Gas phase hydrodechlorination of chlorinated aromatic compounds on nickel catalysts

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Supported Ni/γ-Al_2O_3 catalysts were studied in the gas phase hydrodechlorination of substituted chlorobenzenes. The catalytic properties of the catalysts were shown to be determined by the metal nickel. A correlation between the rate of the gas phase hydrodechlorination of substituted chlorobenzene and donor–acceptor properties of substituents was established. The electron-donor substituents increase and the electron-acceptor ones decrease their reactivity. The correlation analysis of data treated via the Hammett equation shows that hydrodechlorination on Ni/γ-Al_2O_3 catalysts is a reaction of electrophilic type.

Keywords: hydrodechlorination; substituted chlorobenzene; Ni/γ-Al_2O_3 catalysts

1. Introduction

Polychlorinated organic substances (PCOS) are priority toxicants of the environment due to their high carcinogenic and mutagenic activity. Catalytic hydrodechlorination is one of the ways of detoxification of the PCOS which excludes the formation of more toxic compounds, such as polychlorinated dibenzodioxins and dibenzofurans.

Ni-containing systems are known to be active catalysts in hydrogenation. The liquid phase hydrodechlorination of chlorinated pesticides and biphenyls on a 61% Ni/kieselguhr catalyst was reported in several works [1–3]. But the complete dechlorination of parent substances and intermediate products was not achieved. Supported nickel catalysts have not been studied in the gas phase hydrodechlorination of chlorinated aromatic compounds.

The aim of this work is to study the reactivity of chlorinated aromatic compounds in the hydrodechlorination on supported Ni/γ-Al_2O_3 catalysts depending

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on the nature and position of substituents in a benzene ring. Data obtained will be useful both for synthetic organic chemistry and environmental protection concerning the utilization of toxic PCOS.

2. Experimental

The catalysts were prepared by impregnating pelletized γ-Al_2O_3 (0.2–0.5 mm) with an aqueous solution of salt $Ni(NO_3)_2 \cdot 6H_2O$. The support was precalcined in air flow at 673 K. The Ni content was varied from 1 to 40 wt%. After impregnation the samples were dried and calcined in an air flow at 673 K for 4 h. Total areas of fresh and used catalysts were obtained using the BET method from adsorption of Ar at 77 K. The surface areas of used catalysts slightly (10–15%) decrease in comparison with fresh ones.

Before starting the experiments the catalysts were reduced in a hydrogen flow at 573 K for 2 h. The experiments were carried out in a flow microcatalytic set-up with a fluidized-bed reactor using the reaction mixture of the following content (vol%): R–Ar–Cl : H_2 : He = 0.5 : 20 : 79.5. The activity of the catalysts was calculated as the sum of the rates of formation of organic products. The analysis of reaction mixtures was made with a GLC chromatograph equipped with a flame ionization detector and a column packed with 5% PEGA/Inerton-super. Material balance of the reaction on carbon atoms was complete.

3. Results and discussion

The activity of nickel catalysts with different contents of metal was studied in the hydrodechlorination of chlorobenzene. Supported Pd catalysts are known to be deactivated during the hydrodechlorination process [4–6]. That is why the dynamics of the activity of the Ni catalysts with the reaction time was studied. The dependences of the catalyst activities on the reaction time at 523 K are reported in fig. 1. As follows from the data, the activity increases slightly during the first 30–60 min and then does not change during the 6 h of reaction. This shows that the Ni catalysts are stable in the presence of chlorobenzene and hydrogen chloride.

Table 1 presents the rate of hydrodechlorination of chlorobenzene on the Ni catalysts per surface of used catalysts. Benzene was the only organic product of the reaction. The data indicate that the activity of the catalysts rises by three orders of magnitude when increasing the Ni content from 1 to 3–5 wt%. Further increase of Ni content leads to a moderate rise of the activity of the catalysts, its value becoming comparable with those of unsupported 100% Ni catalysts.

The close values of the rate of hydrodechlorination of chlorobenzene on Ni metal and on supported catalysts with Ni content of more than 3 wt% (fig. 1,

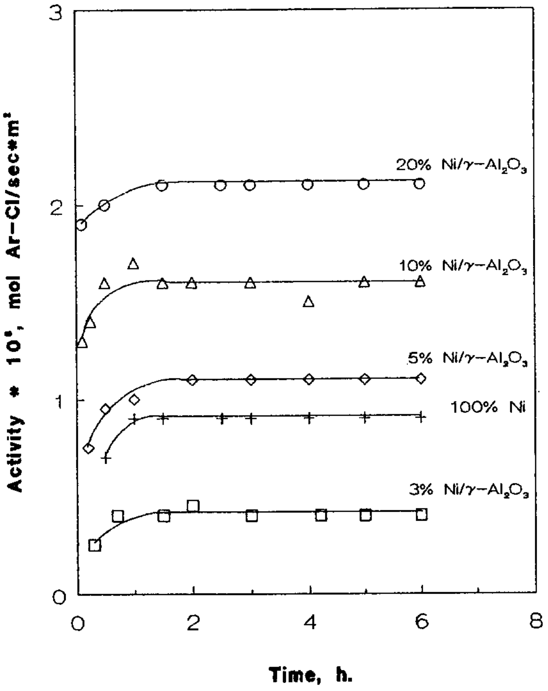

Fig. 1. The dependences of the rate of hydrodechlorination of chlorobenzene on Ni/γ-Al_2O_3 catalysts on time of reaction ($T = 523$ K).

table 1) along with the invariant activation energies (table 1) evidence that the catalytic properties are governed by the metallic Ni. The decrease of the rate and activation energies for 1% Ni/γ-Al_2O_3 is likely to be caused by the low extent of reduction of Ni to its metal state under the conditions applied.

The 10% Ni/γ-Al_2O_3 catalyst, which displays a high stability in reaction mixtures, was selected to study the reactivity of substituted chlorobenzenes in the

Table 1
Catalytic properties of Ni/γ-Al_2O_3 catalysts in the hydrodechlorination of chlorobenzene ($T = 523$ K, conversion 10%, reaction mixture (vol%) ArCl : H_2 : He = 0.5 : 20 : 79.5)

Catalyst composition (wt%)	Activity (mol/s m^2)	Activation energy (kJ/mol)
1% Ni/γ-Al_2O_3	2.6×10^{-11}	58 ± 2
3% Ni/γ-Al_2O_3	0.4×10^{-8}	96 ± 2
5% Ni/γ-Al_2O_3	1.1×10^{-8}	96 ± 2
7% Ni/γ-Al_2O_3	1.6×10^{-8}	96 ± 2
10% Ni/γ-Al_2O_3	1.6×10^{-8}	96 ± 2
20% Ni/γ-Al_2O_3	2.1×10^{-8}	92 ± 3
40% Ni/γ-Al_2O_3	2.9×10^{-8}	96 ± 2
100% Ni	0.9×10^{-8}	92 ± 2

hydrodechlorination reaction. The results obtained are presented in table 2. Hydrogenation of aromatic products was not observed. The rates of hydrodechlorination decrease by more than two orders of magnitude in the sequence: chloroaniline > chlorophenols > chlorotoluenes > dichlorobenzenes > chlorotrifluoromethylbenzene.

Generally, the reactivity of the chlorinated aromatic compounds in hydrodechlorination is determined by the position and nature of substituents in a benzene ring as well as the properties of the catalytic system. In particular, we have established for the Pd catalyst [5,6] that the position of chlorine in the benzene ring affected the relative reactivity of chlorinated benzenes and phenols. It was shown that the reactivity of compounds containing chlorine in para and meta positions was 5–10 times higher than the reactivity in the case of ortho position [5,6].

Unlike the Pd system the rate of hydrodechlorination of substituted benzenes, phenols and toluenes on Ni catalysts is slightly sensitive to the position of the chlorine atom in the benzene ring with respect to another substituent (table 2). The observed differences between Pd and Ni systems could be explained with different activation pathways of the chlorinated aromatic compound and hydrogen on the catalysts. It is known that hydrogen can exist in molecular, atomic and dissolved forms on Ni and Pd metal [7,8]. It should be noted that, at the reaction temperature, the rate of diffusion (permeability) of hydrogen in the metal Pd is greater by more than three orders of magnitude than in the metal Ni [9]. Under the reaction conditions, the ratio of the different forms of hydrogen can vary to a great extent. This has an effect on the reaction route and mechanism.

Based on the reactivity sequence of the substituted chlorobenzenes (RArCl) it is apparent that the rate of hydrodechlorination on Ni catalyst depends on the donor–acceptor properties of substituents ($R = NH_2, OH, CH_3, Cl, CF_3, H$), which vary widely.

Table 2
The reactivity of substituted chlorobenzenes in the hydrodechlorination on 10% Ni/γ-Al_2O_3 catalyst ($T = 523$ K, reaction mixture (vol%) RArCl : H_2 : He = 0.5 : 20 : 79.5, conversion of RArCl 10%)

Compound	Substituent R	Product	Activity (10^{-6} mol/g s)
chlorobenzene	H	benzene	1.9
ortho-dichlorobenzene	*o*-Cl	benzene, chlorobenzene	0.3
para-dichlorobenzene	*p*-Cl	benzene, chlorobenzene	0.6
meta-dichlorobenzene	*m*-Cl	benzene, chlorobenzene	0.3
ortho-chlorophenol	*o*-OH	phenol	3.3
para-chlorophenol	*p*-OH	phenol	3.8
ortho-chlorotoluene	*o*-CH_3	toluene	2.7
para-chlorotoluene	*p*-CH_3	toluene	2.4
para-chloroaniline	*p*-NH_2	aniline	8.5
para-chlorotrifluoromethylbenzene	*p*-CF_3	trifluoromethylbenzene	0.04

The quantitative description of the electron effect of para and meta substituents on the hydrodechlorination rate was made in the context of the Hammett equation [10,11]:

$$\lg(W/W_0) = \rho\sigma,$$

where W is the rate of hydrodechlorination of substituted chlorobenzenes; W_0 the rate of hydrodechlorination of chlorobenzene; ρ a reaction parameter; and σ a constant of the substituents R.

The dependence of the relative rate of hydrodechlorination of substituted chlorobenzenes on the donor–acceptor properties of the substituents is shown in fig. 2. The Hammett constant σ was used as a constant of the substituents [10–12]. The same dependence was found using σ^+ constants and a different one was obtained for Taft's σ^0 constants. As follows from fig. 2, the investigated compounds can be divided into two groups of only electron-donor or electron-acceptor substituents. The electron-donor substituents increase the reactivity of substituted chlorobenzenes, the electron-acceptor ones decrease their reactivity with respect to unsubstituted chlorobenzene.

The reaction parameter ρ is equal to -1.0 (correlation coefficient $\tau = 0.984$) for compounds with electron-donor substituents and -3.0 (correlation coefficient $\tau = 0.963$) for compounds with electron-acceptor ones. The negative value of the

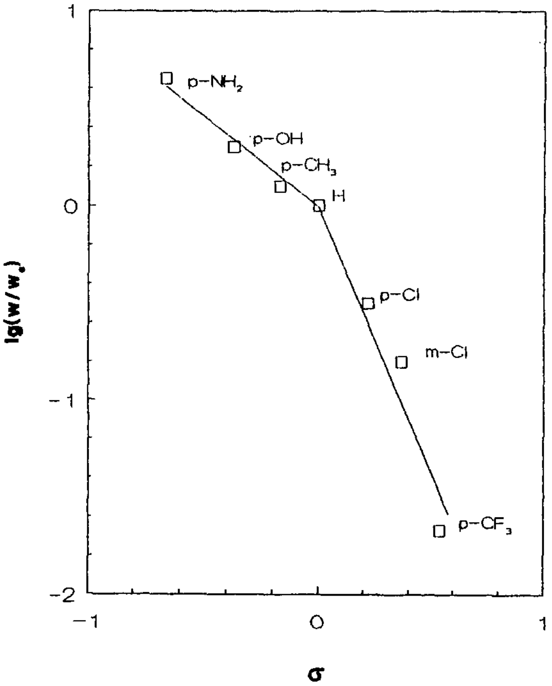

Fig. 2. The dependence of the rate of hydrodechlorination of substituted chlorobenzenes from the σ constant of the substituents.

reaction parameter shows that the hydrodechlorination of substituted chlorobenzenes on the Ni catalyst is an electrophilic reaction, i.e. the transition complex of the limiting step has a partially positive charge.

The decrease of the reaction parameter ρ when passing from electron-donor substituents to electron-acceptor ones could be due to the different electron effect of the substituent on the initial and transitional states of the reacting system resulting from the balance of their inductive and resonance effects [11,13,14].

The decrease of the rate of hydrodechlorination of substituted chlorobenzenes for the electron-acceptor substituents is observed both in liquid phase on Pd/C [15] and in gas phase on Ni/γ-Al_2O_3 catalysts. In the case of the liquid phase hydrodechlorination a slight effect of the electron-donor substituents on the relative reactivity of substituted chlorobenzenes was found. The protonation of substituents leading to sharp changes in their donor–acceptor properties is likely to occur in the presence of acetate buffer. Besides, hydrogen chloride present in the gas phase of the process could affect the hydrodechlorination rate. In the liquid phase reaction hydrogen chloride reacted with the acetate buffer.

It should be noted that the $\rho\sigma$-analysis allows the determination of the type of reaction mechanism in principle. Based on it one can predict the relative reactivity of different chloroaromatic compounds in the hydrodechlorination reaction. More detailed study is necessary to elucidate the relationship between the substituents and state of reagents and intermediates on the catalyst surface.

4. Conclusions

Nickel catalysts supported on γ-Al_2O_3 were studied in the gas phase hydrodechlorination of chlorobenzene. It was shown that properties of catalysts containing more than 3 wt% Ni are determined by the metal Ni. The apparent activation energy of the hydrodechlorination of chlorobenzene on the Ni catalysts was established to be equal to 96 ± 3 kJ/mol. It was shown that the Ni/γ-Al_2O_3 catalysts are not deactivated in reaction mixtures containing hydrogen chloride and chlorobenzene.

The correlation between the rate of the gas phase hydrodechlorination of substituted chlorobenzenes and the donor–acceptor properties of substituents was established. The electron-donor substituents increase the reactivity of substituted chlorobenzenes, the electron-acceptor ones decrease their reactivity. The correlation analysis of data treated via the Hammett equation points to the fact that the hydrodechlorination of substituted chlorobenzenes on 10% Ni/γ-Al_2O_3 is a reaction of electrophilic type.

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