

THEORETICAL APPROACH FOR THE ADSORPTION SITE OF CHLOROBENZENES ON THE SIMPLE MODEL CLUSTER OF A PALLADIUM CATALYST

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Introduction

Chemical disposal of organic chlorinated compounds such as polychlorinated biphenyls (PCBs) and pesticides plays an important role in protecting human health and preserving a clean environment. Among the several disposal methods, hydrogenolysis of the chlorinated compounds using hydrogen molecules with metal catalyst (that is, hydrodechlorination: abbreviated as HDC) is the safest¹. In addition, as the catalyst element for the HDC reaction, palladium is the most active component².

There are many reports on HDC under gas or liquid phase reaction using various types of palladium catalyst²⁻⁷. For example, Kraus and coworker³ studied the kinetics of HDC of chlorobenzenes with Pd/C catalyst in a flow system. In the liquid phase, we examined the HDC of chlorobenzene (abbreviated as CLB) and *para*-amino, methoxy, methyl, chloro, acetyl and cyano substituted chlorobenzenes (abbreviated as CLAN, CLAS, CLTN, DCLB, CLAP and CLBN, respectively) over Pd/C catalyst⁷, and reported that the HDC reactivities were decreased in the order of CLAN < CLAS < CLTN < CLB; CLBN < CLAP < DCLB < CLB, respectively. In relation with the adsorption state and/or the active site on the Pd catalytic surface, however, the reaction mechanism such as the electronic factors affecting the HDC reactivity requires further clarification.

In the present study, quantum calculation by density functional theory (DFT) in B3LYP/LANL2DZ system is applied to several types of "chlorobenzenes-the simple model cluster (Pd₁₀)" complexes that are constructed as the initial geometry, and the adsorption state and/or energy on the catalytic site are checked in connection with the actual HDC reactivity reported previously⁷.

Materials and Methods

The optimization for the initial geometry of "chlorobenzenes-Pd₁₀ cluster" complexes was performed according to spin-restricted density functional theory (DFT: B3LYP/LANL2DZ)^{8,9}, using Gaussian03W software package (Rev.B.04 or D.01) on Windows 2000 or XP. The B3LYP is a hybrid functional method that includes a mixture of Hartree-Fock exchange with DFT. In addition, the used basis set of LANL2DZ¹⁰⁻¹² utilizes D95V (Dunning/Huzinaga valence double-zeta (DZ)) on first row elements from H to Ne, and adapts both inner core orbitals exchanged by Los Alamos effective core potentials (ECPs) and outer valence orbitals of double-zeta on heavy atoms from Na to Bi. The convergence criteria of the maximum force, RMS force, maximum displacement and RMS displacement were below 0.00045, 0.0003, 0.0018 and 0.0012 (default values), respectively. The catalytic model of the Pd₁₀ cluster, of which the lattice constant (a) is 0.389 nm in the point group of O_h⁵-Fm3m (No.225, fcc), was constructed using the "displat" program in the DV-X α ¹³ software distribution. Prior to constructing the "chlorobenzenes-Pd₁₀" complexes, the organic part of the complexes was optimized using the B3LYP/LANL2DZ system.

During the course of the optimization process of the model complexes, the mobile space of the chlorine atom was limited in a range in which the molecular axis is the intersection between the molecular plane (benzene ring) and the vertical reflection plane (σ_v) of the Pd₁₀ model cluster. Except for the chlorine atom, the organic parts were fully optimized. On the other hand, the geometry of the Pd₁₀ cluster was fixed. Except for the CLAS and CLAP complexes, as a result, the complex maintained Cs symmetry property to the vertical reflection plane (σ_v) in the optimization process.

Results and Discussion:

Searching the suitable adsorption point

Various types of adsorption sites were expected in the model catalyst (Pd_{10}) surface, six representative types of “chlorobenzene (CLB)- Pd_{10} cluster” complexes were constructed as an initial geometry (Fig. 1) and the DFT calculations were applied to those complexes in order to search for the most suitable adsorption site where the dissociative adsorption of the C-Cl bond takes place. In the initial geometry, the atomic distance between the chlorine atom of CLB and the palladium atom of the adsorption site in the Pd_{10} model cluster was standardized to 2.0 Å for all six types of model. Furthermore, the molecular plane of CLB was parallelized to the cluster (111) plane in the initial models of type I and type III, and the plane of CLB was inclined to the crystal plane or the ridge line of the cluster at an angle of 45.0° in the models of type II, type IV and type V. In the case of type VI, the molecular plane was inclined to the (111) crystal plane at an angle of 175.0°. Those initial geometries are summarized in Table 1, respectively.

Table 1 Adsorption states of “chlorobenzene-the Pd_{10} model cluster” in initial and final geometry

	type I	type II	type III	type IV	type V	type VI
Initial geometry						
$\text{Pd}_2\text{-Cl}$ distance: l (Å)	2.0	2.0	2.0	2.0	2.0	2.0
$\text{C}_1\text{-Cl}$ distance (Å)	1.825	1.825	1.825	1.825	1.825	1.825
Angle $\text{Pd}_1\text{-Pd}_2\text{-Cl}$ (°)	90.0	90.0	90.0	90.0	90.0	160.5
Angle $\text{Pd}_2\text{-Cl-C}_1$ (°)	90.0	135.0	90.0	135.0	135.0	175.0
Final geometry						
$\text{Pd}_2\text{-Cl}$ distance: l (Å)	2.814	2.799	2.697	2.788	2.646	2.641
$\text{C}_1\text{-Cl}$ distance (Å)	1.840	1.865	1.852	1.869	1.848	1.849
Angle $\text{Pd}_1\text{-Pd}_2\text{-Cl}$ (°)	80.25	109.96	82.27	68.92	143.02	175.40
Angle $\text{Pd}_2\text{-Cl-C}_1$ (°)	93.27	64.23	91.77	102.50	110.62	112.18

In the optimized geometry except for type VI, CLB adsorbed with a chlorine atom on each metallic site at a distance (Cl-Pd_2) of ca. 2.6-2.8 Å and the carbon-chlorine atomic distance ($\text{C}_1\text{-Cl}$) is lengthened at ca. 0.015-0.044 Å. As seen in Table 1, in fact, the magnitude of the Cl-C_1 distance is increased in the order of type IV < type II < type III < type VI < type V < type I, showing that the Cl-C_1 bond is expanded most easily on the ridge line site of the model catalyst. These results suggest that the dissociative adsorption occurred on the catalytic surface of the cluster. On the other hand, as seen in Fig. 1, the magnitude of the adsorption energy (absolute value) of the CLB is decreased in the following order: type II < type III < type I < type IV < type V \approx type VI. From the standpoint of the adsorption energy, it is suggested that the adsorption of chlorobenzenes on the (111) crystal plane are more stable than that of CLB on the ridged line or the top of the tetrahedral cluster. In the following section, the adsorptions of *para*-substituted chlorobenzenes on both the (111) plane and the ridged line of the cluster are examined.

Adsorption of substituted chlorobenzenes on (111) crystal plane

When the DFT calculation applied to the “substituted chlorobenzenes-Pd₁₀ cluster” complex, in which the chlorine atom of chlorobenzenes is put on the center palladium atom of the base of the triangular (111) plane at a height of 2.0 Å and the aromatic ring of the chlorobenzenes is laid parallel to the (111) plane (type I in Fig. 1), the dissociative adsorption of C-Cl bond was observed in all the chlorobenzenes of the optimized structures. Although the dissociative adsorption on the (111) plane occurred in the other two types of complexes (type II and III in Fig. 1), as seen in Fig. 2, the regularity in the order of the magnitude of the adsorption energy (absolute value) was only obtained in the type I complex: CLAN < CLTN < CLAS < CLB for the chlorobenzenes of the electron-donating substituent, and DCLB < CLB < CLAP < CLBN for the electron-withdrawing substituent, respectively. Except for DCLB, this order of the chlorobenzenes possessing the electron-withdrawing substituent is similar to that of the actual HDC reactivity reported previously⁷. For the HDC of substituted chlorobenzenes of the electron-withdrawing substituent, the palladium atom existing in the edge part of the (111) plane may be useful for the active site of the actual Pd/C catalyst.

Adsorption of substituted chlorobenzenes on the ridged line part

Except for CLAP, when the chlorine atom of the substituted chlorobenzenes is put on the center palladium atom of the ridge line of the Pd₁₀ cluster at a height of 2.0 Å and the molecular plane is banked on the ridge line at an angle 45° of the molecular axis (type IV), the dissociative adsorption also occurred between the C-Cl bond in the optimized structure. In the case of CLAP, the DFT calculation did not converge to the stationary point. Furthermore, the adsorption energy in the type IV complex is decreased in the order of CLAN < CLTN ≈ CLAS < CLB, and CLB < CLBN < DCLB, respectively (Fig. 3). This order of the adsorption energy for

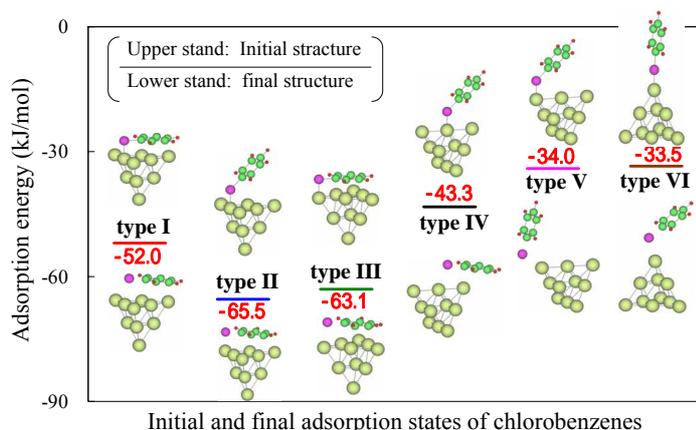


Fig.1 Adsorption energy of chlorobenzenes depending on the adsorption state on the Pd₁₀ cluster

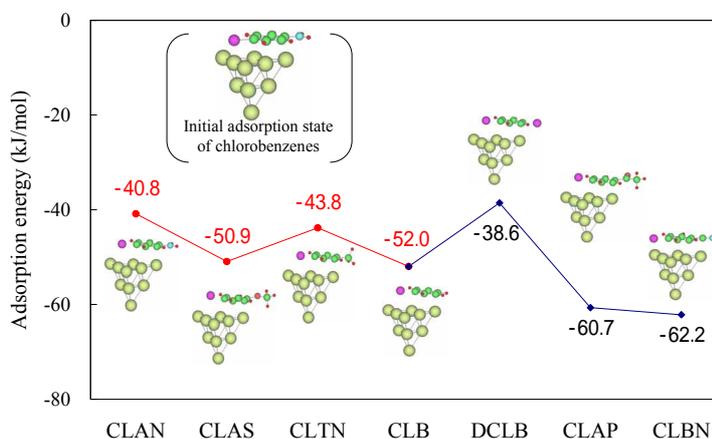


Fig.2 Adsorption energy of chlorobenzenes (type I) on the plane of the Pd₁₀ cluster

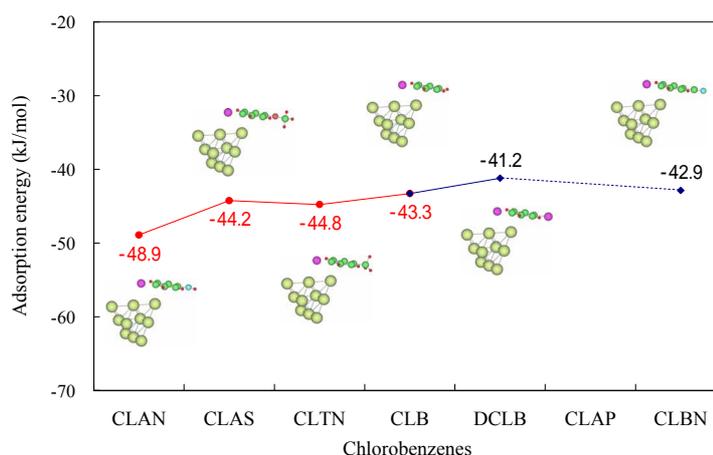


Fig.3 Adsorption energy of chlorobenzenes in type IV adsorption on the edge site of the Pd₁₀ cluster

the chlorobenzenes having the electron-donating substituent is similar to that of the previous experimental reactivity⁷. As a catalytic site, the palladium atom in the ridge line of the catalyst may play an important role for the HDC of the substituted chlorobenzenes with the electron-donating substituent.

Orbital interaction between the chlorobenzenes with the electron-donating substituent and the Pd₁₀ model cluster

To clear up the electronic factors affecting the adsorption stability, for type IV complexes, the features of the orbital interaction between the chlorobenzenes and the model catalyst were checked from the viewpoint of the energy levels of both the chlorobenzenes and the model cluster. As a representative result, the orbital interaction in the CLAN-Pd₁₀ complex is shown in Fig. 4. In the interaction between CLAN and the Pd₁₀ cluster, as shown in Fig. 4, HOMO of CLAN (-0.2065 eV) was predicted to interact with both LUMO (-0.1488 eV) and the doubly-degenerated (HOMO-14) of the cluster, and (HOMO-39) (-0.2589 eV) as the bonding molecular orbital and (LUMO) (0.1322 eV) as the anti-bonding molecular orbital were produced finally. When the molecular plane of CLAN was included in the x-y plane, in the (HOMO-39) orbital, the *p_z*-type orbital on the carbon atom in the C-Cl bond was overlapped by the same phase as the *p_z*-type orbital on the corner palladium atom of the cluster. Furthermore, a node was observed between the *p_z*-type orbital on the carbon atom and that on the chlorine atom. Such feature in the orbital interaction is advantageous to the dissociative adsorption of the chlorobenzenes on the catalytic surface. A similar manner of orbital interaction was observed in all the chlorobenzenes of the type IV complexes. The results described above suggest that the magnitude of the energy levels between HOMO of the chlorobenzenes with the electron-donating substituent and LUMO of the cluster play an important role in the adsorption stability of the chlorobenzenes.

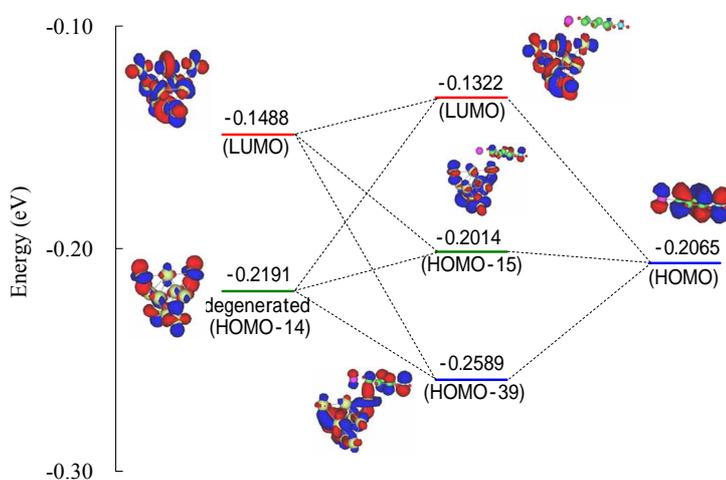


Fig.4 Orbital interaction between HOMO of chloroaniline and both LUMO and HOMO-14 of the Pt₁₀ cluster

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