Hydrodechlorination Reactivity of para-Substituted Chlorobenzenes over Platinum-Carbon Catalyst

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1. Introduction

Since most chlorinated compounds are toxic to human health, their harmless treatment is of utmost importance to maintain a clean natural environment. Among the various methods that render chlorinated compounds harmless, the catalytic hydrotreatment is looked upon as the safest method because it generates a minimal amount of the more toxic compounds such as dioxin as by-products[1, 2)].

To determine the factors that affect hydrodechlorination (HDC) reactivity of chlorinated aromatic compounds, in the present study, the HDC reaction rate of chlorobenzene (abbreviated as CLB) and of *para*-amino, -methoxy, -methyl, -chloro, -trifluoromethyl, -acetyl and –cyano substituted chlorobenzenes (abbreviated as CLAN, CLAS, CLTN, DCLB, CLTF, CLAP and CLBN, respectively) were measured over a platinum catalyst.

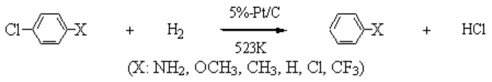
The results were discussed from the viewpoint of the adsorption stability of the chlorobenzenes on the model cluster of the Pt_{14} unit cell, using molecular orbital calculations.

2. Method

HDC Reaction The reaction was carried out in a magnetically stirred autoclave (Sakashita Seishakusho, SUS304, Volume ca.108ml), connected to a sampling tube (SUS316, 0.25mm I.D. × 900mm Length) and a liquid introducing vessel. Quantitative analyses of the reaction product were performed with a gas chromatograph (Shimadzu GC14B) equipped with FID. The detailed procedure was described in a previous paper[3)].

Molecular Orbital Calculation The calculation of the adsorption energy of chlorobenzenes on the Pt_{14} model cluster was performed with Gaussian03W (Revision-B.04)[4)] on a Windows 2000 system, using the density function theory (DFT/B3LYP). Only the organic part of the "chlorobenzenes -Pt_{14} complex" was optimized within the (110) face.

3. Results and Discussion



HDC Reaction In the HDC of *para*-substituted chlorobenzenes over the Pt/C catalyst, except for CLBN and CLAP, the reductive cleavage between the carbon atom and the chlorine atom took place selectively. A ring saturated compound was observed only in the reaction of CLB where a very small amount of cyclohexane was produced.

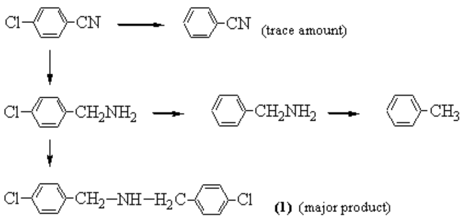


Fig.1 Reaction path suggested for the formation of dimerized product

On the other hand, in the reaction of CLBN, a considerable amount of Bis(4,4'-chloro-benzyl)amine (1) was produced with a small amount of toluene (Fig.1). In the case of CLAP, acetophenone and ethylbenzene were observed. For CLBN and CLAP, product distribution on the Pt/C catalyst differed largely from that on the Pd/C catalyst[3)] in which a simple HDC product was generated.

The reaction rate of the chlorobenzenes, except for CLBN and CLAP, was proportional to the initial concentration with approximate 0.8-1.0 orders. Concerning the chlorobenzenes with electron-releasing substituents and electron-withdrawing substituents, the magnitude of the reaction rate constants decreased in the order of CLAN > CLAS ≥ CLTN ≥ CLB, and CLB > DCLB > CLTF, respectively.

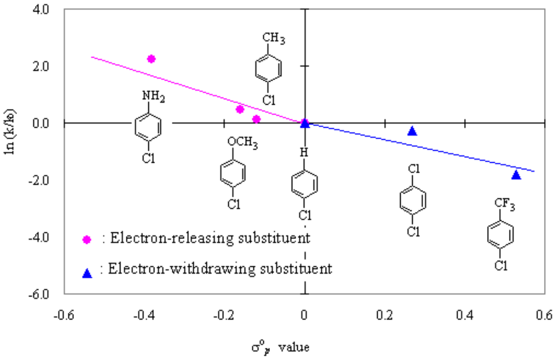


Fig.2 Relationship between rate constant and Hammett constant

Furthermore, the rate constants were plotted to the Hammett constant (σ^o_p), and the electronic effect of the substituent was examined (Fig.2). Although the correlation coefficients were slightly lower, a correlation between the rate constant and the σ^o_p was nonetheless observed in both series of substituted chlorobenzenes. It may thus be inferred that, by the presence of the substituents, the reaction rate of the chlorobenzenes with electron-releasing substituents except for CLTN is slightly accelerated while the rate of the chlorobenzenes with electron-withdrawing substituents is depressed.

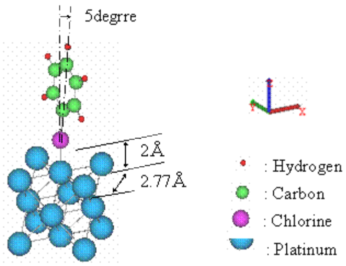


Fig.3 Initial structure of type-I for CLB-Pt_{14}

Adsorption Energy of CLBs on Pt_{14} Model Cluster In order to further investigate the electronic effect of the substituent on HDC reactivity, two types of adsorption states of chlorobenzenes on the Pt_{14} model catalyst were calculated using the ab initio method (Gaussian: B3LYP/LANL2DZ$^{5)}$).

When the chlorobenzenes were placed on the center platinum atom of the (001) face of the Pt_{14} clusters through achlorine atom (type-I), no adsorption stability was observed in the optimized geometry of "CLB-Pt_{14} complex". On the other hand, in the case of CLB placed on the corner platinum atom of the (001) face (type-II) (Fig.4a), a highly stable point was obtained (Fig.4b).

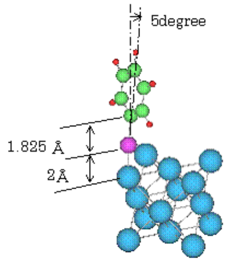


Fig.4a Initial structure of type-II for CLB-Pt_{14} complex

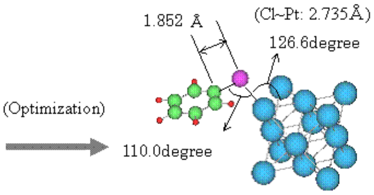


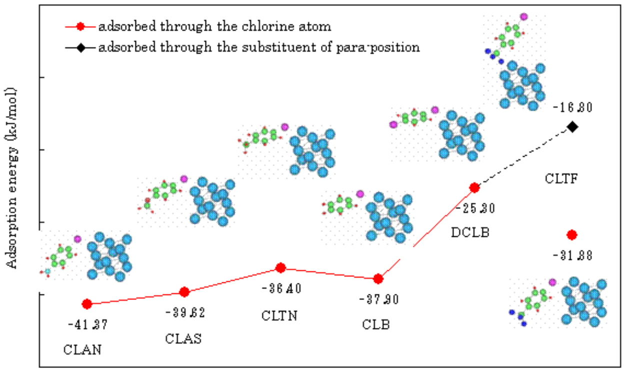
Fig.4b Final structure of type-II for CLB-Pt_{14} complex

When the adsorption energy (E_{ad}) of the chlorobenzenes was defined as below, an interesting result was obtained (Fig.4).

$$E_{ad} = E_{complex} - (E_{CLBs} + E_{Pt14})$$

Where $E_{complex}$ is the total energy in the optimized structure of the "CLB-Pt_{14} complex", E_{CLBs} is the total energy in each optimized structure of each chlorobenzene, and E_{Pt14} is the total energy in the single point calculation of Pt_{14} cluster, respectively.

Concerning the substituted chlorobenzenes with electron-releasing substituents, the magnitude (absolute value) of E_{ad} decreased in the order of CLAN > CLAS > CLB > CLTN. This order is consistent with that of HDC reactivity. As for the chlorobenzenes with electron-withdrawing substituents, on the contrary, a direct relationship was observed only when the unique adsorption state of CLTF was adopted,where CLTF was adsorbed on the corner platinum atom through the *para*-substituent. From these results, it may be predicted that the HDC of CLTF proceeds by Redial-Eley reaction mechanism$^{6)}$.



In conclusion, it may be suggested that the magnitude of the adsorption energy relates largely to HDC reactivity.

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