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Synthesis of *para*-Dichlorobenzene by Chlorobenzene Chlorination on NaY Zeolite Heterogeneous Catalyst

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Abstract—A selective procedure for *p*-dichlorobenzene synthesis, yielding *p*-dichlorobenzene and 1,2,4-trichlorobenzene free of isomeric dichlorobenzenes, was suggested. The chlorination was performed in two steps: with feeding chlorine in an equimolar amount relative to chlorobenzene in the first step and with feeding a small (1.3–1.5-fold) excess of chlorine in the second step. NaY zeolite with the mean particle size of 3–6 μm was used as the heterogeneous chlorination catalyst. The possibility of regeneration and multiple use of the heterogeneous catalyst was demonstrated.

Keywords: chlorobenzene, *p*-dichlorobenzene, chlorination, NaY zeolite

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p-Dichlorobenzene is the starting compound required for preparing polyphenylene sulfides, which exhibit unique chemical and physical properties. *p*-Dichlorobenzene is also used as a deodorant and as a precursor of insecticides and drugs [1]. The development of a process for selective synthesis of this compound is a topical problem of chemical industry.

The main commercially used procedures for synthesizing *p*-dichlorobenzene are as follows:

- liquid-phase chlorination of chlorobenzene (or benzene) in the presence of catalysts until the *p*-dichlorobenzene concentration in the reaction mixture becomes sufficient for its efficient isolation from concentrated solutions (40–82 wt % *p*-dichlorobenzene);
- isolation of *p*-dichlorobenzene from dilute bottoms from chlorobenzene production (1–3 wt % *p*-dichlorobenzene).

Chlorination of aromatic compounds is often accompanied by the formation of an isomeric mixture

and other products, so that subsequent purification and separation of the reaction mixture are required. The use of heterogeneous catalysts such as various mineral compounds, in particular, mixed silicon and aluminum oxides (zeolites), allows the majority of these problems to be avoided owing to the catalyst selectivity. The use of such catalysts allows reaching high conversion of the starting compounds: The chlorobenzene conversion exceeds 90%, and the benzene conversion approaches 100%. One more advantage of such catalysts is the possibility of their regeneration and multiple use. The main factors influencing the selectivity are the presence of ion-exchange sites in zeolite and its acidity and porosity [2]. As shown in [3], to reach high chlorination selectivity, it is preferable to use zeolites with low content of impurities and high crystallinity, in particular, Y zeolite, L zeolite, X zeolite, gmelinite, offretite/erionite-type zeolite, mordenite, and ZSM-5 zeolite [3].

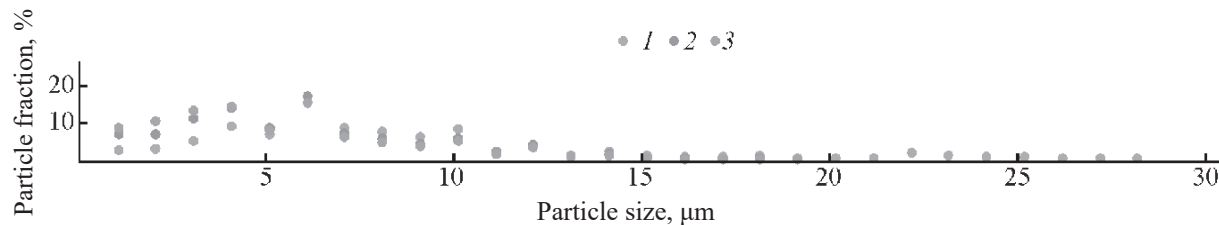


Fig. 1. Particle-size distribution of Ishimbai NaY zeolite depending on the sample treatment conditions in the course of laser diffraction measurements.

Along with zeolites, molecular sieves were also tested in the process. However, wide use of molecular sieves is limited by their easy deactivation and difficult regeneration, which is performed at high temperatures [4, 5].

As reported by Miyake et al. [4], the use of Y-type zeolite as a catalyst ensures high selectivity of *p*-dichlorobenzene formation due to definite size of zeolite pores and presence of sodium chloride molecules in them. The amount of acid sites in the zeolite was determined from the change in the concentration of ammonium chloride after the sorption on the catalyst. The zeolite pore size was 7.4 Å. The authors believe that the optimum silica ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$) for ensuring high selectivity of *p*-dichlorobenzene synthesis is 4.6.

An idea of excess chlorination of chlorobenzene and benzene in the presence of iron and aluminum chlorides as Lewis acids was suggested in patent [6]. According to the patent data, with excess chlorine high selectivity of the formation of *p*- and *o*-dichlorobenzene was reached owing to a decrease in the amount of the *m*-isomer.

The idea of excess chlorination becomes topical when it is necessary to isolate *p*-dichlorobenzene. Usually *p*-dichlorobenzene is isolated from a mixture of dichlorobenzene by repeated recrystallization or freezing [7] because of higher melting point of the *p*-isomer compared to the other isomers. The yield of crystalline *p*-dichlorobenzene in the process usually does not exceed 60% [8]. The separation of the *p*- and *o*-isomers by fractional distillation is difficult because of close volatility of the components. However, at the selectivity with respect to *p*-dichlorobenzene higher than 75% with the subsequent excess chlorination step, which leads simultaneously to a decrease in the *p*-dichlorobenzene concentration to 55–65% and in the concentration of the *o*- and *m*-isomers to a minimum, it

is possible to use fractional distillation to obtain high-purity *p*-dichlorobenzene.

This study deals with monochlorobenzene chlorination on a heterogeneous catalyst, NaY zeolite, and with excess chlorination of the reaction mixture after the first step of the equimolar chlorination in the presence of the zeolite.

EXPERIMENTAL

The NMR spectra were recorded at 25°C with a Bruker Avance-400 NMR spectrometer (400.0 MHz, ^1H ; 100.6 MHz, ^{13}C). The chemical shifts were determined using the residual solvent peak as a reference. The IR spectra of samples prepared as KBr pellets or thin films were recorded with a Bruker Vector 22 spectrometer. The weight fraction of chlorobenzene, dichlorobenzene, and other impurities in the product was determined by gas-liquid chromatography [GOST (State Standard) 646–84: Technical-Grade Chlorobenzene. Technical Specification].

Analysis of *p*-dichlorobenzene samples for the main substance content was performed by gas chromatography with a Crystal-5000.2 laboratory chromatograph (Chromatec, Russia) equipped with a flame ionization detector. The chromatographic analysis data were processed using Chromatec Analytic software (Chromatec). We used a flame ionization detector and an Agilent capillary column (HP FFAP Agilent Technologies, 50 m \times 0.32 mm, film thickness 0.50 μm).

Chromatographic analysis conditions: analysis time 38 min; vaporizer temperature 250°C; column temperature schedule: heating from 80 to 130°C at a rate of 10 deg min^{-1} , keeping at 130°C for 10 min, heating to 230°C at a rate of 10 deg min^{-1} , and keeping at 230°C for 10 min. The carrier gas was fed at a pressure of

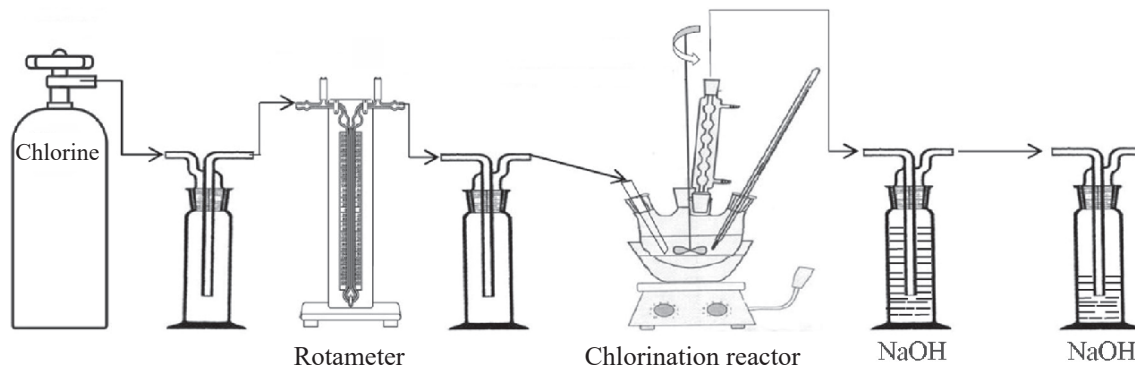


Fig. 2. Installation for *p*-dichlorobenzene synthesis.

82 ± 5 kPa and a flow rate of 25 ± 1 mL min^{-1} . The flame ionization detector was operated at 250°C and air and hydrogen flow rates of 250 and 25 mL min^{-1} , respectively.

As starting chemicals we used chlorobenzene (technical grade, Tatkhimprodukt, Russia) and evaporated chlorine [chemically pure grade, BK-Group (S-Gas), Russia]; NaY zeolite (Ishimbai Specialized Chemical Plant of Catalysts, Russia) was used as a catalyst. We also used sulfuric acid (technical grade 1, Tatkhimprodukt), sodium hydroxide (technical grade RD, Tatkhimprodukt), polymethylsiloxane PMS-300 (Tatkhimprodukt), and nitrogen (grade 5.5, BK-Group).

The melting point was determined by differential scanning calorimetry with a DSC 214 Polyma device (Netzsch-Geratebau GmbH). The melting and crystallization differential scanning calorimetry thermograms of *p*-dichlorobenzene samples were recorded in a nitrogen atmosphere (grade 5.5, BK-Group) in the temperature interval $25\text{--}80^\circ\text{C}$ at a heating rate of 0.5 deg min^{-1} and protective gas (nitrogen) flow rate of 60 mL min^{-1} . Samples ($1.5\text{--}2.5$ mg) were placed in $25\text{-}\mu\text{L}$ aluminum crucibles.

The zeolite particle size was determined with a Horiba LA-960 laser scattering particle size distribution analyzer (Fig. 1). Analysis conditions: measurement method based on Mie scattering theory, measurement range $0.01\text{--}5000$ μm , measurement time 1 min from filling with the dispersion liquid to measurement and washing, sample weight 50 mg, dispersion medium

amount from 180 to 250 mL (using a flow-through cell), viscosity less than 10 mPa s. The optical system consisted of a laser diode (LD, 650 nm, 5.0 mW) and a light emitting diode (LED, 405 nm, 3.0 mW) as light sources and a silicon photodiode as a detector. The transmittance was 84.3% for LD and 75.8% for LED. The circulation system included an ultrasonic sensor (20 kHz). The flow/fraction cell was made of Tempax glass. The circulation and stirring rate was 10 rpm. The working temperature was from 15 to 35°C (from 59 to 95°F). The relative humidity was 85%.

The zeolite was a white powder with the following characteristics: $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio 5.3, specific surface area 822 m^2 g^{-1} , bulk density 0.3 g cm^{-3} . The mean zeolite particle size determined by laser diffraction was $3\text{--}6$ μm .

The internal surface area of zeolite was determined by calculation from the certificate data: 246.6×10^6 m^2 m^{-3} (internal surface area) = 0.3 g cm^{-3} (bulk density) \times 822 m^2 g^{-1} (specific surface area), proceeding from the pore size of $0.42\text{--}0.74$ nm [9].

To synthesize *p*-dichlorobenzene, we assembled an installation consisting of a rotameter for measuring the chlorine flow rate, a glass chlorination reactor, and a trap filled with $10\text{--}15$ wt % aqueous NaOH for capturing HCl and unchanged chlorine. The reactor was heated on an oil bath using polymethylsiloxane PMS-300 as a heat carrier (Fig. 2).

The synthesis of *p*-dichlorobenzene consists of the following steps: chlorination of chlorobenzene and

Table 1. Molecular composition of reaction mixtures after monochlorobenzene chlorination in the presence of NaY zeolite

Component	Content, wt %			
	monochlorobenzene chlorination in the presence of NaY zeolite		monochlorobenzene chlorination with repeated use of NaY zeolite	
	experiment 1	experiment 2	without catalyst regeneration and purification	after catalyst washing and calcination
Chlorobenzene	16.7	4.5	9.2	9.1
<i>p</i> -Dichlorobenzene	73.4	79.7	75.9	77.6
<i>o</i> -Dichlorobenzene	8.9	14.5	11.1	12.2
<i>m</i> -Dichlorobenzene	0.7	1.0	0.9	0.8
Trichlorobenzenes	0.3	0.3	0.3	0.3
Tetra- and polychlorides	0	0	2.6	0
<i>para/ortho</i> Isomer ratio	8.3	5.5	6.8	6.3

Table 2. Yield of dichlorobenzene derivatives and chlorobenzene conversion in multiple use of the same zeolite catalyst after regeneration

Number of catalyst cycles	1	2	3	4	5	6	7
<i>p</i> -Dichlorobenzene yield, wt %	78.14	70.36	72.33	62.66	57.08	50.13	56.00
Chlorobenzene conversion, %	100	100	100	100	100	100	99.93
<i>m</i> -Dichlorobenzene yield, wt %	0	0.02	0	0.02	0.01	0.02	0.02
<i>o</i> -Dichlorobenzene yield, wt %	4.16	1.14	1.41	0.47	0.91	0.16	0.84
Yield of trichlorobenzenes, wt %	17.7	28.48	26.26	36.85	42.0	49.69	43.08

excess chlorination of dichlorobenzenes; capture of the released gases; filtration of the reaction mixture.

Chlorine was fed from a cylinder through a needle-like valve equipped with a straight metal tube acting as a vaporizer to a bubbler through a Drechsel bottle filled with concentrated H₂SO₄. After each experiment, the acid was replaced by a fresh portion.

Prior to use, NaY zeolite was calcined in a muffle furnace at 540°C for 3 h to remove water and activate the zeolite catalytic sites. The mean amount of chlorobenzene taken in an experiment was 110 g; NaY zeolite was taken in an amount of 10 wt % relative to chlorobenzene.

Chlorination was performed as follows: Chlorine was fed at room temperature at a rate allowing the breakthrough to be avoided (70–90 mL min⁻¹) into a reactor charged with chlorobenzene and the catalyst with vigorous stirring using an overhead stirrer. After starting

feeding chlorine, the reaction mixture temperature spontaneously increased to 40–45°C, after which the reaction mixture was heated to 55–57°C over a period of 30 min. Then, the chlorine flow rate and reactor temperature were maintained constant for 6–7 h.

After the chlorination completion, the reaction mixture was purged with gaseous nitrogen to remove dissolved hydrogen chloride and possible traces of chlorine. Then, the reaction mixture preheated to 70°C was unloaded and filtered while hot in a vacuum to remove the catalyst, which was then reused.

In the course of slow cooling of the reaction mixture to room temperature (6–8 h), crystals of the target component are formed in the vessel in a large amount (usually up to 75% of the weight of *p*-dichlorobenzene obtained). The crystals were filtered off, and the content of *p*-dichlorobenzene in them, according to the chromatographic data, was 98.5–99.0 wt %.

1,4-Dichlorobenzene. The pure product was obtained as colorless crystals, mp 53–54°C. ¹H NMR spectrum (400 MHz, CDCl₃, ppm): δ 7.29 (s, 4H). ¹³C NMR spectrum (125.8 MHz, CDCl₃): δ 132.5, 129.8. IR spectrum (KBr, cm⁻¹): 491, 525, 1008, 1090, 1130, 1385, 1481, 1642, 1785, 3034.

RESULTS AND DISCUSSION

The *para/ortho* isomer ratio reached 5.5–8.3, whereas, according to published data, the ratio of these products in processes involving NaY zeolite as a catalyst usually does not exceed 3–4 [4, 10]. Miyake et al. [4] focus attention on the type of the NaY catalyst in which the silica-to-alumina ratio is 2–4. The obtained values of the *para/ortho* selectivity are comparable with the data obtained in chlorination processes performed using L-type zeolite (Linde Type L), 6–10 [11–15]. The *para/ortho* isomer ratio decreases with an increase in the chlorobenzene conversion. This fact suggests that, as chlorobenzene in the reaction solution is consumed, *p*-dichlorobenzene occupies the catalyst pores and thus prevents the access of chlorobenzene molecules to the zeolite catalytic sites, which leads to nonselective reaction of chlorobenzene with chlorine in solution or on the catalyst surface and to an increase in the relative content of the *o*-isomer. However, in [16], when using L-type zeolites, high selectivity (87.8 wt %) of *p*-dichlorobenzene formation in benzene chlorination was reached, which is probably associated with different course of the chlorobenzene and benzene chlorination and with the adsorption of chlorine atoms on zeolite.

In repeated single use of the filtered-off catalyst without regeneration and purification, the catalyst activity and selectivity did not change noticeably. After washing the catalyst and thoroughly drying it by calcination, the catalytic properties are restored (Table 1).

In repeated use of the regenerated catalyst, the selectivity decreases after the fourth cycle, which is probably associated with deactivation of the catalyst pores due to the interaction of HCl with aluminum and possible dealumination and removal of sodium cations; as a result, the ion-exchange properties of the zeolite decrease (Table 2). However, the chlorobenzene conversion in chlorination does not change.

Table 3. Component composition of the reaction mixture under the conditions of excess chlorination

Component	Content, wt %, at indicated chlorobenzene : chlorine molar ratio	
	1 : 1.35	1 : 1.5
Chlorobenzene	0.03	0.02
<i>p</i> -Dichlorobenzene	59.2	55.0
<i>m</i> -Dichlorobenzene	1.9	0.4
<i>o</i> -Dichlorobenzene	0.005	0
Tri- and tetrachlorobenzenes	38.9	44.6

Takahashi and Kai [17] state that the acid sites of HY-type zeolite can be deactivated upon interaction with *p*-dichlorobenzene or *p*-chlorobromobenzene. Zaneskin et al. [18] reached the 67% selectivity of *p*-dichlorobenzene formation using NaX-type catalyst and 71.26% selectivity using KSK silica gel. They also showed that the catalyst pore size significantly influenced the reaction selectivity. The authors believe that the optimum pore size for reaching high selectivity of *p*-dichlorobenzene formation and preventing the catalyst deactivation is 0.6–1 μm. However, our results obtained in chlorination in the presence of finely dispersed NaY zeolite powder disagree with this statement because the catalyst selectivity depends to a greater extent on the amount of acid sites [4]. The interaction of β-type zeolites with *p*-dichlorobenzene can be accompanied by isomerization of the latter with the formation of free radicals, which was studied in [19]. Similar results are given in [20].

In this study, we suggested a procedure for preparing *p*-substituted chlorobenzene chlorination products virtually free of the *o*-isomer impurity by additional chlorination (excess chlorination of the reaction mixture obtained after the first step of equimolar chlorination). This procedure solves the problem of the subsequent separation of the *p*- and *o*-isomers.

The dichlorobenzene chlorination rate decreases in the order *m*-dichlorobenzene > *o*-dichlorobenzene > *p*-dichlorobenzene. Chlorine atoms in the benzene

molecule are orientants of the first kind, which leads to the further electrophilic substitution in the course of excess chlorination in positions 2 and 4 of the aromatic ring in the case of *m*-dichlorobenzene and in positions 4 and 5 in the case of *o*-dichlorobenzene. The content of the *p*-isomer in the reaction mixture thus increases. The by-product of excess chlorination is 1,2,4-trichlorobenzene. In chlorination of any of dichlorobenzene isomers, the reaction selectively yields 1,2,4-trichlorobenzene with a minor impurity of 1,2,3-trichlorobenzene.

To evaluate the process direction and refine changes in the weight fractions of the components, we introduced into the reaction mixture an additional amount of chlorine in 1 : 1.35 and 1 : 1.5 ratios (Table 3).

The reaction mixture obtained can be separated by fractional distillation into two main fractions, because the difference in the boiling points exceeds 35°C (*p*-dichlorobenzene 174.5°C and trichlorobenzenes 211–213°C). A small amount of *o*-dichlorobenzene with the higher boiling point (180°C) compared to the *p*-isomer will be distilled at the end of fractional distillation together with the “bottoms” whose composition is as follows (wt %): 1,2,4-trichlorobenzene 89.0, 1,2,3-trichlorobenzene 6.3, and tetrachlorobenzenes 4.7.

CONCLUSIONS

The results of our study allow the following conclusions:

(1) Chlorobenzene chlorination catalyzed by NaY-type zeolite allows reaching high *para/ortho* isomer ratio, 5.5–8.3, comparable with the selectivity of L-type zeolite as a catalyst.

(2) Excess chlorination of *p*-dichlorobenzene using NaY zeolite as a heterogeneous catalyst (50% chlorine excess) allows simplification of the *p*-dichlorobenzene isolation from the reaction mixture; its yield is 55–60%, and the purity reaches no less than 99.6%.

Thus, in equimolar chlorination of chlorobenzene, the bottom residue is a difficult-to-separate mixture of *o*- and *p*-isomers of dichlorobenzene with impurities of the *m*-isomer and trichlorobenzenes; this mixture can be used only as a solvent. In the case of excess chlorination, the bottom residue is technical-grade trichlorobenzene with approximately 95 wt % content

of the main components (1,2,4- and 1,2,3-isomers). This product can be used in industry as a component of various dielectric liquids, transformer oil, vat dyes, pesticides, and vulcanization accelerators, and also as a high-boiling solvent in organic synthesis.

Therefore, 1,5-fold excess chlorination of chlorobenzene, followed by fractional distillation, is a preferable procedure for the *p*-dichlorobenzene synthesis. Heterogeneous catalysts have a number of advantages due to their higher catalytic selectivity. This allows reaching >99% conversion of the initial chlorobenzene (or benzene) and simultaneously reducing the reaction temperature, thus reducing the formation of by-products. The suggested catalytic system also allows reaching high *para/ortho* isomer ratio (>8), which is important for simplifying the isolation of the pure *p*-isomer.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

AUTHOR CONTRIBUTION

R.M. Akhmadullin: development of the article concept, formulation of goals of the study; A.V. Rakov: determination and calculation of the internal surface area, of the pore size, and of the zeolite particle size by laser diffraction; zeolite sample preparation; L.I. Musin: manuscript preparation, literature analysis; S.A. Irdinkin: chlorination experiments; I.N. Litvinova: gas-chromatographic analysis; I.S. Antipin: development of the article concept, formulation of goals of the study; A.G. Akhmadullina: analysis and systematization of the results obtained, formulation of conclusions.

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