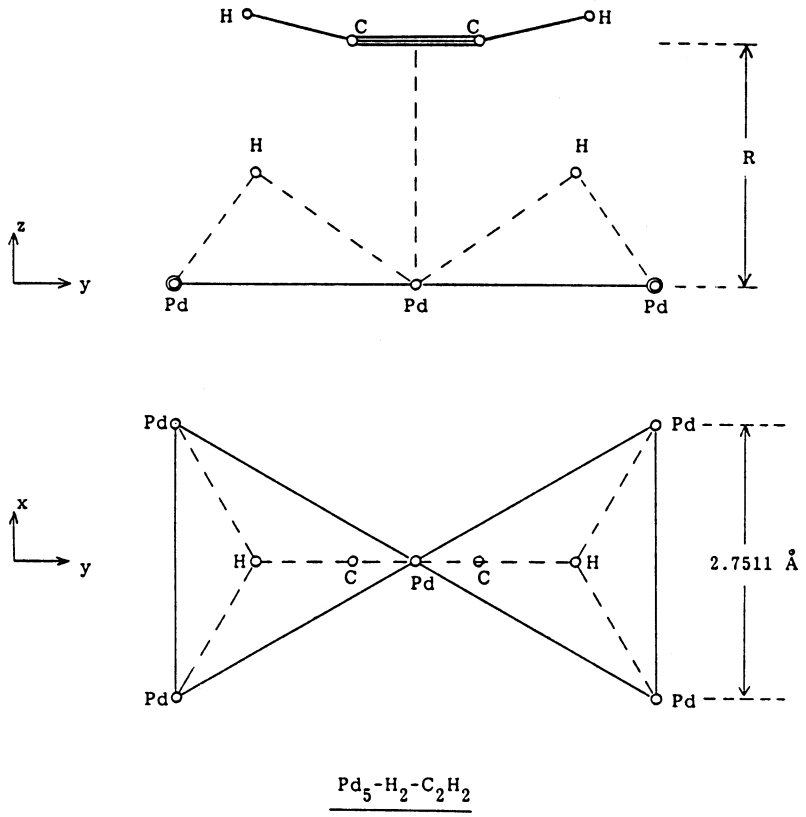
More than fifty years ago, Horiuti and Polanyi [30] studied the surface reaction mechanism for olefin hydrogenations on a metal surface. Olefin adsorbed on a metal surface is attacked by hydrogen also adsorbed on the surface. Bond and Wells [4b] considered a more elaborate mechanism to explain their kinetic experiments for the hydrogenation of acetylene on a palladium surface. We consider here such a surface reaction mode for the hydrogenation of acetylene. This mode is called Langmuir–Hinshelwood (LH) mode [1,14]. It is more realistic than the ER mode as a model for the present catalytic reaction. However, theoretically speaking, this mode is more difficult to study than the ER mode since it involves larger degrees of freedom than the ER mode. To construct a model for the surface reaction complex with a minimum number of necessary degrees of freedom, the previous experimental and theoretical information is valuable.

The stable adsorption site of atomic hydrogen on palladium is reported to be a hollow site which is on the center of the Pd_3 triangle of the surface [31,32]. When H is bound at the bridge site of Pd_2, the binding energy is reduced by about 10 kcal/mol [32].

The geometry of the surface complex of acetylene on a palladium surface is rather complicated. It seems to depend on temperature and the nature of a surface [33–42]. Ozin et al. [33] reported an experimental and theoretical study of ethylene–nickel cluster complexes. They showed that ethylene forms a π complex probably with only one of the Ni atoms. Fischer and Kelemen [36] reported that on the Pd(100) surface the electron spectrum of acetylene differs only moderately from the gas phase spectrum, but on the Pd(111) surface, acetylene forms an olefinic complex which strongly interacts with the neighboring Pd atoms through π and σ bonds. Kesmodel et al. [35] also considered two different bonding states of acetylene (separated by a thermal activation barrier) on a platinum (111) surface. The more weakly bound state involves coordination to basically one surface metal atom (Pt–C bond length of 2.5 Å), whereas attachment to three metal atoms was found for the more strongly

bound state. The π-bond model was assumed for the weakly bound state. More recently, vinylidene ($=C=CH_2$) species were supposed as stable complexes on Pt and Rh surfaces at high temperature [39,40,42]. However, from the viewpoint of the chemical reactivity, the stable species spectroscopically observed does not necessarily correspond to the surface reaction intermediate of the hydrogenation reaction. In particular, the catalytic reaction cycle cannot involve a very stable intermediate. We therefore adopt, for simplicity too, the weakly bound π-complex model for the initial state of the hydrogenation reaction.

The mode of attack of acetylene by hydrogen on a surface is interesting but little seems to be known. Smith [43] reported from an experimental study on the hydrogenation of olefins that hydrogen adds almost exclusively from the surface to the surface side of chemisorbed molecules. Bond and Wells [4b]



Pd_5-H_2-C_2H_2

Fig. 7. Model system for the hydrogenation reaction of acetylene on palladium in the Langmuir–Hinshelwood mode. The upper and lower figures show the projections of the system onto the *yz* and *xy* planes, respectively.

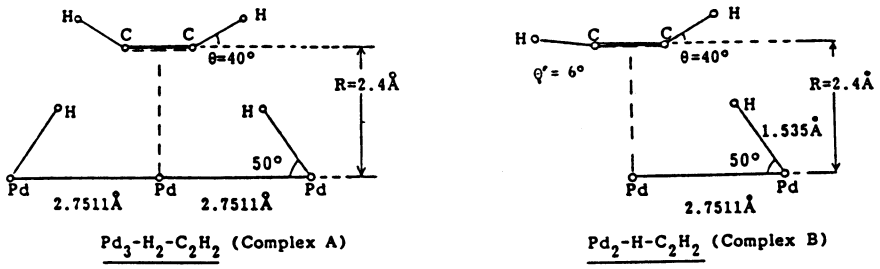


Fig. 8. Model systems used in the present work for the hydrogenation reaction of acetylene on a palladium surface. These models correspond to the initial stage of the hydrogenation reaction.

studied experimentally the elementary steps of the hydrogenation reaction of acetylene on a palladium surface. They proposed a mechanism which involves vinyl radical as an intermediate of the reaction.

Based on this information, we consider a localized model of the surface reaction complex as shown in fig. 7. The Pd–Pd distance is fixed to the experimental value observed for the bulk metal [24]. The Pd–H length is taken from the experimental value for the diatomic PdH molecule [44]. This model system satisfies most of the known information summarized above. However, it contains five palladium atoms, so that this model is too large for accurate ab initio calculations. We therefore rotate the reaction complex by 30° on the surface and leave two Pd atoms out of the consideration.

In fig. 8, we show the models for the surface reaction complexes which we used in the present calculations. We refer to the left and right ones as complexes A and B, respectively. Complex A corresponds to the one-step simultaneous mechanism. Complex B is for the two-step mechanism which involves vinyl radical as a surface reaction intermediate. Complex A includes three palladium atoms and all atoms lie in the same plane. This model also satisfies most of the prerequisites summarized above except that the hydrogen atom initially adsorbed on palladium is placed on the bridge site of Pd_2. We assume a side-on π-complex interaction for acetylene. The geometry is shown in table 2. The C–C length is 1.193 Å which is the optimized value for the Pd–C_2H_2 system by the present calculation. (The C–C length of free acetylene is 1.183 Å by optimization and 1.208 Å by experiment [45].) The distance between acetylene and Pd is fixed to 2.4 Å which is obtained by optimizing for the Pd–C_2H_2 system. The initial position of the hydrogen on palladium is optimized for the Pd_3H_2 system, which is the lower part of complex A without acetylene. The potential curve of the Pd_3H_2 system is shown in fig. 9 for some selected variations of the position of the adsorbed hydrogens. Two hydrogens are moved symmetrically. Besides the central bridging position (1 in fig. 9) optimized by Pacchioni and Koutecky for the Pd_2H system [32], there is another slightly lower minimum near the outer Pd atoms. The electron

Table 2
Geometries of acetylene, ethylene, and vinyl radical in complexes A and B shown in figs. 8 and 10

	C–C (au)	C–H (au)	θ^{f} (deg)	θ'^{f} (deg)
Acetylene	1.193 [a,b]	1.058 [c]	40 [d]	6 [a]
Ethylene	1.339 [c]	1.086 [c]	58.8 [c]	–
Vinyl radical	1.339 [c]	1.086 [c]	58.8 [c]	45 [e]

[a] Optimized values for the Pd–C_2H_2 system.
[b] The C–C length of free acetylene is 1.183 Å by optimization and 1.208 Å by experiment [45].
[c] Experimental value of ethylene [45].
[d] Optimized value for the Pd_2–H–C_2H_2 system.
[e] Optimized value for the vinyl radical C_2H_3.
[f] θ and θ' are defined in fig. 8. θ' is only for complex B.

correlation is very important at this position. The H–Pd(outer)–Pd(central) angle is 50° with the Pd(outer)–H distance fixed at 1.535 Å [44]. We choose this position as an initial position of the hydrogen atoms on the palladium surface. The bending angle θ of acetylene is 6° when it is optimized for the Pd–C_2H_2 system, but 40° when it is optimized for complex B. We use the

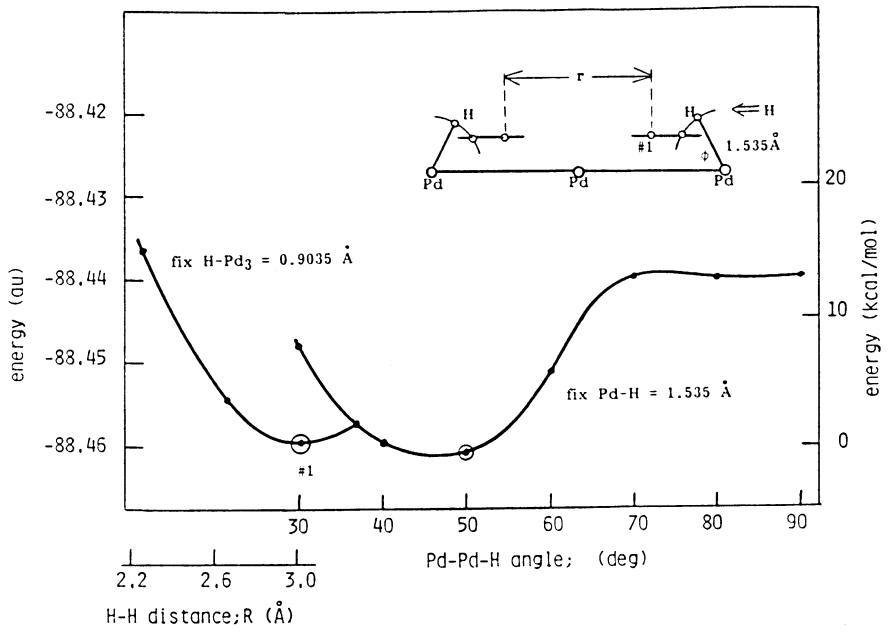


Fig. 9. Potential curves which show the optimal positions of the hydrogen atoms in the Pd_3–H_2 system. The curve on the left-hand side is obtained for the displacement of hydrogens with a fixed H–Pd_3 distance of 0.9035 Å and that on the right-hand side with a fixed Pd–H distance of 1.535 Å.

same angle $\theta = 40°$ for complex A. The stability of the reaction complex depends largely on this angle θ. The difference $E(6°) - E(40°)$ is 34 and 18 kcal/mol for complexes A and B, respectively.

Starting from complex A or complex B shown in fig. 8, we let the system

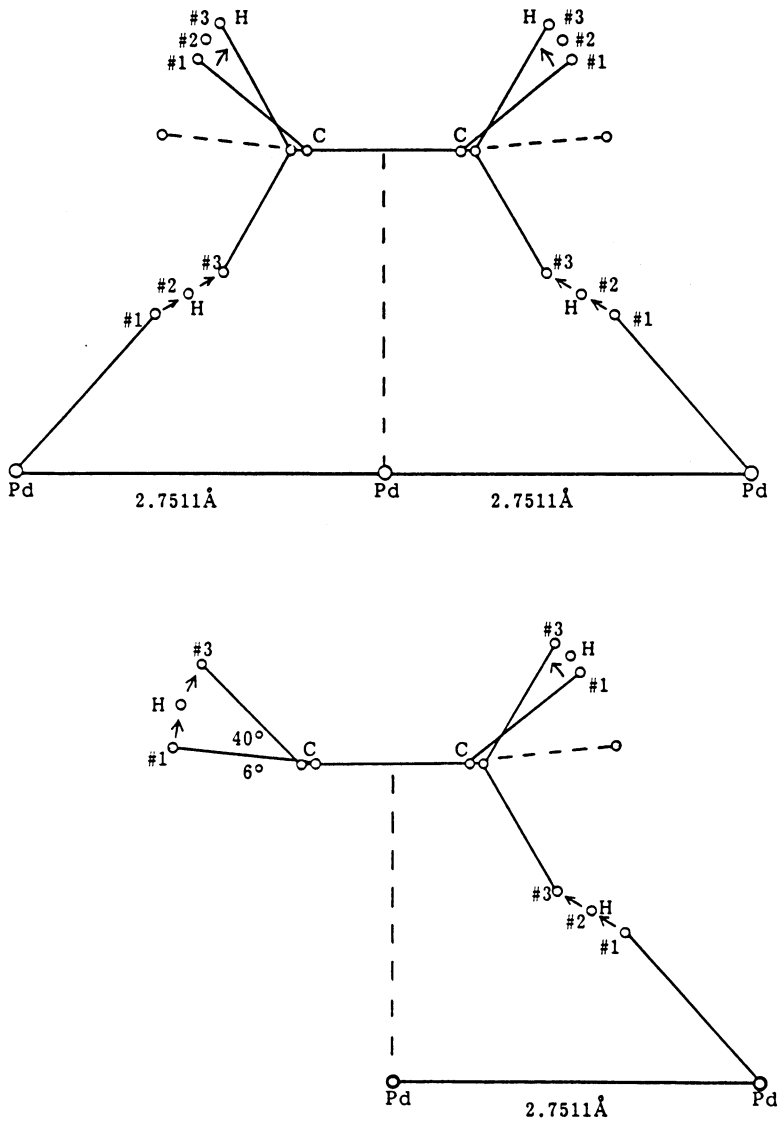


Fig. 10. Assumed reaction phathways in the Langmuir–Hinshelwood mode. The upper and lower pictures correspond to the pathways starting from complexes A and B, respectively. The Pd–Pd and Pd–C_2 distances are fixed throughout the reaction.

react and form ethylene or vinyl radical on the Pd_3 or Pd_2 "surface", respectively. The reaction pathway is shown in fig. 10. We assume that the positions of the hydrogens on Pd_2 or Pd_3, the C–C and C–H distances and the C–C–H angles of acetylene vary linearly, depending on the displacement of the hydrogens on palladium from the initial geometry 1 to the final geometry 3. The intermediate geometry 2 is just the median of the initial and final geometries. At the final geometry 3, we use the geometry of ethylene and vinyl radical shown in table 2. The Pd–C_2 distance is fixed at 2.4 Å throughout the reactions.

4.2. *Energetics of the catalytic reaction*

The energetics of the hydrogenation reaction of acetylene in the LH mode is displayed in figs. 11 and 12. Fig. 11 is for the one-step reaction involving complex A and fig. 12 is for the reaction involving complex B. These figures also show the energetics for the systems without including palladium. They are

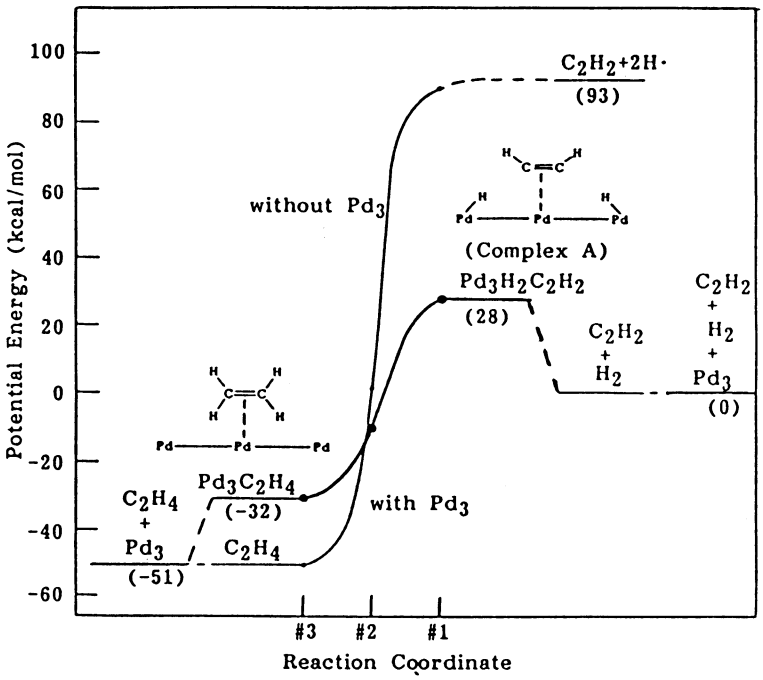


Fig. 11. Energetics for the hydrogenation reaction of acetylene in the Langmuir–Hinshelwood mode involving complex A displayed in fig. 8. The coordinates 1–3 are shown in the upper part of fig. 10. Energetics for the same pathway without Pd_3 is also shown. The numbers in parentheses show relative ene-gies in kcal/mol.

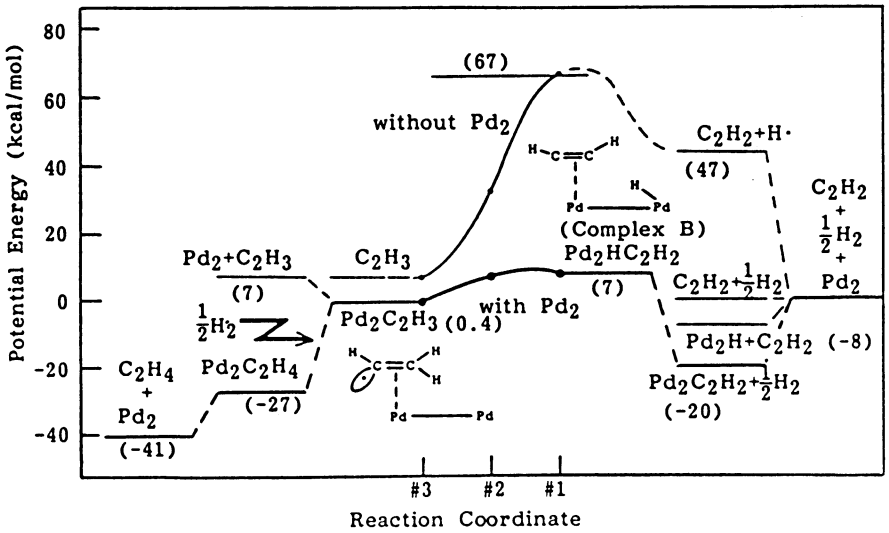


Fig. 12. Energetics for the hydrogenation reaction of acetylene in the Langmuir–Hinshelwood mode involving complex B displayed in fig. 8. The coordinates 1–3 are shown in the lower part of fig. 10. Energetics for the same pathway without Pd_2 is also shown. The numbers in the parentheses show relative energies in kcal/mol.

obtained for the same reaction paths just by omitting Pd_3 and Pd_2 from complexes A and B, respectively.

From fig. 11 we see that complex A is higher in energy than the separated system by 28 kcal/mol. Namely, when two hydrogens attack an adsorbed acetylene simultaneously from the left and from the right, the energy barrier would be of this order. Afterwards, the reaction proceeds without barrier and gives ethylene coplanar with Pd_3. In this geometry, ethylene is repulsive from Pd_3 [25] and automatically released out of the reaction complex. This Pd_3 is again involved in the reaction cycle by adsorbing acetylene, and so on. This is the cycle of the reaction involving complex A. In comparison with the same reaction without Pd_3, the catalytic activity of Pd_3 seems to exist essentially in the dissociative adsorption step of the H_2 molecule. Without palladium, we need 93 kcal/mol (experimentally 104 kcal/mol) to dissociate the H_2 molecule into two atomic hydrogens.

The two-step LH mode involving complex B seems to proceed more smoothly then the one-step simultaneous mode involving complex A. As seen in fig. 12, the energy of complex B is only 7 kcal/mol higher than the separated system. Afterwards, the reaction proceeds smoothly to form a vinyl radical absorbed on Pd_2. The present model is unfavorable for this intermediate complex because the σ radical lobe on the carbon of the vinyl radical cannot have a sufficient interaction with the palladium atom. We need at least

one more Pd atom on the left. The adsorption geometry would also be relaxed. Nevertheless, the present complex of the vinyl radical is more stable than the separated system, $Pd_2 + C_2H_3$, by 7 kcal/mol. In a more complete model this stabilization energy would be larger. Therefore, the vinyl radical still remains on the surface and receives a second attack from the adsorbed hydrogen to form ethylene. In this final product form, ethylene is coplanar with Pd_2 so that it is repelled automatically from the surface. This is the completion of the catalytic cycle. The bare site of palladium thus released adsorbs acetylene and enters again into the cycle. In comparison with the energetics obtained without including Pd_2, the catalytic role of Pd_2 is observed in two steps. One is in the dissociative adsorption step of H_2 on palladium and the other in the surface reaction step to form complex B. Thus, the two-step LH mode involving vinyl radical as a surface intermediate is most favorable among the three modes of the hydrogenation reaction studied in this paper.

5. Selectivity in the hydrogenation reaction

Activity and selectivity are two major roles of a catalyst. The former is related to the ability of a catalyst to reduce the reaction barrier. The latter originates from phenomena such as catalytic surface structure, geometry of interaction between reactant and catalyst, existence of co-adsorbants, etc., which are sometimes very complex.

We explain here the selectivity of the palladium catalyst in the hydrogenation reaction of acetylene included as impurities in ethylene gas [1,4]. It is summarized as follows. (1) Hydrogenation of ethylene does not occur until all acetylene impurities are converted to ethylene. (2) Ethane is generated only scarcely from acetylene. This selectivity, which is of particular importance in chemical industry, occurs despite the fact that palladium is even a better catalyst for the hydrogenation of ethylene.

A possible explanation based on the present calculation is as follows. For the first selectivity, the differences between acetylene and ethylene in the heat of adsorption and in the sticking probability to the catalyst are important. The stabilization energy of acetylene is calculated to be 7 kcal/mol for the Pd atom and 20 kcal/mol for the Pd_2 fragment. The corresponding values for ethylene are 12 and 19 kcal/mol, respectively. Therefore, for an extended surface, the heat of adsorption should be larger for acetylene than for ethylene as observed experimentally [1]. Further, the sticking probability of acetylene should be larger than that of ethylene because acetylene has the active π orbitals in all angles around the C–C axis but ethylene has the π orbitals only in the plane perpendicular to the molecular plane. The second selectivity is explained from all the surface reaction modes studied in this paper. The ethylene just produced by the hydrogenation reaction of acetylene is coplanar

with the active palladium atoms. In this configuration, ethylene is repelled from the surface [25], so that it is released automatically from the reaction cycle. Therefore, the hydrogenation reaction up to ethane does not occur.

6. Concluding remarks

It is theoretically concluded that small palladium clusters show catalytic activity and selectivity for the hydrogenation reaction of acetylene to form ethylene. The reaction proceeds in a smooth cycle involving two main steps. One is the dissociative adsorption of the H_2 molecule on the Pd surface [7,8] and the other is the surface reaction between acetylene and hydrogen. Palladium shows catalytic activity for both steps. Energetically, the catalytic role of palladium seems to be more important in the first step than in the second step. The occurrence of the first step is necessary for the occurrence of the second step as known experimentally [5]. In the second step, the energy barrier seems to be lower for the LH mode than for the ER mode. The hydrogen dissociatively adsorbed on palladium is very reactive in spite of the Pd–H bond with the surface metal. This activity is due to the catalytic role of palladium as shown clearly in the ER mode. Further, the second step is important for the selectivity. The observed selectivity is related to the difference in the affinity of ethylene and acetylene for a Pd surface and the structure of the product ethylene on the catalytic surface. Within the three modes of the hydrogenation reaction studied in this paper, one in the ER mode and two in the LH mode, the two-step LH mode involving vinyl radical as a surface intermediate is the most preferable mechanism. This result seems to agree with the mechanism postulated by experimental chemists for the hydrogenation reactions of olefins [1,4,14]. It would be interested to observe vinyl radical on a Pd surface in the presence of acetylene and hydrogen [38]. It would also be very interesting if the ER mode of the reaction explained here is realized experimentally, for example by a molecular beam technique. This should pose an interesting challenge to experimentalists and we look eagerly forward to their results.

Acknowledgements

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