Interaction of a Hydrogen Molecule with Palladium

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Electronic processes in chemisorption and catalytic action on a metal surface play fundamental roles in chemistry and chemical industry but are still hidden in a veil theoretically. We study theoretically the interaction of a hydrogen molecule with palladium as a model of chemisorption and catalytic action of a metal surface. We use sophisticated ab initio theories explained below. The basic assumption is the local nature of the interaction between hydrogen and palladium.[1-3] We will show that even the Pd_2 fragment shows chemisorptive and catalytic activities for the hydrogen molecule. The H_2 molecule is adsorbed and dissociated very smoothly on the Pd_2 "surface" with almost no barrier and shows an equilibrium with the two atomic hydrogen radicals. The Pd–Pd bond is not weakened in this process, which is related to the stability of the catalytic surface. The mechanism of the catalytic activity is different from the one proposed for a nickel surface.[4] It is a bond alternation mechanism in which the dangling bond of the Pd surface plays an essential role.

We consider first the interaction of a hydrogen molecule with a Pd atom.[5,6] It was shown that the Pd atom in the $^1S(d^{10})$ ground state shows an affinity to the H_2 molecule but does not work to cleave the H–H bond. A long equilateral triangle is a stable form in which the hydrogen molecule is attached weakly to the Pd atom. On the other hand, the excited states of the Pd atom, the $^{1,3}D(d^9s^1)$ states, are repulsive.

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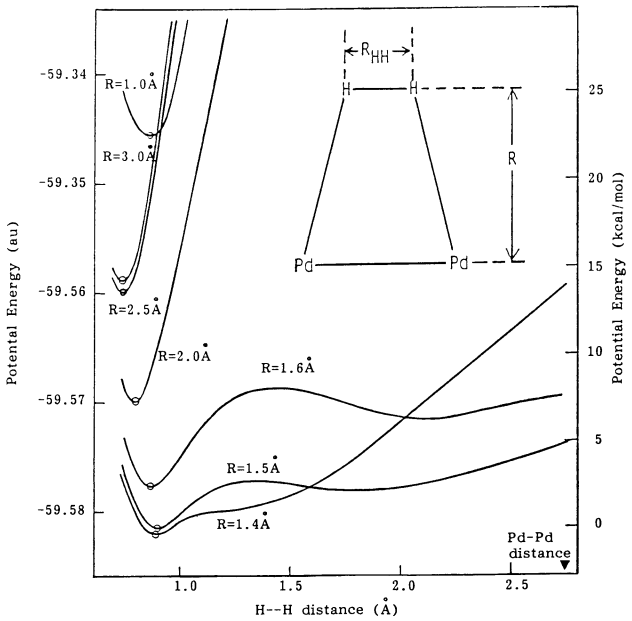

Figure 1. Potential curves for the H–H stretching of the Pd_2–H_2 system at different Pd_2–H_2 separations (CAS–MC–SCF method).

We next consider an approach of the H_2 molecule to the Pd_2 fragment as illustrated in the upper-right corner of Figure 1. The side-on orientation of H_2 shown there was calculated to be most stable at R = 2.5 Å. The Pd–Pd distance was fixed to 2.7511 Å, which is the observed value for the bulk fcc crystal structure.[7] In Figure 1, we showed the potential curves for the H–H stretching motion at several Pd_2–H_2 separations, R. They were calculated by the CAS–MC (complete active space–multiconfiguration) SCF method.[8] When the distance R is larger than 2.5 Å, the potential of the H_2 molecule is essentially the same as that of the free hydrogen molecule. When the H_2 molecule approaches Pd_2 at R = 2.0 Å, the H–H distance becomes longer but the potential is still very sharp. However, at R = 1.4–1.6 Å, the potential curve suddenly (catastrophically) becomes very flat for an elongation of the H–H distance. At R = 1.6 Å, a double-well potential appears, and at R = 1.5 Å, the system becomes considerably more stable than that at R = 1.6 Å. Here, the second minimum appears at R_{H-H} = 1.75 Å besides the first minimum at R_{H-H} = 0.847 Å. At R = 1.4 Å, the first minimum is more stabilized than that at R = 1.5 Å but the second minimum disappears. When the H_2 molecule further approaches Pd_2 up to R = 1.0 Å, the system becomes very much unstable. Thus, a stable adsorption of the H_2 molecule seems to occur at about 1.5 Å from the Pd surface. The calculated heat of adsorption is about 15 kcal/mol which is smaller than the experimental value, 20.8–24.4 kcal/mol, for the bulk Pd surface.[9]

In order to obtain a more reliable potential curve of the H_2 molecule interacting with the Pd_2 fragment at R = 1.5 Å, we calculated the potential curve of the ground state by the SAC (symmetry adapted cluster) expansion method.[10] We also calculated the potential curves of the singlet and triplet excited states by the SAC–CI method.[11] Figure 2 shows the results. In the ground-state curve, we clearly see two potential minima. The minimum at R_{H-H} = ~0.89 Å corresponds to the molecular hydrogen adsorbed on the surface, and the minimum at R_{H-H} = ~2.1 Å corresponds to the dissociative attachment in the form of two atomic hydrogen radicals. This calculation suggests the

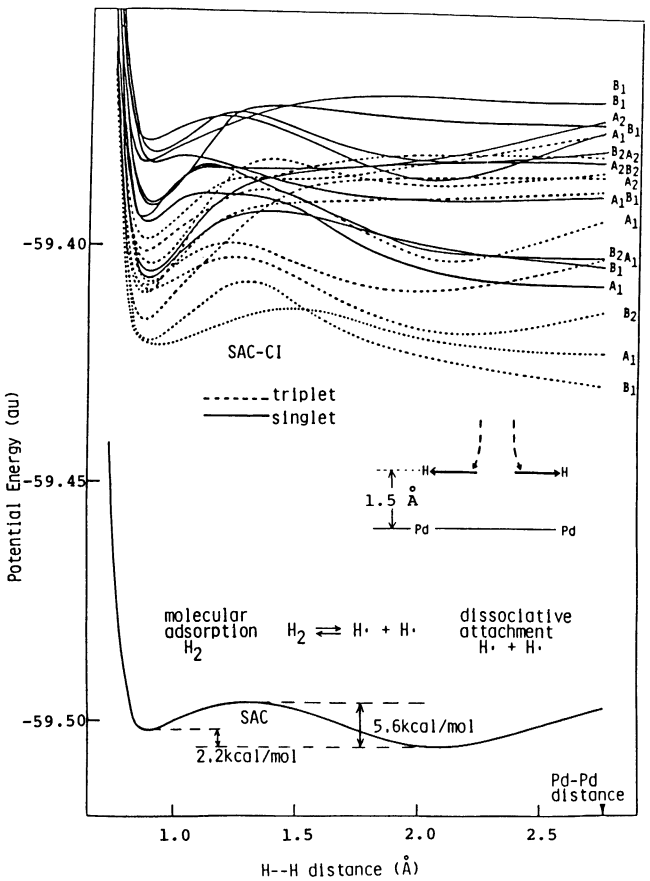

Figure 2. Potential energy curves of the ground and excited states of the Pd_2–H_2 system as a function of the H–H distance of the H_2 molecule at 1.5 Å from the Pd_2 fragment (SAC and SAC–CI methods).

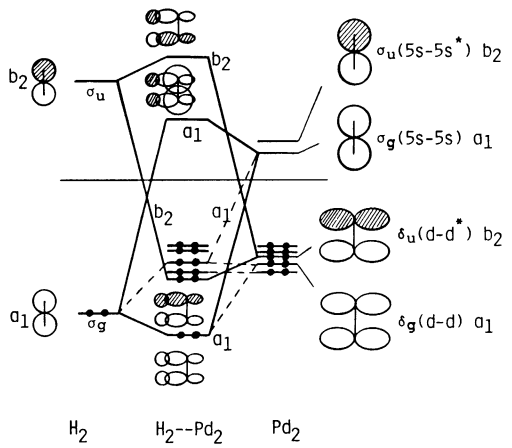

Figure 3. Schematic orbital correlation diagram for the interaction of H_2 and Pd_2.

existence of a smooth equilibrium between molecular hydrogen and two atomic hydrogen radicals on the metal surface, i.e.,

$$H_2 \rightleftarrows H\cdot + H\cdot$$

On the surface 1.5 Å apart from the metal, the dissociative form is more stable than the molecular form by 2.2 kcal/mol and the barrier height is 5.6 kcal/mol. However, since the motion along the metal surface was not energetically optimized, the actual barrier could be smaller. We note that at the second minimum, the Pd–H distance is ~1.5 Å, which is close to the experimental internuclear distance of a free PdH molecule, 1.529 Å.[12]

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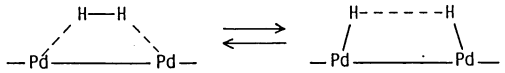
From these results, we conclude that the interaction of the hydrogen molecule with palladium is attractive and that the Pd_2 system is the smallest possible system that shows the catalytic activity for the dissociative adsorption of the H_2 molecule. The H_2 molecule with a binding energy of about 104 kcal/mol is dissociated, with almost no barrier, into two atomic hydrogens on the Pd_2 "surface", like on an extended surface.

From Figure 2, we see that the excited states of the Pd_2–H_2 system are well separated from the ground state, throughout the process, by more than 50 kcal/mol. There is almost no chance for the excited states to participate in the dissociative process. Therefore, we conclude that the mechanism of the dissociative adsorption of the H_2 molecule on the Pd surface is different from that proposed for a Ni surface by Melius et al.[4]

Then, by what mechanism does the Pd_2 show such a catalytic ability? In Figure 3, we have shown a schematic orbital correlation diagram of the Pd_2–H_2 system. It is based on the analysis of the natural orbitals of the MC–SCF calculations. The left-hand side is the MO's of H_2, the right-hand side is the valence MO's of Pd_2, and the center is for the Pd_2H_2 system. Two interactions are important. One is the electron transfer from the δ_u(d–d*) MO of Pd_2 to the antibonding MO of H_2. This transfer works to weaken the H–H bond. The other is the electron back-transfer from the bonding MO of H_2 to the bonding σ_g(5s–5s) MO of Pd_2. This back-transfer also works to weaken the H–H bond. These interactions increase as the H_2 approaches the Pd_2, and finally lead to a cleavage of the H–H bond. Other implications of this diagram are that the d electrons are important in the newly formed Pd–H bond and that the Pd–Pd bond is *not* weakened (rather strengthened) by the adsorption of H_2. The last point is because, on the Pd_2 side, the electron goes out from the antibonding δ_u MO and comes in to the bonding σ_g MO. This aspect seems to be important in relation to the stability of the catalyst, implying that the Pd atom is not exfoliated as a PdH molecule from the metal surface. We note that these $4d_\delta$ and 5s AO's constitute the so-called "dangling" bonds of the metal surface. This mechanism may be simplified as the bond alternation mechanism shown below.



We have obtained a density profile which confirms such a bond alternation.

The present result that even Pd_2 has catalytic activity for the H_2 cleavage shall suggest a design of the palladium catalyst not as a solid but in a more "molecular" form. Molecular beam experiment will also be interesting.

Lastly, we briefly summarize the calculational method used. The accuracy of the method was tested for the PdH molecule.[13-15] The Gaussian basis set for the Pd atom is a (3s3p3d)/[3s2p2d] set and the Kr core was replaced by an effective core potential.[16] For hydrogen, we used the (4s)/[2s] set of Huzinaga–Dunning[17] plus p-type functions which are the first derivatives of the [2s] set. The Hellmann–Feynman theorem is then essentially satisfied for the force acting on the hydrogen nuclei.[18] In the CAS–MC–SCF calculation,[6] we used a modified version of the GAMESS program[19] and adopted 8 (lower) × 2 (upper) active orbital spaces for Pd_2H_2. The SAC and SAC–CI methods[10,11] include a much larger amount of electron correlation than the MC–SCF method. More details will be given elsewhere in the literature.

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(13) To confirm the accuracy of the present calculational method, we carried out the CAS–MC–SCF calculation of the PdD molecule. The ground state was $^2\Sigma^+$ in agreement with experiment. The calculated values of the equilibrium geometry, vibrational frequency, dissociation energy, and dipole moment are 1.570 Å (1.529 Å), 1496 cm^{-1} (1446 cm^{-1}), 54 kcal/mol (~76 kcal/mol), and 2.81 D (1.977 D), respectively, with the values in the parentheses being the experimental values.[12,14] The present result may also be compared with the result of Pacchioni, Koutecky, et al.[3,15]

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