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Complete hydrodechlorination of chlorobenzene and its derivatives over supported nickel catalysts under liquid phase conditions

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Abstract

Liquid phase hydrodechlorination of chlorobenzene was studied over Ni/active carbon (Ni/AC), Ni/γ-Al_2O_3, Ni/SiO_2 and Raney Ni. The complete hydrodechlorination of chlorobenzene was realized at 333–343 K on Ni/AC under hydrogen atmosphere of 1.0 MPa in the presence of alkaline hydroxide. Aryl halides, three chlorotoluenes (*o*-, *m*- and *p*-), three chloroanilines, three chlorobenzotrifluorides, three dichlorobenzenes and two trichlorobenzenes (1,2,3- and 1,2,4-) were also completely hydrodechlorinated under the similar conditions. Chlorobenzene derivatives having either an electron-donating group or an electron-withdrawing group decreased their reactivities with respect to the unsubstituted chlorobenzene. The reactivities of polychlorinated benzenes slightly decreased with the increasing chlorine atom number in a molecule. The steric effect of trichlorobenzene gave a large influence on the product distribution.

The reaction rate did not depend on chlorobenzene concentration and increased with increasing hydrogen pressure. The reaction did not proceed in the absence of alkaline hydroxide. The active catalysts were characterized by hydrogen chemisorption and transmission electron microscopy techniques. The apparent activity strongly depends on the active surface area of nickel on catalyst surface. Based on the above results, the reaction route was discussed.

The deactivation of Ni catalyst was observed in the dechlorinating process. An accumulation of NaCl on the catalyst surface is probably one of the reasons for the deactivation. The deactivated catalysts can be partially recovered by washing with distilled water and reactivating.

Keywords: Hydrodechlorination; Substituted chlorobenzenes; Polychlorinated benzenes; Nickel carbon; Substituent effect

1. Introduction

The disposal of chlorinated organic wastes is a serious environmental problem. Polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are carcinogenic, mutagenic, cumulative and stable chemicals. Among the methods proposed for destruction of chlorinated organic compounds [1], the catalytic hydrodechlorination (HDC) is receiving more and more attention because it is simple, effective and safe. Furthermore toxic compounds, such as PCDDs and PCDFs (generally known as dioxins) will not form under the employed experimental conditions. Noble metal catalysts, like Pd, Rh, Pt, on various supports are active for the reaction under mild conditions [2–9]. Chlorobenzene and its derivatives were hydrodechlorinated on Pd/C catalyst in a flow system [10], and Pd/$AlPO_4$–SiO_2 [3] and Pd/C catalysts [11] in liquid phase, but few of these catalysts are introduced to large-scale applications because of high cost of these catalysts [12,13]. Transition metal catalysts, such as Ni, Ni–Mo on γ-alumina, silica or carbon composite [14–21] required high temperature (>473 K) or high hydrogen pressure (2 MPa) [14,15] to reach significant activity in the gas phase dechlorination process. For example, *para*-substituted chlorobenzenes with amino-, hydroxyl-, chloro-, methyl- and trifluoromethyl were dechlorinated over Ni/γ-Al_2O_3 [19] in the gas phase at 523 K. Little

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literature is reported for liquid phase hydrodechlorination of chlorinated aromatics on Ni based catalysts so far, unless Pd is added into Ni catalysts [22,23].

In our previous communication [24], we have successfully achieved the complete hydrodechlorination of chlorobenzene over Ni/AC catalysts. More information should be gathered on the hydrodechlorination of substituted chlorobenzenes before the reaction is practically applied. In this work, we are to present the hydrodechlorination of aryl halides (iodo and bromo), three chlorotoluenes (*o*-, *m*- and *p*-), three chloroanilines, three chlorobenzotrifluorides, three dichlorobenzenes and two trichlorobenzenes (1,2,3- and 1,2,4-), *p*-chlorophenol and *p*-chloronitrobenzene on Ni/active carbon catalyst in addition to that of chlorobenzene. Based on experimental results, the electronic and the steric effect of substituents, and the reaction route will be discussed.

2. Experimental

2.1. Material and catalyst preparation

All chlorinated compounds were purchased from Lancaster and used as supplied. Ethanol (A.R.) was used as supplied. Hydrogen (99.999%) was used for reaction without purification. Nitrogen (99.999%) was used after the removal of oxygen using manganese(II) oxide.

Commercial active carbon (coconut shell) was crushed and sieved. The active carbon in a fraction of 80–100 mesh was demineralized (agitation in boiling 5 wt.% HNO_3 for 1 h) to remove residual metal impurities, which may contribute to the catalytic activity, and washed with boiling distilled water till the pH of the rinsed solution reached 5.5. The catalysts were prepared by impregnation of the active carbon (1100 m^2/g specific surface area; 2.3 nm average pore diameter) with an aqueous solution of nickel(II) nitrate, as described previously [24]. After dried at 353 K, the samples were dehydrated at 393 K in vacuum for 3 h. Before starting the reaction, the catalysts were activated at 723 K for 2 h in hydrogen flow (15 ml/min) and cooled down to room temperature under the hydrogen flow.

2.2. Catalyst characterization

The hydrogen chemisorption was performed using a CHEMBET 3000 instrument (Quatachrom Co.). The process was similar to the reported literatures [25–27]. In brief, after the catalyst was reduced at 723 K for 2 h in hydrogen stream (15 ml/min), adsorbed hydrogen on the nickel surface was removed under a flowing nitrogen stream (94 ml/min) for 30 min at 723 K. The sample was subsequently cooled to ambient temperature under the nitrogen stream. The hydrogen pulses (0.1 ml) were injected until the eluted areas of consecutive pulses became constant. The amount of nickel atoms on surface were calculated, assuming the stoichiometric adsorption of hydrogen, i.e. one hydrogen molecule occupied two nickel atoms on surface. Nickel surface area was calculated from the nickel atomic cross-sectional area of 6.49×10^{-20} m^2. Crystalline size of nickel metal was calculated on the assumption that nickel crystals formed cubic-shaped structure.

The freshly activated catalyst samples were analyzed by transmission electron microscopy (TEM) using a JEOL JEM-2000EX TEM, which was operated at an accelerating voltage of 100 kV. Catalyst sample in ethanol was ultrasonicated. A drop of the resulting suspension was placed on a holey copper supported grid, evaporated the solvent and used as a sample for TEM measurement. Particle sizes of over 400 individual particles were measured from a TEM picture, and surface area weighted average particle size was calculated using an equation of $\sqrt{\left(\sum N_i \times r_i^2\right)/\sum N_i}$, where r_i is a particle size and N_i is particle number in a particle size range between $r_i + \Delta$ and $r_i - \Delta$.

2.3. Reaction procedure and analysis of reaction products

Hydrodechlorination reaction was carried out in a 300 ml autoclave. In regular experiments, the reaction vessel was charged with 100 ml solution of one of chlorinated benzenes (36 mmol in chlorine atom base, 4.1 g in case of chlorobenzene) in ethanol. Sodium hydroxide (50 mmol, 2.0 g) was added into the mixture to neutralize the evolving HCl. Then, the catalyst was added into the solution under flowing deoxygenated nitrogen (99.999%) at ambient temperature. The catalysts were always handled under air-free condition after the reduction step. The reaction vessel was heated to a designated temperature and was filled with hydrogen to a pressure of 1.0 MPa at a set temperature.

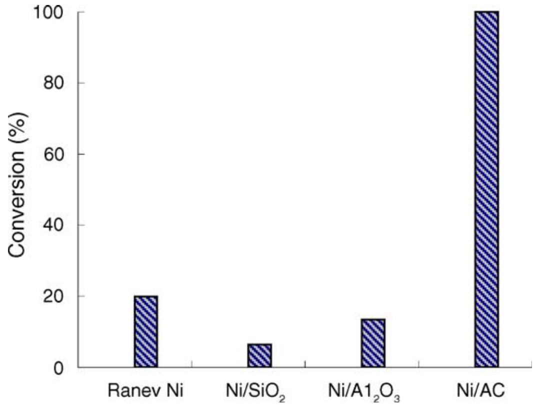


Fig. 1. Hydrodechlorination of chlorobenzene on Ni-based catalysts. Reaction conditions: chlorobenzene 0.36 mol/l; Ni content 10 wt.%; ClBz/Ni = 56 (molar ratio); NaOH/ClBz = 1.4 (molar ratio); H_2 pressure 1.0 MPa; 60 min; 343 K.

Liquid samples were periodically withdrawn from reaction medium during a reaction run. Toluene, benzene or chlorobenzene, which was neither reactant nor product, was used as an internal standard and was added to the liquid sample. The resulting mixture was quantitatively analyzed on a Hewlett-Packard-4890 FID-GC equipped with a HP-5 capillary column (30 m × 0.53 mm × 1.5 μm). The mass balance is >95% for carbon. Except a small amount of cyclohexane (less than 1.0% selectivity in reaction products), no other by-product was detected by Agilent 6890N GC–MS and HPLC (Agilent 1100 series).

The amount of produced NaCl was determined by titrimetric analysis (Mohr method), i.e. the sample was titrated by $AgNO_3$ standard solution using K_2CrO_4 as an indicator. The mass balance is >97% for chlorine.

3. Results and discussion

3.1. Hydrodechlorinaiton of chlorobenzene

Fig. 1 illustrates the results of hydrodechlorination (HDC) of chlorobenzene on different Ni-based catalysts. HDC of chlorobenzene on Raney Ni (without support) gave 20% conversion in 60 min. When nickel was impregnated on γ-alumina, silica and active carbon, the catalytic activities varied in a large extent. The highest activity (100% conversion) was observed on a nickel/active carbon catalyst, while Ni/γ-Al_2O_3 and Ni/SiO_2 showed very poor activity in the liquid phase hydrodechlorination (9 and 13% conversion, respectively). Active carbon (without nickel) was inactive in the reaction. Similar activity trend depending on supports has also been observed in the hydrodechlorination of 1,1,2-trichloro-ethane using Pd/Al_2O_3 and Pd/AC as catalysts [28], where the higher activity of Pd/AC than that of Pd/Al_2O_3 was ascribed to the different adsorptivity of the reactant on catalysts. Similarly, the large difference in activity among Ni/AC, Ni/γ-Al_2O_3 and Ni/SiO_2 may be due to the difference in adsorptivity of chlorobenzene on different support, taking into account that nickel metals of Ni/AC and that of Ni/γ-Al_2O_3 are comparable in crystallite sizes (see *d* in Table 1, entries 1 and 4).

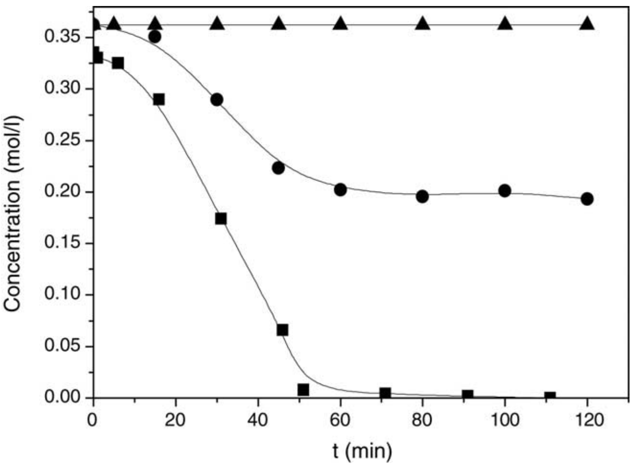


Fig. 2. Time course of the hydrodechlorination of chlorobenzene in the presence or absence of NaOH: (▲) without NaOH, (●) NaOH: Cl = 0.5: 1 (molar ratio), (■) NaOH: Cl = 1.5: 1 (molar ratio). Reaction conditions: 10 wt.% Ni/AC 0.4 g, H_2 pressure 1.0 MPa, 343 K, ClBz/Ni = 56 (molar ratio), ClBz 0.36 mol/l.

Sodium hydroxide is essential for the hydrodechlorination of chlorobenzene (ClBz) on Ni/AC. Fig. 2 shows time course of reaction with or without NaOH. Without NaOH, chlorobenzene was not dechlorinated by hydrogen on Ni/AC. When NaOH was added to the reaction media, the reaction progressed with an induction period. After the induction period, chlorobenzene concentration almost linearly decreased with time. It means that the reaction proceeds nearly zero order of chlorobenzene. The reaction rate could be calculated from the slope of straight line. When NaOH was added in NaOH/ClBz = 0.5 (molar ratio) to the solution, chlorobenzene was hydrodechlorinated up to 45%, similar to the corresponding amount of NaOH to chlorobenzene. Ukisu and Miyadera [29] have reported the incomplete reaction at less than stoichiometric amount of NaOH in the hydrode-

Table 1
Activity and physical characteristics of various Ni supported catalysts

Entry	Catalysts	Conversion[a] (%)	Rate × 10^5		S_{metal} (m^2 g_{metal}^{-1})	d (nm)
			(mol s^{-1} g_{Ni}^{-1})	(mol s^{-1} m^{-2})		
1	10 wt.% Ni/γ-Al_2O_3	13	3	0.3	11	64
2	1 wt.% Ni/AC	100	59	–	–	–
3	5 wt.% Ni/AC	100	49	2.7	18	37 (6.0)[b]
4	10 wt.% Ni/AC	100	45	4.2	11	63 (5.1)[b]
5	15 wt.% Ni/AC	94	24	4.0	6	115 (10.6)[b]
6	20 wt.% Ni/AC	56	14	3.6	4	174
7	10 wt.% Ni/AC (573 K)[c]	100[d]	39	2.5	16	43 (4.8)[b]
8	10 wt.% Ni/AC (773 K)[c]	89	22	2.9	8	89

[a] Reaction conditions: chlorobenzene 0.36 mol/l; ClBz/Ni = 56 (molar ratio); NaOH/ClBz = 1.4; H_2 pressure 1.0 MPa; 343 K; 60 min, pre-calcination temperature 393 K.

[b] Values in parentheses are calculated from TEM (see Section 2).

[c] Pre-calcination temperature.

[d] Reaction time, 50 min.

chlorination of 1,2,4-trichlorobenzene with 2-propanol over Pd/AC catalyst. In the presence of excess NaOH (NaOH/ClBz = 1.5), chlorobenzene was completely converted to benzene. These results show that the reaction proceeds only in alkaline media, and adsorption of chlorobenzene on catalyst is not the rate-determining step.

Next, a series of active carbon-supported nickel catalysts (Ni/AC) were prepared with various Ni loadings. The activity and physical characteristics of the catalysts are summarized in Table 1. The apparent activity of Ni/AC can be easily compared using the conversion of chlorobenzene after a certain time. The conversion in Table 1 was obtained at 60 min of reaction time. It is worth to note that chlorobenzene was completely decomposed at 343 K within 60 min under 1 MPa of hydrogen pressure when nickel loading is less than 10 wt.% (entries 2–4). As far as we know, this is the first example of complete conversion of chlorobenzene under the mild reaction temperature as 343 K. When nickel loading exceeds 10 wt.%, the conversion is considerably decreased with the increase of nickel loadings on active carbon (entries 5–6). More quantitatively than the conversion, the rate was calculated from slope of straight line, assuming the rate of hydrodechlorination is zero order with respect to chlorobenzene concentration, as described previously. As seen in Table 1, the reaction rates at 5 and 10 wt.% loaded Ni/AC catalysts were two times higher than that of 15 wt.% loaded Ni/AC, which, in turn, was about two times higher than that of 20 wt.% loaded Ni/AC. Note here that we compared the activity per gram of nickel metal weight. The higher activity for the catalysts of lower nickel loadings might be due to the higher surface area of nickel on active carbon or vice versa.

Accordingly, nickel surface area and nickel particle size were measured using hydrogen chemisorption and TEM measurements, as shown in Table 1. Here, S_{metal} refers to nickel surface area per nickel weight and d is the particle size. S_{metal} and d outside of parenthesis were estimated from hydrogen chemisorption data, and d values inside parenthesis were from TEM photograph (see Section 2 for more detail). As shown, both of nickel crystallite sizes measured from hydrogen chemisorption and from TEM increased with increase of nickel loading. However, there is a big mismatch in the nickel particle size obtained from the two techniques. Although the discrepancy in particle size depending on methods could ascribe to various reasons, we assumed here that the hydrogen adsorption sites are active for hydrodechlorination, and calculated the rate per metal surface area using S_{metal}. The rate represents the dechlorination ability in unit nickel surface area of the catalyst. It is interesting to note that the dechlorination rate keeps almost a constant value of 3.3×10^{-5} mol s^{-1} m^{-2} (entries 2–6). Decrease of the rate per nickel weight with increase of nickel loading is compensated by the decrease of metal surface area.

Metal surface area could be modified by heat-treatment. As compared with the 10 wt.% Ni/AC catalyst pre-calcined at 393 K (entry 4), the Ni/AC calcined at 573 K (entry 7) has higher and that at 773 K (entry 8) has lower metal surface area. As seen in entries 7–8 of Table 1, the rates per metal surface area keep similar values with each other. 10 wt.% Ni/AC calcined at 573 K promoted the hydrodechlorination of chlorobenzene in the fastest rate among 10 wt.% Ni/AC calcined at various temperatures.

Table 2
Effect of reaction temperature and pressure for HDC of chlorobenzene on 10 wt.% Ni/AC[a]

Entry	Reaction temperature (K)	Pressure (MPa)	Conversion[b] (%)
1	323	1.0	92
2	333	1.0	100
3	343	1.0	100 (45)
4	353	1.0	88
5	343	0.5	49 (12)

[a] Reaction conditions are the same as that of Fig. 1 except for reaction temperature.

[b] Rates ($\times 10^5$) in mol s^{-1} g$_{\text{Ni}}{}^{-1}$ unit are in parentheses.

Table 2 shows the effect of reaction temperature and hydrogen pressure on catalytic performances. The complete dechlorination of chlorobenzene still can be achieved as a low reaction temperature as 333 K. In all cases, benzene was the main reaction product in the hydrodechlorination of chlorobenzene, and cyclohexane was produced less than 1.0% selectivity in reaction products at 333–343 K under hydrogen pressure of 1.0 MPa. From rate of entries 3 and 5 in Table 2, the reaction order with respect to hydrogen pressure was calculated to be 1.9. As described previously, the reaction proceeds only in the presence of sodium hydroxide and the reaction rate does not depend on chlorobenzene concentration or is zero order to chlorobenzene concentration. Generally the reaction Scheme 1 could be proposed. In this scheme, step (1) is not the rate-determining step since the amount of adsorbed chlorobenzene does not depend on chlorobenzene concentration or the reaction kinetics follows zero-order with respect to chlorobenzene concentration. High pressure of hydrogen and the presence of alkali in reaction media facilitate the reaction steps (3) and (4).

3.2. Hydrodehalogenation of aryl halides

Unsubstituted aryl halides (chloro-, bromo- and iodo-) were hydrodehalogenated with molecular hydrogen over

$$\text{Ar-Cl} \rightleftharpoons \text{Ar-Cl (a)} \qquad (1)$$

$$\text{H}_2 \rightleftharpoons \text{2H (a)} \qquad (2)$$

$$\text{Ar-Cl (a)} + \text{2H (a)} \rightleftharpoons \text{Ar-H (a)} + \text{HCl (a)} \qquad (3)$$

$$\text{HCl(a)} + \text{NaOH} \rightleftharpoons \text{NaCl (a)} + \text{H}_2\text{O (a)} \qquad (4)$$

$$\text{Desorption steps for Ar-H, NaCl, H}_2\text{O} \qquad (5)$$

Scheme 1. General scheme for hydrodechlorination of chlorobenzenes.

Table 3
Non-competitive hydrodehalogenation of aryl halides on 10 wt.% Ni/AC

Compounds	Conversion (%)	Time (min)
Chlorobenzene	88	30
Chlorobenzene	100	50
Bromobenzene	100	30
Iodobenzene	35	50

Reaction conditions: concentration of aryl halides 0.36 mol/l; aryl halides/Ni = 56; (molar ratio); NaOH/aryl halides = 1.5 (molar ratio); H_2 pressure 1.0 MPa; 343 K.

supported nickel catalyst in liquid phase. Table 3 shows the conversion obtained in the non-competitive hydrogenolysis of aryl halides. The reactivity in the non-competitive hydrogenolysis decreased in the following sequence of bromobenzene > chlorobenzene > iodobenzene. The reactivity order is the exactly same as that reported by Aramendia et al. [3] for liquid phase hydrodehalogenation over palladium supported on $AlPO_4$–SiO_2 catalyst.

Fig. 3 shows the time course of the competitive dehalogenation reaction using an equimolar mixture of chlorobenzene, bromobenzene and iodobenzene. Iodobenzene was preferentially dehalogenated and was followed by bromobenzene and chlorobenzene. Ukisu and Miyadera [29] had reported the same activity order in the dehalogenation of aryl halide over Pd/AC. The carbon–halogen bond strength was estimated to be 340.2, 281.4 and 222.6 kJ/mol for C–Cl, C–Br and C–I, respectively [30]. The ease of halogen removal in the competitive experiment was related inversely to the carbon halogen bond strength, as expected. In contrast, the rates of reduction in non-competitive hydrogenolysis did not follow this order. The availability of hydrogen may be a reason why the orders of reactivity are different in non-competitive and in competitive hydrodechlorination reaction. Wiener et al. [31] have reported 3% conversion of iodobenzene and 96% conversion of chlorobenzene to benzene in their transfer hydrogenolysis with formate ion on Pd/AC. The low conversion of iodobenzene is attributed to nearly full coverage of Pd/AC surface with iodobenzene and to no available sites for the adsorption of formate ion since the presence of iodobenzene hinders the hydrogen evolution via formate ion decomposition. Similarly, lower rate of iodobenzene than those of bromo and chlorobenzene in non-competitive hydrodehalogenation could be attributed to its lower hydrogen coverage. In competitive hydrodehalogenation, intrinsic reactivities of aryl halides are revealed under the same hydrogen coverage. In fact, 70% of non-competitive activity was reserved in competitive hydrodehalogenation of iodobenzene while only 20–30% of these activities were retained in competitive hydrodehalogenation of bromo and chlorobenzene.

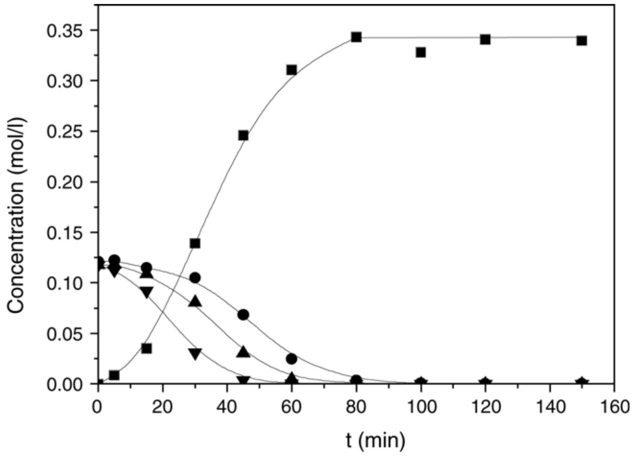


Fig. 3. Competitive hydrodehalogenation on Ni/AC using an equimolar mixture of aryl halides: (■) benzene, (●) chlorobenzene, (▲) bromobenzene, (▼) iodobenzene. Reaction conditions: 343 K; concentration of each aryl halide 0.12 mol/l; total aryl halides/Ni = 18.6 (molar ratio); NaOH/total aryl halides = 1.5; H_2 pressure 1 MPa.

3.3. *Effect of substituents to benzene ring on hydrodechlorination of chlorobenzenes*

Several papers have focused on identifying the electronic factor affecting the hydrodechlorination of chlorobenzene derivatives. In the gas phase reaction of substituted chlorobenzenes over a supported Ni/γ-Al_2O_3 catalyst [17], Suzdorf et al. [19] observed a correlation between reaction rates and the donor-properties of the substituents. Konuma and Kameda [11] hydrogenolyzed chlorobenzenes *para*-substituted such groups as amino, methoxy, methyl, chloro, acetoxy and nitrile over Pd/AC catalyst in liquid phase, and found that the reactivities are accelerated by the presence of both electron-donating groups and electron-withdrawing groups. Aramendia et al. [3] have sorted out the hydrodechlorination reactivity of *para*-substituted chlorobenzenes over Pd/$AlPO_4$–SiO_2 catalysts using the Taft equation but not with the simple Hammett equation. However, very few studies have been conducted on the reactivities of chlorobenzene derivatives with substituents on different position in the benzene ring.

Effect of the substitutes in the hydrodechlorination of chlorobenzenes was investigated over 10 wt.% Ni/AC catalyst using a series of *ortho*-, *meta*- and *para*-substituted chlorobenzenes possessing an electron-donating group or an electron-withdrawing group, as shown in Table 4. Here, time

Table 4
Time (min) required for 90% conversion in competitive hydrodechlorination using an equimolar mixture of *o*-, *m*- and *p*-isomers over 10 wt.% Ni/AC[a]

Substituent position	NH_2	CH_3	Cl	CF_3
o	53	59	109	53
m	44	61	140	112
p	46	59	193	85
Order[b]	0	0	1	1

[a] Concentration of each isomer in chlorine base 0.12 mol/l; total isomers/Ni = 56 (molar ratio); NaOH/total isomers = 1.5; H_2 pressure 1.0 MPa; 343 K.

[b] Reaction order to the concentration of substituted chlorobenzenes.

required for 90% conversion shows that shorter the time refers to faster the rate of reaction. In competitive reaction using an equimolar mixture of *o*-, *m*- and *p*-isomers, substituted chlorobenzenes such as chlorotoluenes, chlorobenzotrifluorides, chloroanilines, dichlorobenzenes were completely hydrodechlorinated to convert corresponding mono-substituted benzenes or benzene within 200 min.

Table 4 also shows that the reaction kinetics of hydrodechlorination of chlorotoluenes and chloroanilines were zero-order with respect to the concentration of each reactant, as the same as the case of chlorobenzene. In contrast, the dechlorination of chlorobenzotrifluorides and dichlorobenzenes obeyed the first order kinetics to the concentration of corresponding reactants. Further, a sterically hindered *ortho*-derivative was the most active among isomers in the hydrodechlorination in chlorobenzene derivatives having an electron-withdrawing group: chlorobenzotrifluorides or dichlorobenzenes. On the other hand, other *ortho*-chlorobenzenes bearing an electron-donating group were similarly active or less active than *meta*- and *para*-counterparts. Similar activity trends have been observed on Ni/SiO_2 catalyst in gas phase hydrodechlorination of chlorotoluenes [32] and chlorobromobenzenes [17]. Chlorobenzene bearing higher electron-withdrawing group, NO_2, as compared with CF_3 or Cl group, did not hydrodechlorinate but hydrogenate at NO_2 position, and produced chloroaniline. These results suggest strong interaction among electron withdrawing groups (NO_2, CF_3, Cl) and catalyst surface, and the hydrogenation or hydrodechlorination proceeds in a close vicinity of the substituents. Possibly benzene ring stands up from surface with the electron-withdrawing group as an anchor.

The Hammett equation [33,34] can be used to quantitatively describe the electronic effect of *para*- and *meta*-substituents on the hydrodechlorination rate:

$$\log\left(\frac{k}{k_{\mathrm{H}}}\right) = \rho\sigma$$

where k is the rate of hydrodechlorination of substituted chlorobenzenes; k_{H} the rate of hydrodechlorination of chlorobenzene; ρ the reaction constant; σ the substituent constant. Fig. 4 shows the Hammett plot of σ values against the logarithms of ratio of reaction rate constant $\log(k/k_{\mathrm{H}})$ obtained from non-competitive experiments. Chlorobenzenes having either an electron-donating group (O^-, NH_2 or CH_3) or an electron-withdrawing group (Cl, CF_3 or NO_2) decreased their reactivities with respect to unsubstituted chlorobenzene. A discontinuity in the Hammett plot is indicative to a change in the rate-determining step [33]. Reactant should be adsorbed on catalyst surface with proper strength of adsorptivity. A strongly adsorbed reactant may repel the other weakly adsorbed reactant from catalyst surface, as shown in the case of aryl halides. This possibility was checked by competitive reaction using an equimolar mixture of three chlorobenzene derivatives, which were representing chlorobenzenes bearing an electron-donating group (*p*-methyl), an electron-withdrawing group (*p*-trifluoromethyl), and hydrogen as a reference, as shown in Fig. 5. The reaction rates were in the following order: chlorobenzene > *p*-chlorotoluene > *p*-chlorobenzotrifluoride, which was the exactly same order as that in non-competitive experiments. The results show that a reactant adsorbed on catalyst does not prevent the adsorption of the other reactant. At this stage, we do not have rational reason why chlorobenzenes having either an electron-donating group or an electron-withdrawing group react slower, as compared with the parent unsubstituted chlorobenzene.

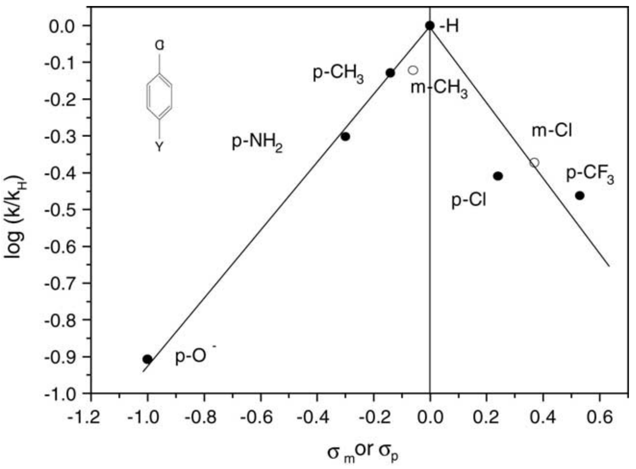


Fig. 4. Hammett plot of $\log(k/k_{\mathrm{H}})$ against σ_{m} (open symbol) and σ_{p} (closed symbol).

3.4. Effect of number of chlorine atoms in a benzene ring

Polychlorinated benzenes were hydrodechlorinated over 10 wt.% Ni/AC. For comparison, the concentration of poly-

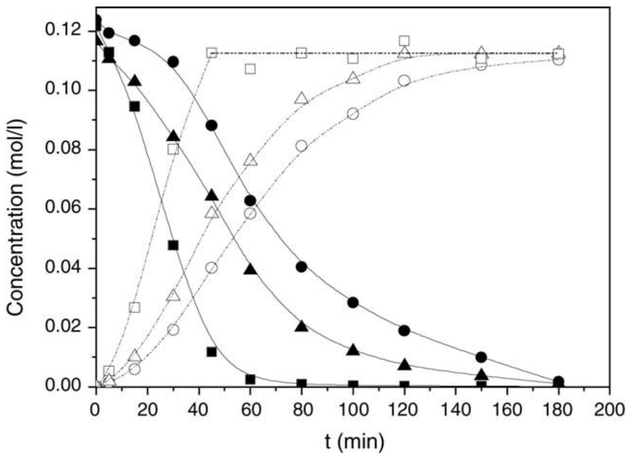


Fig. 5. Competitive reaction on Ni/AC using an equimolar mixture of chlorobenzene, *p*-chlorotoluene and *p*-chlorobenzotrifluoride: (■) chlorobenzene, (□) benzene, (▲) *p*-chlorotoluene, (△) toluene, (●) *p*-chlorobenzotrifloride, (○) benzotrifluoride. Reaction conditions: 343 K; concentration of each chlorobenzenes 0.12 mol/l; total chlorobenzenes/Ni = 18.6 (molar ratio); NaOH/total chlorobenzenes = 1.5; H_2 pressure 1 MPa.

Table 5
Non-competitive hydrodechlorination of chlorine substituted benzenes over 10 wt.% Ni/AC[a]

Substrate	Rate constant[b] (mol/l min g_{Ni})	Products distribution[c] (%)				
		Bz	ClBz	*o*-DCB	*m*-DCB	*p*-DCB
ClBz	0.178	99.9	–	–	–	–
o-DCB	0.097	99.9	0.1	–	–	–
m-DCB	0.075	99.5	0.5	–	–	–
p-DCB	0.069	98.5	1.5	–	–	–
1,2,3-TCB	0.044	95.1	1.4	3.5	–	–
1,2,4-TCB	0.051	84.2	3.9	5.8	3.1	3.0

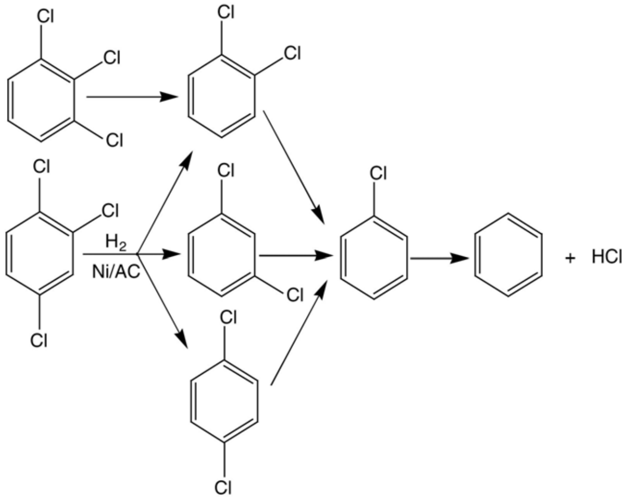
[a] Reaction conditions: same as in Fig. 1. Bz, ClBz, DCB and TCB refer to benzene, chlorobenzene, dichlorobenzene and trichlorobenzene, respectively.

[b] Zero reaction order.

[c] Product distribution at 60 min of reaction time.

chlorinated benzenes was set to 0.36 mol/l in chlorine atom base. The number and the position of chlorine atom in the benzene ring gave a large effect on the hydrodechlorination activity of chlorinated benzenes. Table 5 summarizes the rate constant (zero order) in the hydrodechlorination of chlorobenzene, three dichlorobenzenes and two trichlorobenzenes, and corresponding product distributions at 60 min. All of these chlorobenzenes were completely dechlorinated within 80 min on Ni/AC under mild condition of temperature (343 K). The reactivity of these chlorobenzenes decreased in the order of chlorobenzene > *o*-dichlorobenzene > *m*-dichlorobenzene > *p*-dichlorobenzene > 1,2,4-trichlorobenzene > 1,2,3-trichlorobenzene. The reactivity of polychlorinated benzenes decreases with the increase of chlorine number, as chlorobenzene > dichlorobenzene > trichlorobenzene.

During the hydrodechlorination reaction, partially dechlorinated products were observed along with a fully dechlorinated product, benzene. The appearance of partially dechlorinated products is the typical character of consecutive reaction, as described in Scheme 2. Chlorobenzene was always produced from all three dichlorobenzene isomers (*o*-, *m*- and *p*-) in their hydrodechlorination reactions. Hydrodechlorination of 1,2,3-trichlorobenzene yielded only *o*-dichlorobenzene, indicating that the chlorine atom located between two chlorine atoms (2-position) is hardly dechlorinated, and only the chlorine atoms located in 1 and 3 position are active under the conditions employed. On the other hand, 1,2,4-trichlorobenzene produced *o*-, *m*- and *p*-dichlorobenzene isomers. It is worth noting that a ratio of *o*-, *m*- and *p*-dichlorobenzene isomers was observed to be 1.9:1.0:1.0 at 60 min of reaction time. The concentration of these dichlorobenzenes depended on production and consumption rate of these compounds. As described in Table 4, *o*-, *m*- and *p*-dichlorobenzene isomers were dechlorinated at almost same rate although the rate for *o*-dichlorobenzene was 20–30% higher than the others. In addition, the ratio did not change much with reaction time: 2.4:1.2:1.0 at 15 min and 2.6:1.2:1.0 at 30 min. Therefore, the ratio of dichlorobenzenes mainly depended on the removal rate of chlorine atom in the trichlorobenzene hydrodechlorination. If the adsorbed hydrogen species could attack a C–Cl bond from a site of next carbon bearing no chlorine (or big) atom, it is easily understandable that 1,2,4-trichlorobenzene was hydrodechlorinated to *o*-, *m*- and *p*-dichlorobenzene in 2:1:1 ratio, and 1,2,3-trichlorobenzene was dechlorinated to *o*-dichlorobenzene but not to *m*-isomer. Clearly the steric effect prevails in this reaction. Similar preferential formation of *o*-dichlorobenzne in the gas phase hydrodechlorination of 1,2,4-trichlorobenzene has been reported on Ni/Al_2O_3 [35], Ni/$NiAl_2O_4$ [25] and Ni/Mg/Al [26] catalysts. The results have been attributed to the inductive and steric effects.



Scheme 2. Reaction pathways in the hydrodechlorination of chlorinated benzenes over Ni/AC.

The coincidence of the 2:1:1 ratio between the observed ratio and the statistical probability implies that the substrates might adopt a parallel adsorption on the catalyst surface. In fact, it is well established that benzene adsorbs parallel to many metal surface [36,37] including nickel by means of a π-complex. The parallel adsorption is also demonstrated for chlorobenzene on Cu (1 1 1) single crystal [38].

3.5. Reuse of nickel catalyst

10% Ni/AC was used to evaluate the life of the catalyst. After chlorobenzene was completely converted (average rate: 36.4 mmol l^{-1} h^{-1}), the same amount of chlorobenzene was added into the reaction system as substrate without further separation of catalyst. The activity of catalyst decreased (average rate: 3.6 mmol l^{-1} h^{-1}). After analyzing the product mixture, it was found that only a minor amount of NaCl (0.006 mol/l) existed in the liquid reaction mixture, which is close to the poor solubility of NaCl in pure ethanol (0.009 mol/l, 25 °C) [39]. Most of the produced NaCl precipitated from the solution as a solid residue.

Accumulation of NaCl layers on the catalyst surface covered on the active site, therefore, reduced the activity of catalyst. A similar phenomenon was reported for the dechlorination of aromatic chlorides over Rh–Pt/AC catalyst [9]. To confirm the hypothesis, the used catalysts was separated, washed with distilled water and dried. Then, the catalyst was re-activated and used to catalyze the reaction again. The catalytic activity (average rate: 7.3 mmol l^{-1} h^{-1}) is about two times higher than that of the catalyst without separation.

The results indicated that the deactivation of Ni catalyst accompanied with the dechlorinating process. An accumulation of NaCl on the catalyst surface is probably one of the reasons for the deactivation. The deactivated catalysts can be partially recovered by washing with distilled water and reactivating.

4. Conclusions

Results are summarized as follows:

(1) The complete hydrodechlorination of chlorobenzene was realized over 10 wt.% Ni/active carbon catalyst in liquid phase at 333–343 K under hydrogen pressure of 1.0 MPa in the presence of alkaline hydroxide.

(2) Aryl halides (iodo- and bromo-), chlorobenzenes substituted at *ortho*-, *meta* and *para*-positions with amino, chloro, methyl and trifluoromethyl groups and trichlorobenzenes (1,2,3- and 1,2,4-) were also completely hydrodechlorinated within 200 min under the similar conditions.

(3) Chlorobenzenes with either the electron-donating group or electron-withdrawing group were dechlorinated at lower rates than the parent chlorobenzene. In the presence of electron-withdrawing group, a sterically hindered *ortho* C–Cl bond was preferentially hydrodechlorinated among isomers or electron withdrawing group itself was hydrogenated in case of NO_2. These results suggest strong interaction among electron withdrawing groups (NO_2, CF_3, Cl) and catalyst surface, and the hydrogenation or hydrodechlorination proceeds in a close vicinity of the substituents.

(4) In hydrodechlorination of 1,2,3-trichlorobenzene, only the chlorines located at the C1 and C3 position were dechlorinated under the conditions employed. While in hydrodechlorination of 1,2,4-trichlorobenzene, C4-chlorine was two times more reactive than C2-chlorine and C1-chlorine. These results are rationalized if the adsorbed hydrogen species could attack a C–Cl bond from a site of next carbon bearing no chlorine (or big) atom. Clearly the steric effect prevails in this reaction.

(5) The reaction proceeds only in the presence of sodium hydroxide and the reaction rate does not depend on chlorobenzene concentration or zero order to chlorobenzene concentration. The reaction order to hydrogen is 1.9. These results can be explained when the reaction steps but not diffusion steps are the rate determining

(6) The active catalysts were characterized by hydrogen chemisorption and transmission electron microscopy techniques. The apparent activity strongly depends on the active area of nickel on catalyst surface.

(7) The deactivation of Ni catalyst was observed in the dechlorination process. An accumulation of NaCl on the catalyst surface is probably one of the reasons for the deactivation. The deactivated catalysts can be partially recovered by washing with distilled water and reactivating.

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