THEORETICAL APPROACH FOR THE FACTORS AFFECTING THE HYDRODECHLORINATION REACTIVITY OF CHLOROBENZENES OVER A PLATINUM CATALYST

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Abstract

In order to investigate the factors affecting the hydrodechlorination (HDC) reactivity of organic chlorinated compounds over a platinum catalyst, the adsorption energy of chlorobenzene and *para*-substituted chlorobenzenes on the model cluster of platinum metal crystal were calculated according to the density functional theory (DFT) method, and the relevance to the adsorption energy of the HDC reactivity was checked in connection with a dissociative adsorption of the carbon-chlorine bond of the chlorobenzenes on the catalyst. When a platinum cluster (Pt_{10}) constructed of four Pt (111) planes on crystallography was used as a model cluster, the chlorobenzenes adsorbed on the edge though the chlorine atom with the angle of the molecule axis at about 20 to 23 degrees, and the carbon-chlorine bond length was extended. For all chlorobenzenes possessing electron-donating and electron-withdrawing substituents, the adsorption stabilization decreased in the order of *p*-chloroaniline (CLAN) > *p*-chlorotoluene (CLTN) ≥ *p*-chloroanisole (CLAS) > chlorobenzene (CLB) and chlorobenzene (CLB) > *p*-dichlorobenzene (DCLB) >> *p*-chlorobenzenetrifluoride (CLTF). These adsorption energies are ca. -48 to +5kJ/mol in the above system. The reason for the adsorption stability of these chlorobenzenes on the Pt_{10} cluster is discussed from the standpoint of energy level according to frontier orbital theory.

Introduction

Since most organic chlorinated compounds involved in industrial waste and household garbage are toxic substances[1], their detoxification is a very important process for maintaining a clean environment. In the various methods of detoxification of these chlorinated compounds, catalytic hydrogenolysis is the safest method.

In order to shed light on the factors affecting the hydrodechlorination (HDC) of the reactivity of organic chlorinated compounds, recently, we studied the HDC of chlorobenzene (CLB) and five types of *para*-isomers (*p*-chloroaniline, *p*-chloroanisole, *p*-chlorotoluene, *p*-dichlorobenzene, *p*-chlorobenzenetrifluoride; abbreviated as CLAN, CLAS, CLTN, DCLB, CLTF, respectively) on the platinum catalyst[2], and reported that the HDC reactivity of these substituted chlorobenzenes was related to the degree of electron-donating or electron-withdrawing ability of the substituent as well as the electronic property of the metal catalyst. Furthermore, we obtained the interesting result that the chlorobenzenes with higher HDC reactivity show a larger absolute value of the adsorption energy using quantum calculation by the density functional theory (DFT) method for the simple complex model of “chlorobenzenes-Pt_{14} cluster”.

Although the above calculation result might provide some clues for the reaction mechanism, we need more detailed research on the adsorption states of chlorobenzenes, because the optimized structure obtained in our calculation was not the dissociative adsorption among the carbon-chlorine bond but the one-point adsorption through the chlorine atom of chlorobenzenes onto the corner platinum atom of the Pt_{14} cluster.

In the hydrogenolysis of mono-halogenated benzenes over the sulfided Ni-Mo/Al_2O_3, Ni-W/Al_2O_3 and Co-Mo/Al_2O_3 catalysts, in fact, Moreau *et al.*[3, 4] suggested that the cleavage of the C_{sp2}-X (X: Br, Cl, F) bond occurs via the two-site adsorption of a molecule. From the kinetic study for the hydrogenolysis of chlorobenzenes and chlorocyclohexanes on a nickel-chromina catalyst, furthermore, Serguchev *et al.*[5] proposed the HDC reaction mechanism in which the dissociative adsorption of the C-Cl bond occurred.

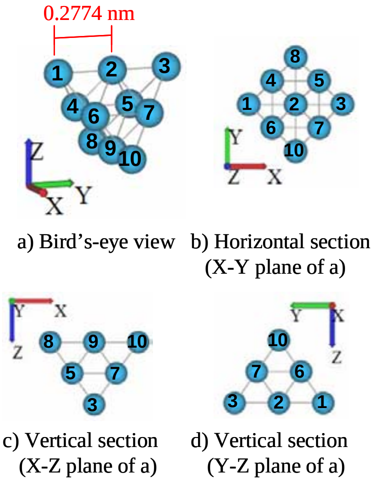
In this presentation, therefore, we aim to describe the dissociative adsorption mechanism, and calculate a stable point of chlorobenzenes on a regular tetrahedron structure of platinum atoms (Pt_{10} cluster) constructed of four (111) planes.

Materials and Methods

Quantum calculations were performed according to the spin-restricted density functional theory (DFT) method[6,

[7] implemented in the software package of GAUSSIAN03 (Gaussian, Inc., Rev.C.01) or GAUSSIAN03W (Rev.D.01). Geometry optimizations of chlorobenzene and five types of *para*-substituted chlorobenzenes with or without platinum cluster (Pt_{10}) were optimized by the B3LYP/LANL2DZ system. The B3LYP method, which consists of Becke plus LYP parameters[8, 9], has a hybrid functional, including a mixture of Hartree-Fock exchange with DFT exchange-correlation terms. The LANL2DZ basis set exchanges inner core orbitals of heavy atoms for Los Alamos effective core potentials. Convergence criteria were default values as follows: the maximum force is below the cutoff value of 0.00045, the RMS force is below the cutoff value of 0.0003, the maximum displacement is below the cutoff value of 0.0018, the RMS displacement is below the cutoff value of 0.0012.

As the highest intensity plane was (111) on platinum metal by X-ray diffraction analysis, a Pt_{10} cluster similar to a regular tetrahedron structure using four (111) planes of platinum crystal was constructed by the lattice constant (a=0.391nm) of the point group of O_h^5-Fm3m (No.225, fcc)[10], as described in Fig.1. Bond lengths, angles and dihedral angles between platinum atoms were fixed in all optimized computations. On the other hand, chlorobenzenes were fully optimized onto the Pt_{10} cluster fixed in all calculations.



a) Bird's-eye view

b) Horizontal section (X-Y plane of a)

c) Vertical section (X-Z plane of a)

d) Vertical section (Y-Z plane of a)

Fig.1. Structure of Pt_{10} cluster

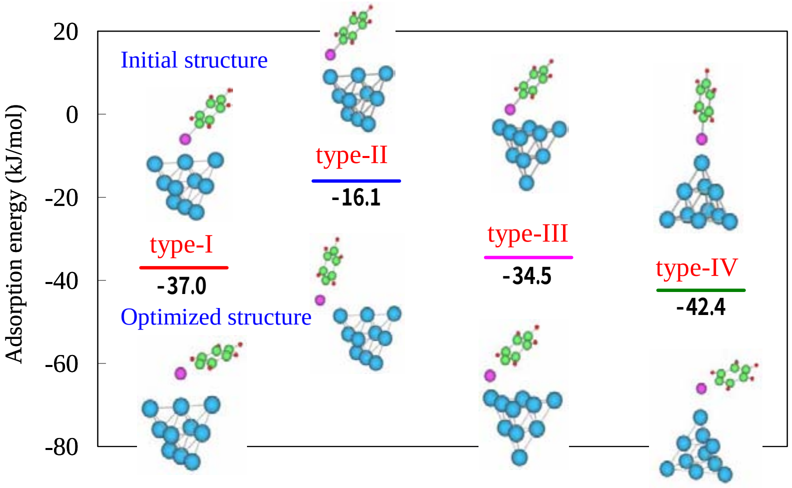


Fig.2. Adsorption energies of CLB depending on several adsorption states (type-I to type-IV)

Results and Discussion

Adsorption of chlorobenzenes: In order to search for a suitable dissociative mechanism on a Pt_{10} cluster, as described in the upside pictures shown in Fig.2, four types of adsorption states (type-I to type-IV) were screened according to the magnitude of the adsorption energy of CLB on the Pt_{10} cluster.

When CLB was arranged at 0.200nm directly above the ridge of the platinum atom (I, II), on the center atom of the edge of (111) plane (III), or on the edge atom (IV) at 45 degrees, optimization was completed with the adsorption states of the downside pictures shown in Fig.2. The adsorption energy (absolute value) decreases in the sequence of type-IV > I > III > II. (Fig.2)

Although a great deal of stability was observed in type-IV, this type of adsorption is beyond the scope of this discussion since the adsorption of chlorobenzene is not dissociative but one-point type through the chlorine atom (Cl) on the top position of the platinum atom in Pt_{10} cluster. In the previous paper[2], we have already reported a similar type of adsorption to this phenomenon. Therefore, the type-I adsorption, in which a certain degree of the dissociative mechanism of the chlorine-carbon bond on the cluster is expected, is discussed here due to the relative larger adsorption energy.

Concerning the type-I adsorption of chlorobenzenes on the Pt_{10} cluster, the chlorine atom was placed on the middle atom (Pt_2) of the ridge (Pt_1-Pt_2-Pt_3) of the cluster, and the organic molecular axis leaned at an angle of 45 degrees. The stabilization of potential energy, that is adsorption energy, was defined by the following equation:

$$E_{\mathrm{ad}} = E_{\mathrm{complex}} - (E_{\mathrm{CLBs}} + E_{\mathrm{Pt10}})$$

where E_{complex} is the total potential energy in optimized geometry of "CLBs-Pt_{10}" complex; E_{CLBs} is the potential energy in optimized geometry of chlorobenzenes; E_{Pt10} is the potential energy in single point calculation of the

Pt_{10} cluster, respectively.

As shown in Fig.3, the absolute value of the adsorption energy (E_{ad}) degreased in the following order: CLAN < CLTN ≤ CLAS < CLB; CLB < DCLB < CLTF. This tendency is similar to that of the actual HDC reactivity, although the reversed order was observed between CLTN and CLAS as compared with the reactivity. As for factors affecting the HDC reactivity, it is suggested that difference in the electronic affinity (that is, the magnitude of the adsorption energy) of the chlorine atom of chlorobenzenes onto the catalytic surface is very important. As the positive value of adsorption energy is only observed in CLTF, however, further study of a more suitable model is probably required to CLTF.

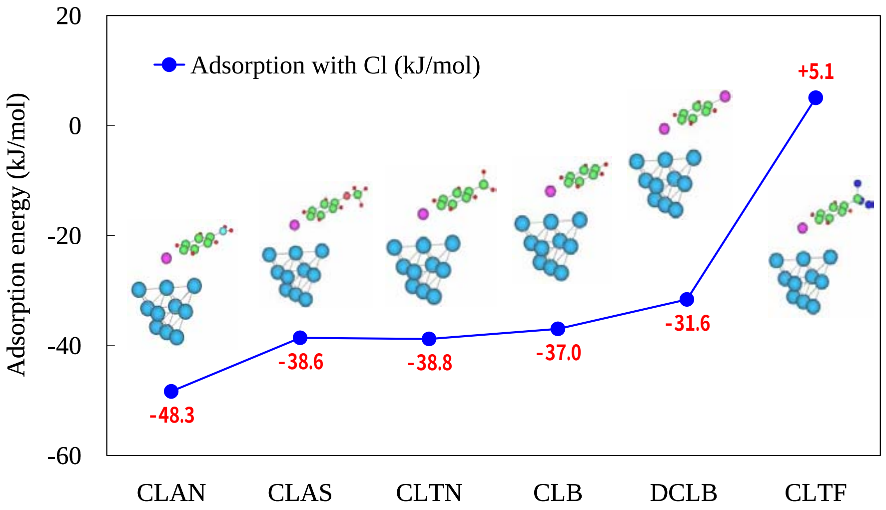


Fig.3. Adsorption energy of chlorobenzenes (CLBs) on Pt_{10} cluster (type-I)

Molecular orbital interaction: In order to obtain the reason for the difference in the adsorption stability for the type-I complex, the orbital interaction was analyzed from the standpoint of the energy levels between the organic molecules and the cluster.

In the orbital interaction between the chlorobenzenes and the Pt_{10} cluster, as seen in the left side in Fig.4, two orbitals of the HOMO-20 (E=-0.2551eV) and degenerated LUMO+2 (E=-0.1701eV) of the cluster were estimated to play an important role in every case. HOMO-20 of the cluster consisted of the linear combination of $5d_{z2}$ and $5d_{yz}$ atomic orbitals (No.1, 3 in Fig.1-a), $5d_{z2}$ and $5d_{xz}$ atomic orbitals (No.8, 10), and $5d_{z2}$ and $5d_{x2-y2}$ atomic orbitals (No.2, 9), respectively. Also, the main component of LUMO+2 was the linear combination of three pieces of atomic orbital of $5d_{z2}$, $5d_{x2-y2}$, and 6s (No.2, 9), respectively.

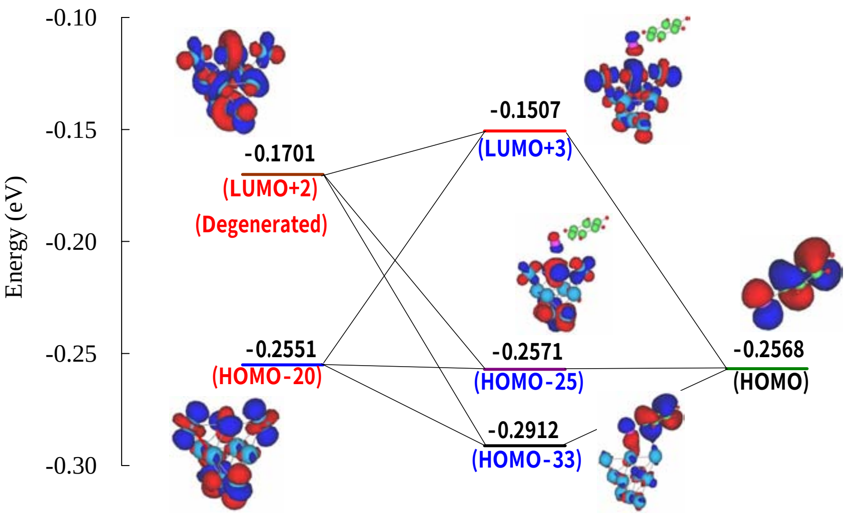


Fig.4. Orbital interaction between CLB and Pt_{10} cluster (type-I)

On the other hand, HOMO of chlorobenzene, which is composed of p_z atomic orbitals on both the chlorine atom and carbon atom of the benzene ring, was expected to overlap both the orbitals of the two platinum atoms (No.2,3) in the cluster. (The right side in Fig.4)

In the case of the interaction between CLB and the Pt_{10} cluster, for example, three orbitals are produced by the interaction of HOMO (*E*=-0.2586ev) of CLB with HOMO-20 (*E*=-0.2551ev) and LUMO+2 (*E*=-0.1701ev) of the cluster. As shown in the center part in Fig.4, these orbital are HOMO-33 (*E*=-0.2912eV) as a bonding orbital, and HOMO-25 (*E*=-0.2571eV) and LUMO+3 (*E*=-0.1507eV) as an anti-bonding orbital. By this interaction, it is clear that the Pt-Cl bond is enhanced whereas the C-Cl bond is weakened. Similar interactions were also observed in the case of the *para*-substituted chlorobenzenes. Therefore, it was suggested that the HOMO of the organic part and LUMO+2 of the cluster plays an important role in these interactions.

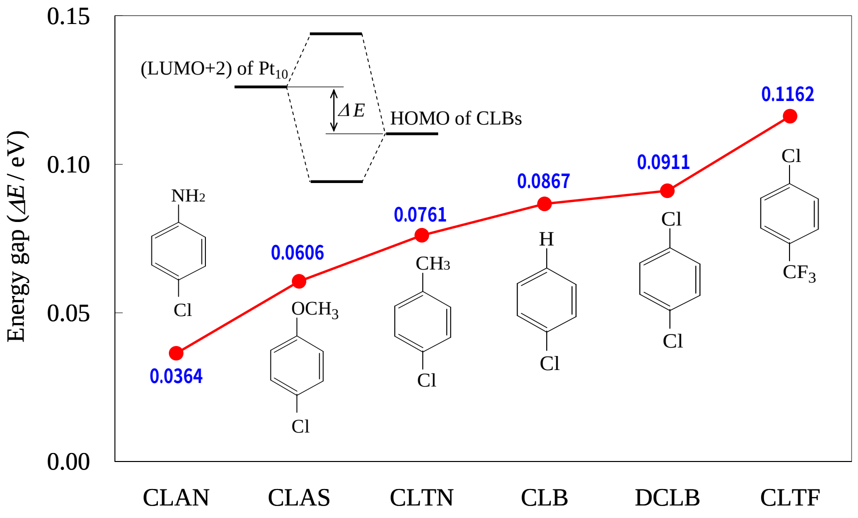


Fig.5. Energy gaps between LUMO+2 of Pt_{10} cluster and HOMO of CLBs (type-I)

To obtain further information on the interaction, energy gaps (ΔE) between the HOMO of each chlorobenzenes and LUMO+2 of the Pt_{10} cluster are checked. As described in Fig.5, the energy gaps are increased in the order of CLTN < CLAS < CLTN < CLB; CLB <DCLB <CLTF, respectively. A smaller energy gap between HOMO and LUMO generates a larger orbital interaction. According to this molecular orbital theory, the HDC reactivity decreased in the opposite order: CLTN > CLAS > CLTN > CLB; CLB > DCLB > CLTF, respectively. These expected orders are in good agreement with that of the actual reactivity[2]. In the present calculation, it may be concluded that the difference in the energy gap between the HOMO of chlorobenzenes and LUMO+2 of the Pt_{10} cluster is due to the difference in the HDC reactivity.

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