

# Dipped adcluster model for chemisorptions and catalytic reactions on a metal surface

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We propose a model for chemisorptions and surface reactions in which "adcluster" (admolecule + cluster) is dipped onto the electron "bath" of a solid metal and an equilibrium is established for the electron and/or spin transfer between them. The equilibrium condition is described with the use of the chemical potentials of the adcluster and the solid surface. Since the adcluster is a partial system, the number of the transferred electrons  $n$  is not necessarily an integer. Some typical behaviors of the energy  $E(n)$  of the adcluster are explained. A molecular orbital model is proposed to calculate the energy  $E(n)$  and the electronic structure of the adcluster. The electrostatic energy due to a charge polarization is also important though it is insensitive to the chemical structure of the adcluster. Sample application is given for the Pd-O<sub>2</sub> system.

## I. INTRODUCTION

Chemisorptions and surface reactions like catalytic reactions involve a formation of a chemical bond between a solid surface and an admolecule. In the delocalized model, this interaction is described as a coupling between the orbitals of the admolecule and the band electrons of the solid.<sup>1-4</sup> There, the local states on the surface and the extended nature of the solid are, in principle, described in equal footing, though it is difficult to calculate both of these features in chemical accuracy (in kcal/mol). This method is particularly useful for studying the properties of the solid metal on adsorption of atoms and molecules.<sup>4</sup> A method for improving the description of the molecule-solid surface interactions using CI treatment and larger basis set for the local surface region was also proposed.<sup>5</sup> In the cluster model, on the other hand, the interaction between a molecule and a small cluster of metal atoms is studied as a model of the interaction on a real surface. Quantum chemical studies of catalytic processes mostly use this model. Since the size of the system can be made small, the advanced theories of quantum chemistry can be applied for investigating this interaction in chemical accuracy. Electron correlation is sometimes very important<sup>6,7</sup> and the catalytically active states often involve lower excited states of the cluster as well as the ground state.<sup>8</sup> For example, the chemisorptions of a hydrogen molecule on Ni,<sup>6</sup> Pd,<sup>7</sup> and Pt<sup>8</sup> surfaces and the succeeding hydrogenation reaction of acetylene on Pd<sup>9</sup> have been studied successfully by this model.

The lattice size of a metal surface is usually larger than the bond distance of ordinary molecules. For example, the lattice sizes of alkali metals and transition metals are 3-5 and 2.5-3 Å, respectively, while the typical H-H, C-C, and O-O distances are 0.75-1.6 Å.<sup>10</sup> The van der Waals radii of the first row atoms are 1-1.5 Å.<sup>10</sup> Thus, the molecule approaching on a surface can see only a few atoms of the surface. This locality of the interaction is a basis of the cluster model. However, when only a few metal atoms are isolated out from the surface, it cannot exchange electrons and spins with the metal bulk. There are cases in which electron transfer is crucial as an elementary process: oxygen and halogen chemis-

orptions on a metal surface<sup>11,12</sup> and an addition of alkali metals as promoters and cocatalysts.<sup>13</sup> Generally speaking, the ability of a metal surface for dissociative adsorption increases with increasing electronegativity difference between an admolecule and a metal.<sup>14</sup> There is a rough correlation between electronegativities and Fermi energy levels of metals.<sup>15</sup> The elementary process of the scanning tunneling microscope (STM)<sup>16</sup> also involves the electron transfer between needle atoms and the surface of a substrate.

We define "adcluster" as a combined system of a metal cluster and admolecules (and adatoms) on it. We here propose a model in which the adcluster is "dipped" onto the electron "bath" of the solid metal and an equilibrium is established for the electron exchange between the adcluster and the bulk metal. This equilibrium would be defined by

$$\frac{\partial E(n)}{\partial n} = -\mu, \quad (1)$$

where  $E(n)$  is the energy of the adcluster with  $n$  being the number of electrons transferred from the solid into the adcluster and  $\mu$  the chemical potential of the electrons of the metal surface. The electron transfer occurs until the chemical potential of the adcluster (left-hand side<sup>17</sup>) becomes equal to that of the electrons of the surface  $\mu$ . Since the adcluster is not a total system but a partial system,  $n$  is not necessarily an integer. We call this model the *dipped adcluster model*. (The conventional cluster model corresponds to the isolated adcluster model.) Since  $E(n)$  is not necessarily a monotonic function of  $n$ , as shown below, this equation should be extended in general as follows:

*The adcluster is at the min[ $E(n)$ ] in the range*

$$\frac{\partial E(n)}{\partial n} < -\mu. \quad (2)$$

When a reverse flow of electrons is considered,  $n$  in the above equations should be replaced by  $-n$ .

For metals, Fermi levels and work functions are used for  $\mu$ , and for semiconductors and insulators  $I_p$  (or  $E_v$ ),  $E_a$  (or  $E_c$ ), or the Mulliken's electronegativity  $(1/2)(I_p + E_a)$  is used for  $\mu$ , depending on the nature of the electron transfer under consideration. For some metals, the chemical poten-

tial for the density of active states may be used. The effects of promoters, cocatalysts, and supports are taken into account through  $\mu$ , as well as the effects of temperature, light, electric potential, etc. In the dipped adcluster model, the cluster atoms need not supply all the electrons transferred into the admolecule: some are supplied from the electron bath of the solid metal. The metal atoms of the adcluster play not only as an interaction counterpart of the admolecule, which is chemically very specific, but also as a passage of electrons and spins. The charge polarization locally produced in this way is also very important. We give below a molecular orbital model for calculating the electronic structure and the energy  $E(n)$  of the dipped adcluster as a function of  $n$ . Some typical behaviors of the  $E(n)$  curve are illustrated and the implications are explained. Test applications are given for the palladium- $O_2$  system.

## II. BEHAVIOR OF THE $E(n)$ CURVE AND THE IMPLICATIONS

Let us consider general behaviors of the energy  $E(n)$  of the dipped adcluster as a function of  $n$  and the implications of the equilibrium conditions given by Eqs. (1) and (2). Generally speaking,  $E(n)$  is a continuous function of  $n$ , but its derivative is not necessarily continuous at  $n$  being an integer.<sup>17</sup> Several typical behaviors of the  $E(n)$  curve are illustrated in Fig. 1. In case A, (1) the gradient becomes  $-\mu$  at  $n = n_0$ , and (2) in the region  $\partial E(n)/\partial n < -\mu$  the minimum energy is lower than the energy of the initial state  $E(0)$ . In case A-1, (3) the curvature is lower convex, and in case A-2, (3) the curvature is upper convex. In case A-1, the electrons flow into the adcluster up to  $n_0$ , as Eq. (1) implies, since the potential of the adcluster is lower than that of the electron of the metal. The energy of the adcluster is  $E(n_0)$ .

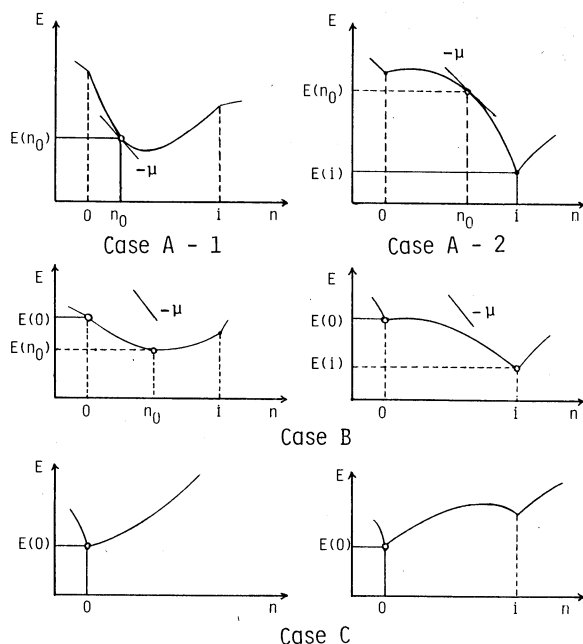


FIG. 1. Some typical behaviors of the  $E(n)$  curve as a function of  $n$ , the number of electrons transferred into the adcluster. On the horizontal axis,  $i$  denotes an integer number of electrons. The gradient  $\mu$  is the chemical potential of the metal surface.

In case A-2, there is a barrier for electron flow: the electron flow would not occur until  $n_0$  electrons "sink" into the adcluster through, say, a tunneling effect or an activation, but afterwards, the electrons flow into it up to  $i$ , as Eq. (2) indicates, with  $i$  being an integer. At  $n = i$ , the system is most stable, and when  $n$  exceeds  $i$ , the potential suddenly becomes very high (even positive), so that the electron flow ceases at  $n = i$ . The energy of the system is  $E(i)$ . It is interesting to note that in case A-2, the transfer of an *integral* number of electrons has resulted in very naturally, so that case A-2 is, in some sense, quantum. We note that, case A-1 has occurred for the paired spin coupling and case A-2 for the highest spin coupling explained below.

In case B, (1) there is a region of  $n$  where  $E(n)$  is lower than  $E(0)$ , but (2) the gradient is smaller than  $\mu$  in that region. In this case, the electron flow does not occur, since the potential of the metal is always lower than that of the adcluster. However, when the chemical potential of the metal is modified by an addition of promoters, raising temperature, applying electric field, exposing it to light, etc., the electron flow may be able to be realized. Such a device is important for catalyst design.

In case C, (1)  $E(0)$  is most stable in some wide region of  $n$ . In this case, the electron transfer can not be expected, and the isolated adcluster model, which is the conventional cluster model, would be appropriate.

We note that the above case is not an intrinsic property of the admolecule-solid pair, but a property depending on the distance, geometry, etc., and other external conditions as described above. In particular, when an electric potential is applied between an admolecule and a solid, as in STM, the electron flow would be facilitated and regulated. In the above considerations, an electron flow from the bulk metal to the adcluster has implicitly been assumed. The reverse flow is realized simply by changing  $n$  to  $-n$ .

## III. MOLECULAR ORBITAL MODEL OF THE DIPPED ADCLUSTER

We here propose a molecular orbital model of the dipped adcluster and calculate the energy  $E(n)$  and the electronic structure. We assume that the adcluster exchanges electrons and spins with the solid through its HOMO (highest occupied MO), LUMO (lowest unoccupied MO), SOMO (singly occupied MO), or some other active MO, with the other MO's being doubly occupied or completely unoccupied. Such active MO is denoted by  $m$ . Two types of spin coupling are assumed for the electrons occupying the  $m$ th MO. One is called *highest spin coupling*, in which the  $m$ th MO is first occupied by  $\alpha$  spin electron and after its occupation becomes equal to unity, it is then occupied by  $\beta$  spin electron. The other is *paired spin coupling* in which the same amounts of  $\alpha$  and  $\beta$  spin electrons occupy the  $m$ th MO. The energy of the adcluster with  $x$  electrons occupying the  $m$ th MO, which is assumed to be nondegenerate, is given by

$$E^{(0)} = 2 \sum_k H_k + \sum_{k,l} (2J_{kl} - K_{kl}) + x \sum_k (2J_{km} - K_{km}) + xH_m + Q, \quad (3)$$

where  $k, l$  run over the doubly occupied MO's.  $H_k, J_{kl}$ , and  $K_{kl}$  denote core-Hamiltonian integral, Coulomb repulsion integral, and exchange repulsion integral, respectively. The meaning of the superscript (0) will be self-evident later. The quantity  $Q$  represents the electron repulsion in the active orbital  $m$  and depends on the spin coupling described above. It is given by

$$Q = \|x - 1\|J_{mm} \quad (4a)$$

for the highest spin coupling and

$$Q = (x/2)^2 J_{mm} \quad (4b)$$

for the paired spin coupling. Here,  $\|a\| = 0$  if  $a < 0$ ,  $\|a\| = a$  if  $0 \leq a \leq 1$ , and  $\|a\| = 1$  if  $a > 1$ . It is easy to prove that  $Q$  is minimum for the highest spin coupling and maximum for the paired spin coupling. Therefore, the energy of the adcluster itself is lowest in the highest spin coupling. The actual preference of the spin coupling would also depend on the nature of the solid and of the interaction between the adcluster and solid. For example, when some amount of  $\alpha$  spin is transferred from the solid metal to the adcluster, the system is spin polarized near the adcluster.

When the orbital  $m$  is twofold degenerate, the energy of the dipped adcluster is calculated as

$$E^{(0)} = 2 \sum_k H_k + \sum_{k,l} (2J_{kl} - K_{kl}) + \frac{x}{2} \sum_k \sum_m (2J_{km} - K_{km}) + \frac{x}{2} (H_m + H_n) + Q, \quad (5)$$

where  $Q$  is written as

$$Q = \|x - 1\|(J_{mn} - K_{mn}) + \|x - 2\|J_{mn} + \|x - 3\| \times (2J_{mn} - K_{mn}) + \|\frac{1}{2}(x - 2)\|(J_{mm} + J_{nn}) \quad (6a)$$

for the highest spin coupling and

$$Q = \left(\frac{x}{4}\right)^2 \sum_m \sum_n (2J_{mn} - K_{mn}) \quad (6b)$$

for the paired spin coupling.

When  $n$  electrons flow from the solid into the adcluster, positive  $n$  holes are created in the solid near the adcluster. The electrostatic interaction due to this charge polarization is important for stabilization of the system, so that the holes in the solid would not easily be neutralized. If these  $n$  holes are distributed to the  $M$  solid atoms, nearest neighbor to the metal atoms of the adcluster, the gross charge  $g$  of such solid metal atoms is  $n/M$ . The molecular orbital of the adcluster may be calculated under the influence of the electrostatic field of these positive holes with the use of the energy expression given by

$$E^{(1)} = - \sum_k \lambda_k \langle \psi_k | \sum_R g_R / r_R | \psi_k \rangle + \sum_A \sum_R Z_A g_R / R_{AR} + \sum_{R>S} g_R g_S / R_{RS}, \quad (7)$$

or such electrostatic interaction is taken into account after solving the MO's without such field by

$$E^{(1)} = \sum_A \sum_R g_A g_R / R_{AR} + \sum_{R>S} g_R g_S / R_{RS}, \quad (8)$$

where  $A$  runs over the atoms of the adcluster,  $R, S$  over the solid metal atoms, and  $\lambda_k$  is the occupation number of the MO  $\psi_k$ . The energy of the system thus becomes

$$E = E^{(0)} + E^{(1)}. \quad (9)$$

The geometry of the solid surface, such as (111) and (100) planes and a step, kink, terrace, etc., is described by the structure of the cluster part of the adcluster and by the spatial distribution of the holes in Eqs. (7) and (8). Because of the long-range nature of the Coulombic interaction, the electrostatic energy  $E^{(1)}$  is insensitive to the detailed chemical structure of the adcluster.

The energy of the open-shell restricted Hartree-Fock (RHF) method is written as<sup>18</sup>

$$E = \sum_k \lambda_k H_k + \frac{1}{2} \sum_k \sum_l \lambda_k \lambda_l (\alpha_{kl} J_{kl} - \beta_{kl} K_{kl}). \quad (10)$$

By a comparison between Eq. (10) and Eqs. (3) or (5), the occupation parameter  $\lambda_k$  and the spin coupling parameters  $\alpha_{kl}$  and  $\beta_{kl}$  in Eq. (10) are fixed. So, performing the RHF-MO SCF calculation involving the nonintegral occupation number  $x$ , we obtain the molecular orbitals and the energy  $E(x)$ .

The molecular orbital model of the dipped adcluster given above may be viewed in a different way, as described in the Appendix. Namely, the molecular orbitals of the dipped adcluster under the electrostatic influence of the surrounding solid atoms are obtained from the MO formalism for the total (adcluster plus solid) system with the approximations, zero-differential overlap and zero bond order between the AO's belonging to the adcluster and the surrounding solid. Namely, in this approximation, the Fock matrix of the total system is written in a block-diagonal form of the Fock matrices of the adcluster and the solid. The same is true for the overlap matrix. Therefore, the adcluster and the solid system are *separately* solved with mutually giving electrostatic influences. The number of the electrons of each system need not be an integer, though the sum of them should be an integer.

#### IV. PALLADIUM-O<sub>2</sub> SYSTEM

We apply the dipped adcluster model to the palladium-O<sub>2</sub> system, representing a palladium surface by a single Pd atom. The O<sub>2</sub> molecule is put at end-on, on-top position of the Pd atom, so that the adcluster is a linear Pd-O<sub>a</sub>-O<sub>b</sub> system. At an infinite separation, the O<sub>2</sub> molecule is in the <sup>3</sup>Σ<sub>g</sub> state and the Pd atom is in the <sup>1</sup>S(*d*<sup>10</sup>) state. The highest spin coupling model is adopted, since it gives a continuous picture leading to the correct separation limit, but the paired spin coupling model does not. The electrons are transferred into the degenerate π\* MO's of the PdO<sub>2</sub> system from the Pd solid. We have used Eqs. (5) and (6a) with  $x = n + 2$ . The electrostatic energy due to the charge polarization is calculated by Eq. (8). The holes produced in the solid are equally distributed to the nine Pd atoms, nearest neighbor to the Pd atom of the adcluster in the (111) plane, with six atoms in the first layer and three atoms in the second layer. The calculations have been performed with the use of the *ab initio* RHF SCF MO program. For Pd, the (3s3p3d)/[3s2p2d] set has been used for valence electrons and effective-core potential for the Kr core.<sup>19</sup> For oxygen, the 4-31G set of Ditchfield

*et al.*<sup>20</sup> has been employed.

Figure 2 is a display of the  $E(n)$  curve, calculated as a function of  $n$ , the number of the electrons transferred into the adcluster. This figure is for the Pd–O<sub>a</sub> distance fixed at 2.0 Å, which is almost the most stable distance. The O–O distance is changed from 1.207 52 Å which is an equilibrium length  $R_{\text{eq}}$  of O<sub>2</sub>,<sup>21</sup> to 1.35 Å which is an equilibrium length of O<sub>2</sub><sup>-</sup>,<sup>21</sup> and further to 1.5 Å. The chemical potential of the solid palladium metal is 5.12 eV,<sup>22</sup> which is given by the gradient in Fig. 2. Clearly, the behavior of the curves corresponds to case A-2: the curve is upper convex and the curvature is discontinuous at  $n = 0$  and  $n = 1$ . At  $n = 0$ ,  $R_{\text{OO}} = R_{\text{eq}}$  is most stable, but at  $n = 1$ ,  $R_{\text{OO}} = 1.35$  Å is most stable. The tangents of the curves coincide with the chemical potential  $-\mu$  at  $n = 0.85$ , 0.73, and 0.63 for  $R_{\text{OO}} = R_{\text{eq}}$ , 1.35 Å, and 1.5 Å, respectively. Therefore, after some barrier, one electron flows from the bulk metal into the adcluster, so that the adcluster becomes (Pd–O<sub>2</sub>)<sup>-</sup>. The energy of this charged state is lower than that of the neutral one. On the right-hand side of Fig. 2, the stabilization energy of the system, relative to the separated system Pd + O<sub>2</sub>, is given in kcal/mol. The calculated heat of adsorption is 54 kcal/mol in comparison with the experimental adsorption energy of 70.2 kcal/mol.<sup>23</sup> Since the energy at  $R_{\text{OO}} = 1.35$  Å is lower than that at  $R_{\text{OO}} = 1.5$  Å, the O–O dissociation would not occur in this adsorption mode.

Figure 3 shows the potential energy curve for the end-on approach of the O<sub>2</sub> molecule to the palladium. In the conventional cluster model, which corresponds to  $n = 0.0$ , the calculated result is that the O<sub>2</sub> molecule is not adsorbed by Pd in this orientation. This is seen from the upper curve of Fig. 3 which has been obtained for  $R_{\text{OO}}$  fixed at 1.2075 Å, the equilibrium length. A similar repulsive curve has also been obtained for  $R_{\text{OO}}$  fixed at 1.35 Å. Due to matrix isolation method, Huber *et al.* have shown that the PdO<sub>2</sub> molecule does not take an end-on geometry, but takes a side-on geometry.<sup>24</sup> The dipped adcluster model, on the other hand, gives the lower curve of Fig. 3. When the electron transfer from the solid to the adcluster is admitted, the system becomes stable as O<sub>2</sub> approaches Pd and finds a minimum at  $R_{\text{PdO}} = 2.04$  Å when  $R_{\text{OO}}$  is fixed at 1.35 Å. Imbihl and Demuth<sup>25</sup>

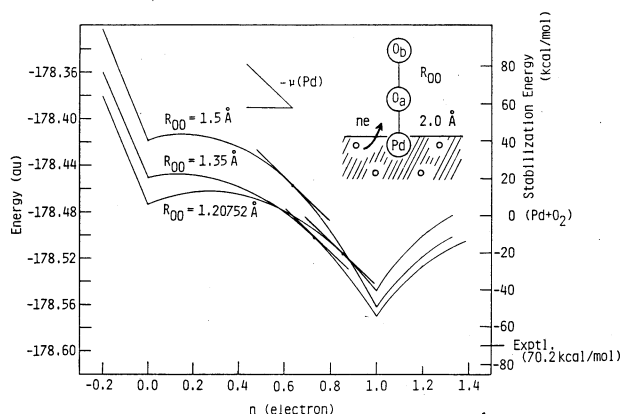


FIG. 2. Dipped adcluster model calculation with the highest spin coupling for the Pd–O<sub>a</sub>–O<sub>b</sub> system with the O–O distances of 1.207 52, 1.35, and 1.5 Å and the Pd–O<sub>a</sub> distance fixed at 2.0 Å. The energy scale on the right-hand side is in kcal/mol relative to the free Pd plus O<sub>2</sub> system.

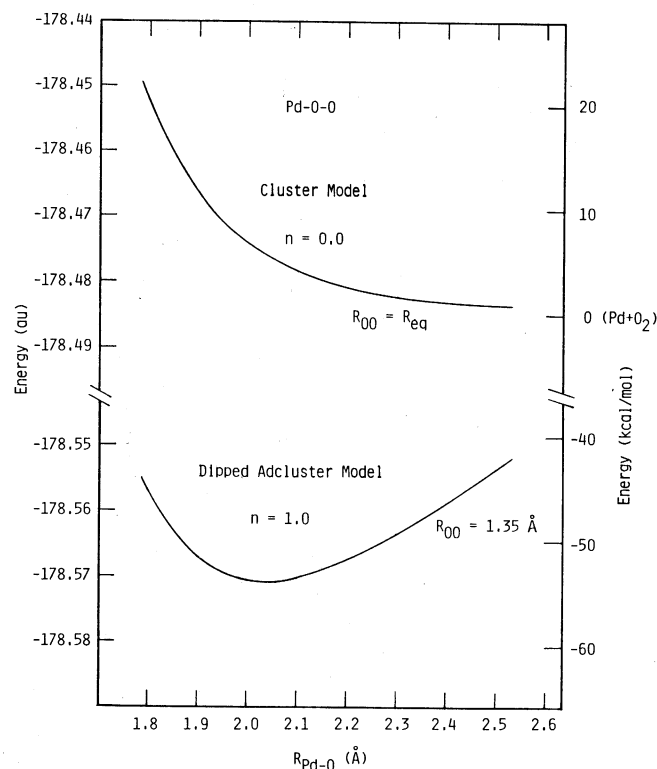


FIG. 3. Potential energy curves for the end-on approach of the O<sub>2</sub> molecule to the Pd atom in the cluster model (upper,  $n = 0.0$ ) and in the dipped adcluster model (lower,  $n = 1.0$ ). The O–O length is fixed at 1.207 52 Å (equilibrium length of the free O<sub>2</sub>) for the upper one and at 1.35 Å for the lower one. The energy scale on the right-hand side is in kcal/mol relative to the free Pd plus O<sub>2</sub> system.

reported that at 30 K, O<sub>2</sub> is adsorbed on a Pd(111) surface in a molecular form. Gland *et al.*<sup>26</sup> reported that on a Pt(111) surface, O<sub>2</sub> is adsorbed in a molecular form with an end-on geometry. Thus, for the adsorption of the O<sub>2</sub> molecule on palladium, we need the dipped adcluster model, instead of the conventional cluster model, at least when the size of the cluster is limited to be small. For this adsorption, the electron transfer from the metal to the adcluster is essentially important.

We have separately examined the side-on approach of the O<sub>2</sub> molecule to the Pd atom. In this case, the stabilization energy of about 20 kcal/mol has been calculated even for the isolated molecule, PdO<sub>2</sub> with  $n = 0.0$ , in agreement with the experiment of Huber *et al.*<sup>24</sup> Further, the heat of adsorption of the O<sub>2</sub> molecule on a Pd surface calculated for the side-on approach by the dipped adcluster model is about 56 kcal/mol in comparison with the experimental value of 70.2 kcal/mol.<sup>23</sup> The corresponding value calculated for the end-on approach is 54 kcal/mol as seen from Figs. 2 and 3. Thus, the side-on geometry is more stable than the end-on geometry in both the Pd–O<sub>2</sub> molecule and the O<sub>2</sub> molecule adsorbed on an extended Pd surface.

Figure 4 shows the calculated potential curves for the O<sub>2</sub> vibration in the free gaseous state and in the adsorbed state on Pd in the dipped adcluster model ( $n = 1.0$ ). On the surface, the O<sub>2</sub> molecule is very much relaxed. The equilibrium O–O distance is calculated to be 1.20 and 1.37 Å for the free and adsorbed states, respectively. The experimental value

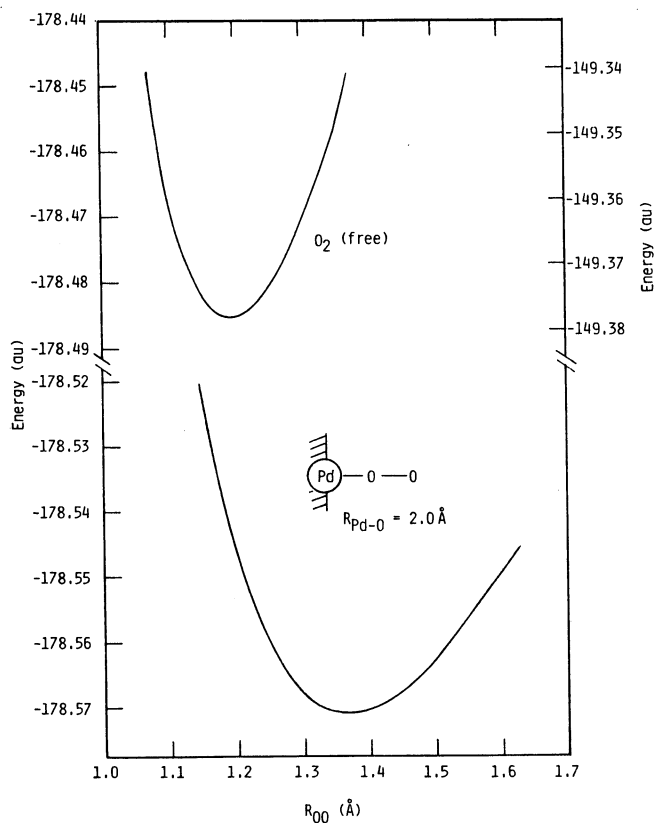


FIG. 4. Potential energy curves for the O–O vibrations of the free O<sub>2</sub> molecule (upper) and of the adsorbed O<sub>2</sub> molecule on Pd in the dipped adcluster model with the Pd–O distance fixed at 2.0 Å. The energy on the left-hand side is for the Pd + O<sub>2</sub> system and on the right-hand side for the O<sub>2</sub> molecule alone.

for the former is 1.207 52 Å.<sup>21</sup> The O–O stretching vibration frequency is calculated to be 1707 and 1023 cm<sup>-1</sup> for the free and adsorbed states, respectively, in comparison with the experimental values, 1580 and 1035 cm<sup>-1</sup>, respectively. The experimental values are due to Huber *et al.*<sup>24</sup> for the former and Imbihl *et al.*<sup>25</sup> for the latter. As seen from Fig. 4, the potential curve of the O<sub>2</sub> molecule is considerably more anharmonic on a surface than in the free state. The vibrational frequency for the Pd–O stretching mode is calculated to be 372 cm<sup>-1</sup> from the potential curve shown in Fig. 3. This value should be an underestimate since in Fig. 3 the O<sub>2</sub> molecule vibrates as a whole. The experimental value is 485 cm<sup>-1</sup> for the O<sub>2</sub> molecule on a Pt(111) surface.<sup>26</sup> A similar value 480 cm<sup>-1</sup> was reported for the Pd–O vibration of the dissociated oxygen on a Pd surface.<sup>25</sup>

TABLE I. Energy (a.u.) and atomic charge of the Pd–O<sub>a</sub>–O<sub>b</sub> system<sup>a</sup>

$R_{OO}$ (Å)	$n = 0.0^b$					$n = 1.0$					
	$E^{(0)}$	Pd	O <sub>a</sub>	O <sub>b</sub>	O <sub>a</sub> + O <sub>b</sub>	$E^{(0)}$	$E^{(1)}$	Pd	O <sub>a</sub>	O <sub>b</sub>	O <sub>a</sub> + O <sub>b</sub>
1.207 52	-178.474 28	+0.093	-0.120	+0.027	-0.093	-178.469 29	-0.079 24	-0.218	-0.480	-0.303	-0.783
1.35	-178.451 72	+0.169	-0.140	-0.029	-0.169	-178.491 80	-0.078 70	-0.193	-0.555	-0.252	-0.807
1.50	-178.419 73	+0.261	-0.063	-0.198	-0.261	-178.486 11	-0.076 49	-0.172	-0.563	-0.266	-0.829

<sup>a</sup> Pd–O<sub>a</sub> length is at 2.0 Å.

<sup>b</sup> For  $n = 0.0$ ,  $E^{(1)}$  vanishes identically.

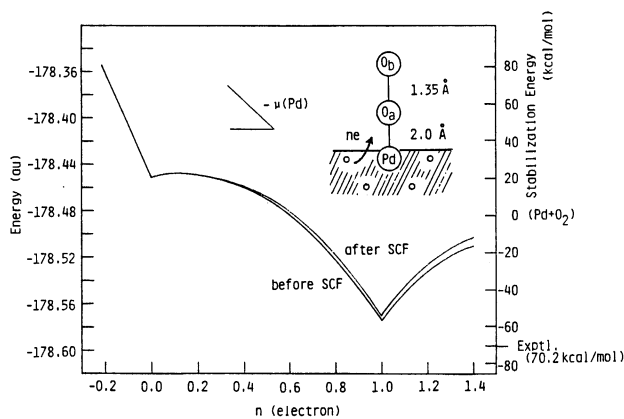


FIG. 5. Dipped adcluster model calculation with the highest spin coupling for the Pd–O<sub>a</sub>–O<sub>b</sub> system with the O–O and Pd–O<sub>a</sub> distances fixed at 1.35 and 2.0 Å, respectively. For the lower and upper curves, the electrostatic effect is included before and after SCF calculations of the MO's with the use of Eqs. (7) and (8) of the text, respectively.

When one electron is transferred to the adcluster, it is mostly distributed into the O<sub>2</sub> molecule. Table I shows the atomic charge of the PdO<sub>2</sub> system. When  $n = 1.0$ , about 0.56 electron lies on O<sub>a</sub>, 0.25 electron on O<sub>b</sub>, and 0.19 electron on the Pd atom. When  $n$  is fixed to zero, the negative charge of the O<sub>2</sub> molecule is donated only by the Pd atom, so that the amount of the electron transfer is limited and the Pd atom becomes very positively charged. In the dipped adcluster model, such electrons are offered by the electron bath of the solid metal. It is interesting to note that on palladium, the O<sub>2</sub> molecule is as if it breathes the electron gas; viz., when the O–O distance is elongated, the electron enters into the O<sub>2</sub> region and vice versa. This implies that the intensity of the vibrational peaks of O<sub>2</sub> should be larger on a metal surface than in a gas phase. There is an experimental observation for this result.<sup>27</sup>

The electrostatic interaction between the adcluster and the holes produced on the metal atoms of the solid is important for the present system. Without this interaction, the curvature of the  $E(n)$  curve is too flat to effect the electron transfer between the adcluster and the solid. Table I shows the energies  $E^{(0)}$  and  $E^{(1)}$  calculated by Eqs. (5) and (8), respectively. At  $n = 0.0$ , the electrostatic contribution  $E^{(1)}$  vanishes identically, but at  $n = 1.0$ , it amounts as large as 48–49 kcal/mol. However, we note that  $E^{(1)}$  is insensitive to the change in the molecular geometry. This is in fact our general experience; viz., the chemical difference is described by  $E^{(0)}$  rather than  $E^{(1)}$ . This is because the electrostatic

Coulombic interaction is long range in nature. Further, we have found that the account of the electrostatic effect after the SCF calculation with the use of Eq. (8) is a very good approximation to the inclusion of this electrostatic field into the SCF process of the MO's with the use of Eq. (7). Figure 5 shows the  $E(n)$  curves due to these two methods. The closeness of the two curves is surprising.

## V. CONCLUDING REMARKS

In this paper, we have proposed the dipped adcluster model for the study of chemisorptions and catalytic reactions on a metal surface which involve large electron transfer between an admolecule and a metal surface. The size of the cluster necessary to investigate such electronic processes would be reduced if the dipped adcluster model is adopted instead of the conventional cluster model. This merit is practically very important since the electron correlation is often very important to describe the model reactions on a cluster surface<sup>7</sup> and further since sometimes the catalitically active state is not necessarily the ground state but an excited state of the surface cluster.<sup>8</sup> We therefore want to make the size of the cluster as small as possible. Although we have restricted the present formulation only within the molecular orbital model, an inclusion of electron correlation is a necessary step in the future. It is also interesting to investigate the effect of the cluster size on the dipped adcluster model. If the size is large enough to be able to describe the real surface, the dipped adcluster model would, in principle, become unnecessary.

In the dipped adcluster model, it is rather easy to include the external effects such as an addition of promoters and cocatalysts, the effect of supports, temperature, electric potential, light, etc., through a variation of chemical potential  $\mu$ . We have confirmed from the application to the palladium- $O_2$  system that the dipped adcluster model gives the reasonable results in comparison with the experiments, even for those cases the conventional cluster model does not.

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## APPENDIX

The molecular orbital model of the dipped adcluster given in Sec. III may be viewed in a different way. Let us apply the molecular orbital method to the total adcluster plus solid system which is in equilibrium for the electron exchange. We use the indices  $a, b, c, d$  to denote the AO's of the adcluster,  $r, s, t, u$  for the solid AO's, and  $i, j, k, l$  for the general AO's. The Fock operator of the total system is written as

$$F_{ij} = H_{ij} + \sum_{kl} P_{kl} \{ (ij|kl) - \frac{1}{2}(ik|jl) \}, \quad (A1)$$

and the equation

$$FC = SCE \quad (A2)$$

determines the MO's of the total system. Here,  $P$  is the bond-

order density matrix,  $C$  the matrix of the LCAO-MO expansion coefficients,  $S$  the overlap matrix, and  $E$  the diagonal matrix of the orbital energy. We now introduce two approximations: (1) zero-differential overlap,  $\chi_a \chi_r = 0$ , and (2) zero bond order,  $P_{ar} = 0$  for the AO's  $\chi_a$  and  $\chi_r$ , belonging to the adcluster and solid, respectively. This approximation is similar to the one introduced for the  $\sigma$ - $\pi$  separation in the  $\pi$  electron theory of conjugated  $\pi$ -electron systems. Then, the Fock matrix of the adcluster is written as

$$F_{ab} = H_{ab} + \sum_{cd} P_{cd} \{ (ab|cd) - \frac{1}{2}(ac|bd) \} + \sum_{rs} P_{rs} (rs|ab) \quad (A3)$$

and that of the solid as

$$F_{rs} = H_{rs} + \sum_{tu} P_{tu} \{ (rs|tu) - \frac{1}{2}(rt|su) \} + \sum_{ab} P_{ab} (ab|rs) \quad (A4)$$

and the off-diagonal element between the adcluster and solid as

$$F_{ar} = -\frac{1}{2} \sum_{bs} P_{bs} (ab|rs) \quad (A5)$$

which vanishes due to the second approximation above. Then the matrices  $F$  and  $S$  become block diagonal, i.e.,

$$F = \begin{bmatrix} F^{\text{adcluster}} & 0 \\ 0 & F^{\text{solid}} \end{bmatrix}, \quad S = \begin{bmatrix} S^{\text{adcluster}} & 0 \\ 0 & S^{\text{solid}} \end{bmatrix}, \quad (A6)$$

so that the Fock equation (A2) is *separately* solved for the adcluster and the solid system with mutually giving electrostatic influences. The number of the electrons of the total system is written as

$$N = \sum_{ij} P_{ij} S_{ij} = \sum_{ab} P_{ab} S_{ab} + \sum_{rs} P_{rs} S_{rs} = N^{\text{adcluster}} + N^{\text{solid}}. \quad (A7)$$

Though  $N$  should be an integer, those of the adcluster and the solid need not be integers. We note that no electron flow between the adcluster and solid is described in this approximation. Initial number of electrons is kept throughout the SCF processes. The variation of the system with the variation in the number of the transferred electrons is calculated by performing independent calculations for a set of different  $n$ 's.

We rewrite the Fock operator of the adcluster given by Eq. (A3). The core-Hamiltonian matrix  $H_{ab}$  is written as

$$H_{ab} = H_{ab}^{(0)} - \langle a | \sum_R Z_R / r_R | b \rangle \quad (A8)$$

with

$$H_{ab}^{(0)} = \langle a | -\frac{1}{2} \Delta - \sum_A Z_A / r_A | b \rangle, \quad (A9)$$

where  $A$  and  $R$  run over the nuclei of the adcluster and solid, respectively. With the use of the approximation,

$$\begin{aligned} & \sum_{rs} P_{rs}(rs|ab) - \langle a | \sum_R Z_R / r_R | b \rangle \\ &= \langle a | \int \frac{1}{r_{12}} \cdot \rho^{\text{solid}}(2) dr_2 - \sum_R Z_R / r_R | b \rangle \\ &\approx - \langle a | \sum_R g_R / r_R | b \rangle, \end{aligned} \quad (\text{A10})$$

the Fock operator is rewritten as

$$F_{ab} = F_{ab}^{(0)} - \sum_R g_R \langle a | \frac{1}{r_R} | b \rangle \quad (\text{A11})$$

with

$$F_{ab}^{(0)} = H_{ab}^{(0)} + \sum_{cd} P_{cd} \{ (ab|cd) - \frac{1}{2}(ac|bd) \}, \quad (\text{A12})$$

where  $g_R$  is the gross charge of atom  $R$ . Using this equation and the equation

$$E = \frac{1}{2} \sum_{ab} P_{ab} (H_{ab} + F_{ab}) \quad (\text{A13})$$

we obtain the energy expression which is the basis of Eqs. (7)–(9) of the text.

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