Applied Catalysis B: Environmental 84 (2008) 667–677

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Hydrodechlorination of *para*-substituted chlorobenzenes over a ruthenium/carbon catalyst

Tetsuya Yoneda [a,*], Toshio Takido [b], Kenji Konuma [a]

[a] *Department of Liberal Arts and Science, College of Science and Technology, Nihon University, Narashinodai 7-24-1, Funabashi, Chiba 274-8501, Japan*
[b] *Department of Materials and Applied Chemistry, College of Science and Technology, Nihon University, Kanda-surugadai 1-8-14, Chiyoda, Tokyo 101-8308, Japan*

ARTICLE INFO

Article history:
Received 29 September 2007
Received in revised form 24 May 2008
Accepted 26 May 2008
Available online 5 June 2008

Keywords:
Hydrodechlorination
Para-substituted chlorobenzenes
Ru/C catalyst
DFT
Adsorption energy

ABSTRACT

The hydrodechlorination (HDC) of chlorobenzene (abbreviated as CLB) and seven types of *para*-substituted chlorobenzenes (*para*-amino, -methoxy, -methyl, -chloro, -trifluoromethyl, -acetyl and -cyano: abbreviated as CLAN, CLAS, CLTN, DCLB, CLTF, CLAP and CLBN, respectively) were performed over 5%-ruthenium/carbon (Ru/C) under a hydrogen pressure of 0.5–1.5 MPa at 523 K.

In the HDC of these model compounds, except for CLAP and CLBN, reductive cleavage between the carbon and chlorine atoms took place and dechlorinated compounds were produced preferentially. In the reaction of CLAP and CLBN, on the other hand, hydrogenation and/or hydrogenolysis of the substituent coincided with the HDC and a wide variety of products was observed accompanying the HDC product.

For the chlorobenzenes of the simple HDC, the HDC reaction rate constants decreased in the orders of CLAN $\gg$ CLB $\approx$ CLTN $\approx$ CLAS and CLB $>$ DCLB $\gg$ CLTF, respectively.

In the reaction of the chlorobenzenes of the electron-donating substituent, the reaction constant ($\ln k/k_0$) has no relevance to the Hammett substituent constant (σ_p^0). In the case of the chlorobenzenes possessing the electron-withdrawing substituent, on the other hand, it was indicated that the electron-withdrawing substituent suppressed the HDC reactivity of chlorobenzenes, although no proportional relationship was observed between the reaction rate constant and the Hammett substituent constant.

To explore the factors affecting the HDC reactivity, quantum calculation according to the DFT method (B3LYP/LANL2DZ) was applied to the "chlorobenzenes-Ru_{10}" complex. As a result of the calculation, chlorobenzenes were adsorbed through a chlorine atom on the edge atom of the Ru_{10} cluster. The magnitude of the adsorption energy, moreover, decreased in the order of CLAN $>$ CLAS $\approx$ CLB $\approx$ CLTN and CLB $>$ DCLB $>$ CLTF, respectively. These orders of adsorption energy are similar to that of the HDC reaction rate constant. It was concluded that adsorption energy is a useful parameter for the reactivity index of the HDC.

1. Introduction

Since organic chlorinated compounds such as PCBs and HCH are harmful not only in rubbish and waste but are also carcinogenic substances, appropriate chemical disposal is required to protect human health and preserve the environment. Chlorinated compounds can be degraded by combustion [1,2], pyrolysis [3], electrolysis [4,5], ultra-violet irradiation [6], ultrasonic reaction [7,8], biological disposal [7,9], microwave reaction [10] and catalytic hydrogenolysis [11–28]. Of these methods, catalytic hydrodechlorination (HDC) is simple, safe, and effective [11], because hydrogen chloride is easily separated from the process as a by-product, and refined hydrocarbons can be recycled.

For the HDC reaction, many reports deal with the reaction mechanism [12,13], catalytic activity [14,15] and the preparation or modification of the catalyst [16–18]. However, few studies focus on the HDC reactivity of chloro-aromatics [19–23]. For instance, in the gas phase reaction of chlorobenzene and its derivatives with electron-donated substituents over the Ni/SiO_2 catalyst, Keane [19] suggested that the higher dechlorination rates were indicative of an electrophilic mechanism.

In the liquid phase reaction of the HDC of the substituted chlorobenzenes over Pd/C catalyst [20], we found that both the electron-releasing groups and the electron-withdrawing groups accelerate the HDC, and that linear relationships between the reaction rate constant ($\ln(k/k_0)$) and the Hammett constant (σ_p^0) were observed in each group. In contrast, Wu et al. [22] reported

---

* Corresponding author. Tel.: +81 47 469 5310; fax: +81 47 469 5310.
E-mail address: yoneda@chem.ge.cst.nihon-u.ac.jp (T. Yoneda).

0926-3373/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcatb.2008.05.024

that electron-donating and electron-withdrawing groups suppressed the reaction rate constants in the liquid phase reaction over Ni/C, Ni/γ-Al_2O_3, Ni/SiO_2 and Raney Ni. Recently, we showed that the effect of the electron-withdrawing substituent over the platinum/carbon (Pt/C) catalyst suppresses the reaction rate of the substituted chlorobenzenes [23].

However, for these distinct kinetic studies, consensus on the electronic factors affecting the HDC reactivity of chlorobenzenes has not been reached beyond the differences in the catalytic elements and other reaction conditions. We are currently searching for a certain unity of HDC activity about the platinum group catalysts according to periodic metal elements or groups. To elucidate the electronic factors affecting these HDC, hence, we need to study other metal catalysts such as Ru, Rh, Co, Ni and so forth, comprehensively.

In the present study, chlorobenzene (abbreviated as CLB) and seven types of *para*-substituted derivatives: amino-, methoxy-, methyl-, chloro-, trifluoromethyl-, acetyl- and cyano-chlorobenzene (abbreviated as CLAN, CLAS, CLTN, DCLB, CLTF, CLAP and CLBN, respectively) were hydrogenolyzed over a ruthenium-carbon (Ru/C) catalyst under hydrogen pressure of 1 MPa at 523 K in a batch reactor. Since the substituent effect in the HDC of chlorinated organic compounds has not been reported for the ruthenium catalyst [15,24–27], the reaction rate was measured and the relevancy of the rate constants to Hammett's substituted constants was checked. Furthermore, in order to explain the HDC reactivity from the standpoint of the adsorption energy, the quantum calculation was performed according to the density functional theory method.

2. Experimental

2.1. Materials

Chlorobenzene, the *para*-isomers of chlorotoluene (CLTN), dichlorobenzene (DCLB), and chlorobenzonitrile (CLBN) were obtained from Kanto Kagaku Co. Ltd. The *para*-isomers of chloroaniline (CLAN), chloroanisole (CLAS), chloroacetophenone (CLAP) and trifluoromethyl-chlorobenzene (CLTF) were purchased from Tokyo Kasei Kogyo Co. Ltd. Solvents of 1,3,5-trimethylbenzene and hexadecane were produced by Kanto Kagaku Co. Ltd. These substrates and solvent, except for hexadecane, were purified according to a conventional method before use. The carbon-supported 5%-ruthenium catalyst (Ru/C), supplied by Sigma–Aldrich Co., was used without purification and the particle size of the catalyst was less than 45 μm (>330 mesh).

2.2. Apparatus and reaction procedure

The HDC reaction was carried out in a test tube (Pyrex glass, i.d. 28 mm × height 130 mm, volume: approx. 77 ml) that was placed into a magnetically stirred autoclave (Sakashita Seisakusho, SUS316, volume: approx. 108 ml) in a batch system. Both the sampling tube (i.d. 0.25 mm × length 600 mm) and the liquid introducing vessel (SUS304, volume: 50 ml) were equipped with an autoclave lid. In order to maintain effective agitation of the reactants, three rectangular turbulence boards (length 60 mm × width 4 mm × thickness 1.5 mm, glass) were fusion-bonded onto the inner wall of the test tube with three points. This experimental apparatus is described in a previous paper [20].

The Ru/C catalyst (0.01 g) was placed into the test tube in the autoclave. After purging the air of the autoclave with hydrogen gas, the catalyst was reduced at a hydrogen flow rate of 100 ml/min under 0.5 MPa at 573 K for 1 h and a liquid introducing vessel was placed on the inlet part of the autoclave. Hexadecane (35 ml), as the main solvent, was deposited into the vessel and then purged by hydrogen gas. At the termination of this reduction, the residual hydrogen gas in the autoclave was rapidly released, and the hexadecane in the vessel was introduced to the test tube with 0.3 MPa of hydrogen pressure. As soon as the pressure in the reactor was adjusted to 0.5 MPa at 558 K, both the solvent and catalyst in the test tube were stirred at 1200 rpm. When the temperature of the reactor was maintained at 523 K, the reactant solution (concentrations: 25×10^{-3} to 100×10^{-3} mol/l) of 1,3,5-trimethyl-benzene (5 ml) was added from the liquid introducing vessel, using hydrogen gas of 0.8 MPa and following a pressure adjustment to 1.0 MPa.

In the course of the reaction, the hydrogen pressure and temperature were kept at 1.0 ± 0.05 MPa and 523 ± 1 K, respectively. Concerning the chlorobenzenes except for DCLB, the range of the starting Cl (mol)/Ru (g) ratios was ca. 2–8 mol/g. For DCLB, possessing two chlorine atoms in the molecule, the range was estimated at ca. 4–16 mol/g. The HDC conversion was stopped within 15 mol%, in order to avoid the effect of products on the reaction rate. In the course of the reaction, reaction products were periodically extracted via the pressure-resistant valve.

2.3. Catalyst characterization

For a Ru/C catalyst, the metal content was measured by an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Shimadzu Co., CPS-8100) from the diluted dissolution, following fusion by sodium peroxide and dry ashing.

The BET surface area and pore size distribution measurement were determined using the BELSORP-mini (BEL Japan Inc.) apparatus. After outgasing at 393 K, a nitrogen adsorption isotherm was employed to determine the total surface area using the standard multiple point BET method at 77 K. Mesopore and micropore volumes were measured using BJH, MP and *t*-plot methods, which are based on a carbon standard curve endorsed by BEL Japan.

The metal surface area, dispersion and average metal particle size were obtained from gas-chemisorption analyses of both carbon monoxide (CO) and hydrogen (H_2) (BEL-METAL-3SP, BEL Japan Inc.). The samples (0.03 g) were loaded into a U-shaped Pyrex glass cell (i.d. 3.5 mm, volume 5 ml) and reduced in hydrogen at 573 K for 60 min, as same as in the experimental pre-reduction of the catalyst. Following the reduction, the samples were swept with 50 ml/min inert gases dried for 90 min (helium gas in CO chemisorption, argon gas in H_2 chemisorption), cooled to 323 K and subjected to each chemisorption using a pulse (10 %-CO/He or 10 %-H_2/Ar, ca. 0.13–0.14 ml at a time) titration procedure in He flow (50 ml/min).

Temperature-programmed experiments on both the decomposition of the functional group on the carbon surface (TPD) and reduction (H_2-TPR) on the Ru/C catalyst were carried out in an apparatus consisting of a differential flow reactor coupled to a mass spectrometer (TPD-1-ATw, BEL Japan Inc.). In both cases, approximately 0.1 g of sample was heated at 20 K/min up to 1073 K. During the TPD experiments, helium was passed thorough the reactor at a flow rate of 60 ml/min. For H_2-TPR experiments, a mixture of 5%-H_2 in helium was used with a flow rate of 60 ml/min, while the gas analyses were carried out by mass spectrometry.

Powder X-ray diffractograms (XRD) were recorded with a D8-Focus (Bruker AXS K.K.) using nickel filtered Cu Kα radiation. The samples were mounted in a low background sample holder and scanned at a rate of 0.02° per step over the $5^\circ \le 2\theta \le 70^\circ$ range at a scan speed of $0.06^\circ\ \mathrm{min}^{-1}$ at 298 K. The diffractograms were compared with the JCPDS-PDF references (No. 6-0663 [29], 26–1079, and 40–1290: Ru, C, and RuO_2, respectively) for identification purposes.