THEORETICAL STUDY ON THE CATALYTIC ACTIVITIES OF PALLADIUM FOR THE HYDROGENATION REACTION OF ACETYLENE

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ABSTRACT. Small palladium clusters show catalytic activity for the hydrogenation reaction of acetylene to form ethylene. The catalytic effect is important in both the dissociative adsorption step of hydrogen molecule and in the surface reaction step between acetylene and hydrogen. Energetically, the effect is larger for the first step. In the second step, we considered the Eley-Rideal mechanism and the Langmuir-Hinshelwood mechanism. In any case, the hydrogen adsorbed on palladium is very reactive despite of the PdH bond. Among the three modes of the reaction studied here, the two step Langmuir-Hinshelwood mechanism involving vinyl radical as a surface intermediate seems to be the most probable mechanism. We explained the selectivities in the hydrogenation of acetylene included as impurities in ethylene gas.

1. INTRODUCTION

Electronic processes on catalytic surfaces are of fundamental importance in both chemistry and chemical industry. Palladium shows especially a variety of catalytic activities.[1-3] We report here a theoretical study on the catalytic activities of palladium for the hydrogenation reaction of acetylene. This reaction consists of two steps. One is the chemisorption of hydrogen molecule on a palladium surface and next is the subsequent attack of hydrogen to olefins on a metal surface. Experimentally, it is known that the first step, namely the dissociative adsorption of hydrogen molecule, is the necessary step for the occurrence of the second hydrogenation reaction step.[4]

Previously, we studied theoretically the chemisorption of a hydrogen molecule on a small palladium cluster.[5-7] We have shown that even the Pd_2 fragment shows a catalytic activity for the dissociative adsorption of the hydrogen molecule.[6,7] The H_2 molecule with a binding

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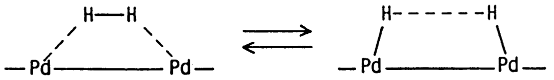
energy of 104 kcal/mol is dissociated, *with almost no barrier*, into two atomic hydrogens on the Pd_2 'surface', like on an extended surface. We found a very smooth equilibrium $H_2 \rightarrow H\cdot + H\cdot$ about 1.5Å apart from the Pd_2 'surface'. We clarified the electronic mechanism of the catalytic activity and showed that the $4d_\delta$ and secondly the 5s AO's of the Pd_2 fragment, which constitute the so-called 'dangling' bond of the metal surface, play an essential role. This mechanism may be sketched as


(1)

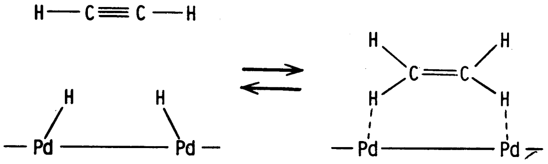
Note that in this bond alternation mechanism, the Pd-Pd bond is not weakened. This is important, suggesting a stability of the catalytic surface. Otherwise, the Pd atom would be exfoliated as a PdH molecule from the surface. This mechanism of the catalytic activity of palladium is different from the one proposed for a nickel surface,[8,9] and also for a calcium surface.[9]

After we have thus been able to produce the dissociatively adsorbed hydrogens on the Pd_2 fragment on a purely theoretical ground, so to speak, in a file of a computer, instead of a test tube, the first thing we wanted to do next was to investigate the activity of this system for the hydrogenation reaction. We have chosen acetylene as a reactant because the catalytic reaction

$$C_2H_2 + H_2 \rightarrow C_2H_4 \tag{2}$$

is one of the most popularly used reactions in chemical industry to convert acetylene included as impurities in ethylene gas.[1,10] Palladium is a good catalyst of this reaction.[10] As far as acetylene exists in the mixture, it is hydrogenated selectively to ethylene, and ethane is not formed. Another reason we have chosen this reaction is that it is typically a symmetry-forbidden reaction.[11-13] Without an existence of the catalyst the barrier of this reaction is too high to occur smoothly. Then, an actual occurrence of this reaction on a palladium surface is essentially due to the catalytic activity of palladium. We want to know the electronic origin of this catalytic activity.

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


(3)

We considered this mode to solve the following question. Is the hydrogens on Pd_2 we obtained active enough, despite of the newly formed Pd-H bonds in Eq.(1)? We will call this pathway as Eley-Rideal (ER) mode. Experimentally this mode is not realistic since acetylene is more easily adsorbed on palladium than hydrogen.[1] However, Bond and Wells[10] considered this mechanism for the hydrogenation of ethylene when excessive amount of H_2 molecule exists.

Another mode of the reaction we considered is that the hydrogen dissociatively adsorbed on palladium attacks acetylene also adsorbed on a palladium surface. We call this mode as Langmuir-Hinshelwood (LH) mode. Experimentally, this mode is natural.[1,10,14] Theoretically, this mode is more difficult to study, because we have to clarify the mode of the adsorption of acetylene and further the mode of the interaction between acetylene and hydrogen both on a palladium surface. We will explain our way of investigation later in the corresponding section.

2. CALCULATIONAL METHOD

The calculations were carried out by the CAS(complete active space)-MC-SCF method. We considered electron correlations within the active MO's of the reaction. The SCF process was performed within an adequate space of the MO's. The gaussian basis set we used are (3s3p3d)/[3s2p2d] set for Pd and the Kr core was replaced by the relativistic effective core potential.[15] For hydrogen we used (4s)/[2s] set[16] and for carbon 4-31G set.[17] In the calculations of the ER mode, we added further the derivatives of the basis set for the carbons and hydrogens, so that the Hellmann-Feynman theorem is essentially satisfied for the forces acting on these nuclei.[18]

3. ELEY-RIDEAL MODE

We have shown in Figure 1 the assumed pathway of the reaction. The acetylene molecule attacks from a side-on orientation the two hydrogen atoms dissociatively adsorbed on the Pd_2 fragment. For the Pd_2-H_2 system, we used the optimum geometry calculated previously by the SAC method.[6,7] For acetylene, the geometry is assumed to change gradually as a function of R, shown in Figure 1, and at $R = 0$ we adopted the geometry of ethylene. The dependence of the geometrical parameters on R was assumed to be the same as the change of the H-H distance in the molecular adsorption step of the hydrogen molecule on Pd_2.[7]

The potential energy curve of the system along this

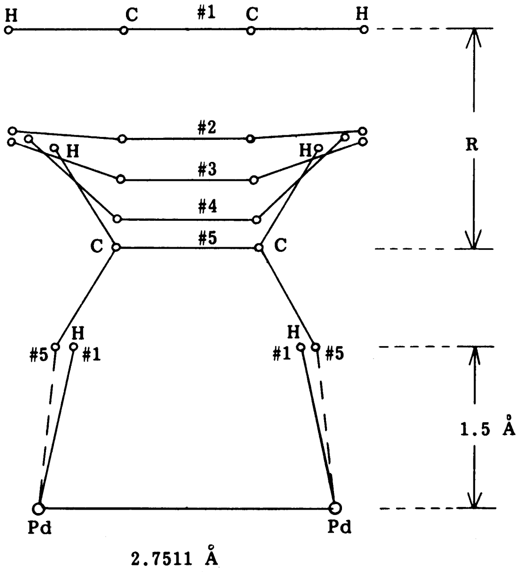


Figure 1. Assumed reaction pathway for the Eley-Rideal mode of the reaction

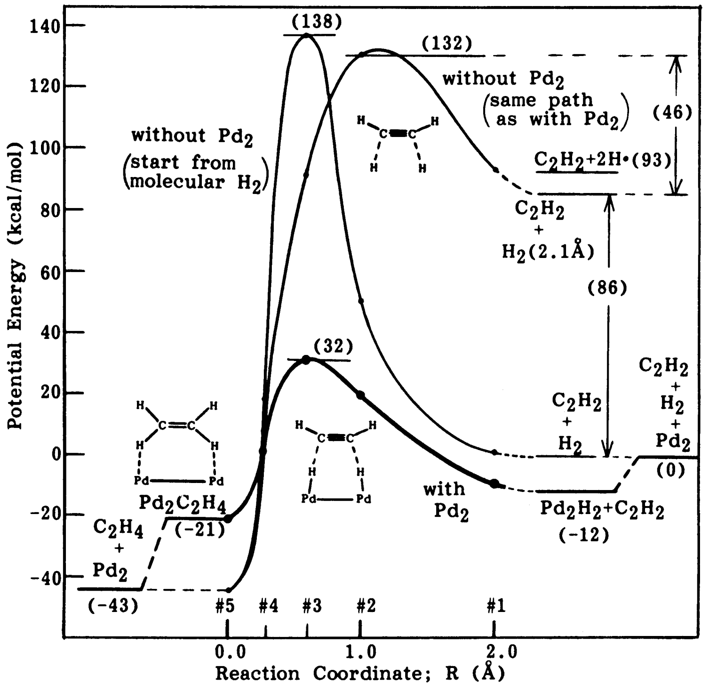


Figure 2. Potential energy curves for the hydrogenation reaction of acetylene with Pd_2 in the Eley-Rideal mode and without Pd_2. For the reactions without Pd_2, see the text. The numbers show relative energies in kcal/mol.

reaction coordinate is shown in Figure 2. It also shows the potential curves for the same reaction without Pd_2. The curve starting from the level, C_2H_2 + H_2(2.1Å), is the potential curve of the system entirely the same as that shown in Figure 1 except for the non-existence of the Pd_2 fragment. Another sharp curve is also without Pd_2 starting from C_2H_2 and molecular hydrogen. The dependence of the H-H distance on *R* is the same as that used in defining the reaction coordinate shown in Figure 1.

The barrier of the reaction with the existence of Pd_2 is about 32 kcal/mol with respect to the free system. When ethylene is formed on Pd_2, it leaves out from the complex automatically, 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. The Pd_2 fragment thus generated again adsorbs H_2 as reported previously and enters again into the reaction cycle. This is the catalytic cycle of the hydrogenation reaction in the ER 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. When we start from C_2H_2 and H_2 with the H-H distance of 2.1Å, the H-H distance of the dissociatively adsorbed Pd_2H_2 system, the barrier is about 46 kcal/mol, but to elongate H_2 up to 2.1Å, 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 reaction 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 also 44 kcal/mol even with Pd_2. 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 fragment. Since this process occurs without barrier,[6,7] we see that the catalytic activity of Pd_2 reduces the barrier of this step by more than 86 kcal/mol. Second, we notice that the hydrogen dissociatively adsorbed on Pd_2 is essentially as reactive as the free atomic hydrogen, despite of the existence of the Pd-H bond in the Pd_2-H_2 system as shown in Eq. (1). This is surprising indeed and shows the catalytic activity of Pd_2 in the hydrogenation step. If the hydrogens were tightly bound by the Pd_2, much larger energy barrier would have been resulted in the hydrogenation reaction step!

Now, what is the origin of this catalytic role of Pd_2 in the hydrogenation reaction step? In Figure 3, we have shown the orbital correlation diagram of this system in the earier 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 depicted in the previous paper[7] as the key 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 can interact with the π* MO of acetylene to form new C-H bonds. However, this interaction alone does not explain the repelling role of H_2 from the Pd_2 fragment. It is due to 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, so that the occupation number is 0.14 even in the free Pd_2-H_2 system. As the interaction increases, the second a_1 MO of the interacting system becomes more and more unstable. This is the origin of

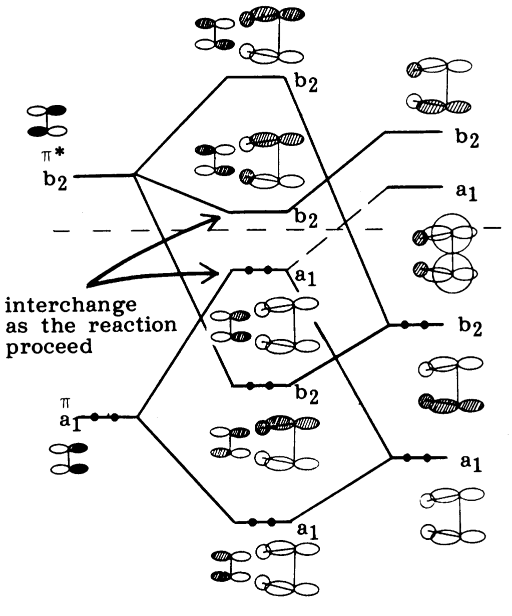


Figure 3. Orbital correlation diagram for the earier stage of the reaction, C_2H_2 + H_2-Pd_2 → C_2H_4--Pd_2.

the existence of the barrier. The spacing between the occupied a_1 and 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 MO's is inverted. We thus understand that in the hydrogenation reaction step, the b_2 orbital interactions and the electron correlation are important in reducing the barrier. We note that in these b_2 MO's the dominant palladium orbitals are the d_δ AO's, which constitute the 'dangling' bonds of a palladium surface.

4. LANGMUIR-HINSHELWOOD MECHANISM

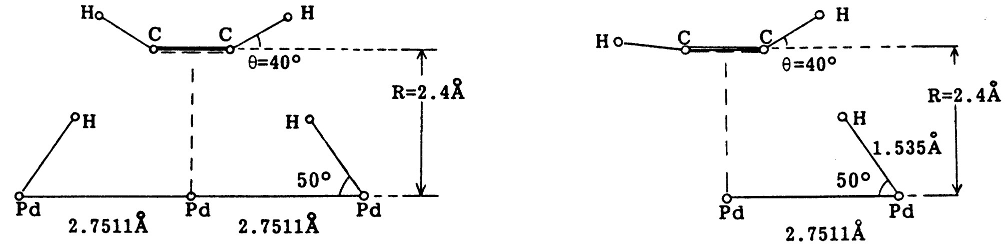
In the Langmuir-Hinshelwood mechanism, the hydrogen dissociatively adsorbed on palladium reacts with acetylene also adsorbed on the surface. Theoretically, this mode of the reaction includes much more freedoms than the ER mode. To construct a model of the surface reaction complex within a minimum number of necessary freedoms, the previous experimental and theoretical informations are 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.[19,20] The Pd-H bond is 1.69Å .[19c] When H is trapped at the bridge site of Pd_2, the binding energy is reduced by about 10 kcal/mol.[20b]

The geometry of the surface complex of acetylene on palladium is rather complicated. It seems to depend on temperature and the nature of a surface.[21] Fischer and Kelemen[21c] reported that on the (100) surface the electron spectrum of acetylene differs only moderately from the gas phase spectrum, but on the (111) surface, acetylene forms an olefinic complex which strongly interacts with the neighbouring Pd atoms through π and σ bonds. Ozin, Goddard, et al.[22] reported an experimental and theoretical study on ethylene-nickel cluster complexes. They showed that ethylene forms a π-complex probably with only one of the Ni atoms.

The mode of the attack of hydrogen to acetylene on the surface is interesting but little seems to be known. Smith[23] reported from the experimental study on the hydrogenation of olefins that hydrogen adds almost exclusively from the surface to the surface side of chemisorbed molecules. Experimentally, the elementary steps of the hydrogenation reaction are considered to involve vinyl radical formation as an intermediate step of the reaction.[10]

Based on these informations, we constructed two models of the surface reaction complex of the LH mechanism as illustrated in Figure 4. We refer to the left and right ones as complexes A and B, respectively. Complex B is the model leading to a vinyl radical formation and is a simplified one of complex A. We assumed a side-on π-complex interaction for acetylene. The distance between acetylene and Pd was settled to 2.4 Å which was obtained by optimizing Pd-C_2H_2 system. The initial position of the hydrogen on palladium was optimized for Pd_3H_2 system. Besides of the central bridging position,[20b] there was another slightly lower minimum near the outer Pd atoms. The H-Pd(outer)-Pd(central) angle was 50° with the Pd(outer)-H distance fixed at 1.535Å .[24] The bending angle θ of acetylene was 6° when optimized for the Pd-C_2H_2 system, but



Pd_3-H_2-C_2H_2 (Complex A)

Pd_2-H-C_2H_2 (Complex B)

Figure 4. Model of the surface reaction complex in the Langmuir-Hinshelwood mechanism.

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

In Figures 5 and 6, we have shown the energetics of the hydrogenation reaction of acetylene in the LH mechanism. Starting from the geometries shown in Figure 4 (#1 on the coordinate), we let the systems to react and to form ethylene and vinyl radical on the Pd_3 and Pd_2 'surfaces', respectively (#3 on the coordinate). Figure 5 is for the reaction involving complex A and Figure 6 for complex B. The reaction involving complex B consists of two steps, one corresponding to the change from acetylene to vinyl radical and the other to the change from vinyl radical to ethylene. These figures also show the energetics for the systems without including palladium. The curves were obtained for the same reaction paths just by deleting Pd_3 and Pd_2 from complexes A and B, respectively.

From Figure 5 we see that complex A is higher in energy than the separated system by 28 kcal/mol. Namely, when two hydrogens attack the adsorbed acetylene simultaneously from left and right, the energy barrier would be in this order. Afterwards, the reaction proceeds barrierlessly and leads to ethylene coplanar with Pd_3. In this geometry, ethylene is repulsive from Pd_3 and released automatically out of the reaction complex. The remaining Pd_3 is again involved in the reaction cycle by adsorbing acetylene, and so on. This is the cycle of the reaction involving the reaction 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 Pd_3, we need 93 kcal/mol (experimentally 104 kcal/mol) to dissociate the H_2 molecule into two atomic hydrogens.

The two step LH mechanism involving the reaction complex B seems to proceed more smoothly than the one step simultaneous LH mechanism involving the reaction complex A. In Figure 6, the energy of complex B is only 7 kcal/mol higher than the separated system. Afterwords, the reaction proceeds smoothly to form vinyl radical adsorbed on Pd_2. The

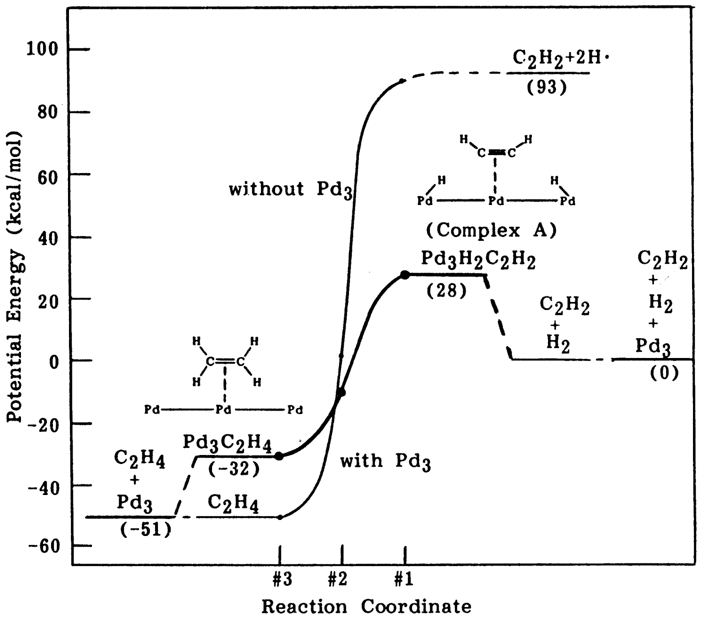


Figure 5. Energetics for the hydrogenation reaction of acetylene in the Langmuir-Hinshelwood mechanism involving complex A shown in Figure 4 with and without Pd_3. The numbers show relative energies in kcal/mol.

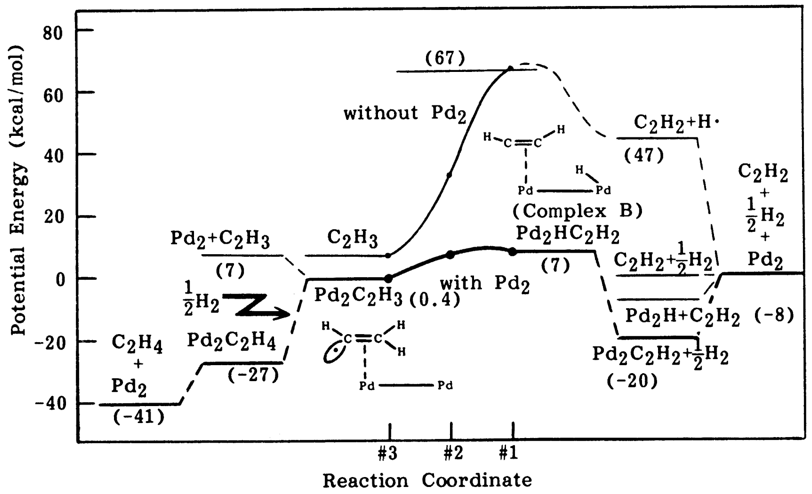


Figure 6. Energetics for the hydrogenation reaction of acetylene in the Langmuir-Hinshelwood mechanism involving complex B shown in Figure 4 with and without Pd_2. The reaction proceeds in two steps and involves vinyl radical as the reaction intermediate. The numbers show relative energies in kcal/mol.

present model is incomplete for this intermediate complex because the σ radical lobe on carbon cannot have a sufficient interaction with palladium (we need at least one more Pd atom on the left). 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 of adsorbed hydrogen to form ethylene. In this final product form, ethylene is coplanar with Pd_2 so that it is repelled from the surface and goes out of the reaction cycle. This is the completion of the catalytic cycle. The naked 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 the palladium and the other in the surface reaction step to form complex B. Thus, the two step LH mechanism involving an intermediate formation of vinyl radical is most favorable within the three modes of the hydrogenation reaction studied here.

5. CONCLUDING REMARKS

Lastly we explain briefly the selectivities in the hydrogenation reaction of acetylene included as impurities in ethylene gas.[10] They are 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. These selectivities, which are of special importance in chemical industry, occur despite of the fact that palladium is even a better catalyst for the hydrogenation reaction of ethylene. A possible explanation based on the present calculations is as follows. For the first selectivity, we think that 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 was calculated to be 7 kcal/mol for the Pd atom and 20 kcal/mol for the Pd_2 fragment. The corresponding values for ethylene were 12 kcal/mol 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 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 mechanisms studied here. The product ethylene generated by the hydrogenation reaction of acetylene is coplanar with the active palladium atoms. In this configuration ethylene is repelled from the surface and goes out of the reaction cycle so that the hydrogenation reaction up to ethane does not occur.

In this study, we have shown that the small palladium clusters show catalytic activity for the hydrogenation reaction of acetylene to form ethylene. The reaction proceeds in a smooth cycle involving the two main steps. One is the dissociative adsorption of the H_2 molecule on the Pd surface and the other is the surface reaction step 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.[4] In the second step, the hydrogen dissociatively adsorbed on palladium is very reactive despite of the Pd-H bond with the surface metal. This activity is due to the catalytic role of palladium. Further, the second step is more important than the first step to manifest a selectivity, which is another important role of catalyst. An example is explained above. Within the three mechanisms of the hydrogenation reaction studied here, one in the ER mode and two in the LH mode, the two step LH mechanism involving vinyl radical as a surface intermediate is the most probable mechanism. This result seems to agree with the mechanism frequently used by experimental chemists in the hydrogenation reactions of olefins.[1,10,14] It would be interesting to observe vinyl radical on a Pd surface in the presence of acetylene and hydrogen.[21e]

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REFERENCES

1. G. C. Bond, *Catalysis by Metals*, Academic Press, New York, 1962.
2. F. A. Lewis, *The Palladium-Hydrogen System*, Academic Press, New York, 1967.
3. P. M. Maitlis, *The Organic Chemistry of Palladium*, Academic Press, New York, 1971, Vols.1 and 2.
4. B. J. Wood and H. Wise, J. Catalysis, 5, 135 (1966).
5. H. Nakatsuji and M. Hada, Croatica Chemica Acta, 57, 1371 (1984).
6. H. Nakatsuji and M. Hada, in *Proceeding of the Nobel Laureate Symposium on Applied Quantum Chemistry (PAC' CHEM '84 Honolulu)*, Ed. by V. H. Smith, Jr, Reidel, Dordrecht, 1985.
7. (a) H. Nakatsuji and M. Hada, J. Am. Chem. Soc. to be published.
   (b) H. Nakatsuji, M. Hada, and T. Yonezawa, to be published.
8. (a) C. F. Melius, Chem. Phys. Lett. 39, 287 (1976).
   (b) C. F. Melius, J. W. Moskowitz, A. P. Mortola, M. B. Baillie, and M. A. Ratner, Surf. Sci. 59, 279 (1976).
9. C. Satoko and M. Tsukada, Surf. Sci. 134, 1, 1983.
10. G. C. Bond and P. B. Wells, J. Catalysis, 4, 211 (1965); 5, 65 (1965).
11. R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Academic Press, New York, 1970.

12. G. Henrici-Olive and S. Olive, *Coordination and Catalysis*, Verlag Chemie, Weinheim, 1977.
13. (a) R. G. Pearson, Acc. Chem. Res. 4, 152 (1970).
    (b) F. D. Mango, Topics in Current Chem. 45, 39 (1974).
14. J. Horiuti and M. Polanyi, Trans. Faraday Soc. 30, 1164 (1934).
15. P. J. Hay, J. Am. Chem. Soc. 103, 1390 (1981).
16. S. Huzinaga, J. Chem. Phys. 42, 1293 (1965).
    T. H. Dunning, Jr., J. Chem. Phys. 53, 2823 (1970).
17. R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys. 54, 724 (1971).
18. H. Nakatsuji, K. Kanda, and T. Yonezawa, Chem. Phys. Lett. 75, 340 (1980); H. Nakatsuji, T. Hayakawa, and M. Hada, Chem. Phys. Lett. 80, 94 (1981); H. Nakatsuji, K. Kanda, M. Hada, and T. Yonezawa, J. Chem. Phys. 77, 3109 (1982).
19. (a) H. Conrad, G. Ertl, and E. E. Latta, Surf. Sci. 41, 435 (1974).
    (b) R. J. Behm, K. Christmann, and G. Ertl, Surf. Sci. 99, 320 (1980).
    (c) W. Eberhardt, S. G. Louie, and E. W. Plummer, Phys. Rev. B28, 465 (1983).
20. (a) R. P. Messmer, D. R. Salahub, K. H. Johnson, C. Y. Yang, Chem. Phys. Lett. 51, 84 (1977)
    (b) G. Pacchioni and J. Kouteckey, *Theoretical Investigation of the Interaction between the Hydrogen Atom and Pd Clusters*, private communication.
21. (a) J. E. Demuth and D. E. Eastman, Phys. Rev. Lett. 32, 1123 (1974).
    (b) L. L. Kesmodel, R. C. Baetzold, and G. A. Somorjai, Surf. Sci. 66, 299 (1977).
    (c) T. E. Fischer and S. R. Kelemen, Surf. Sci. 74, 47 (1978).
    (d) H. Ibach and S. Lehwald, J. Vac. Sci. Technol. 15, 407 (1978).
    (e) J. E. Demuth, Surf. Sci. 80, 367 (1979).
    (f) J. E. Demuth and H. Ibach, Surf. Sci. 85, 365 (1979).
22. G. A. Ozin, W. J. Power, T. H. Upton, and W. A. Goddard, J. Am. Chem. Soc. 100, 4750 (1978).
23. G. S. Smith, J. Catalysis, 5, 152 (1966).
24. K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1979.