

Hydrodechlorination Polychlorinated Benzenes and Biphenyls in the of the Presence of the Bimetallic Catalysys on Carbon Supports.

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Introductuon

Design of new processes for the the efficient removal of highly toxic chlorinated dibenzo-p-dioxins, polychlorinated aromatic hydrocarbons attracts much interest nowadays, since these compounds represent a major environmental problem and as a synthetic method for producing specific isomers of chloroaromatic compounds[1]. Analysis of the various methods of detoxification of organic chlorides leads to the conclusion that reductive methods are more ecologically favorable then oxidative ones [2]. The fact the catalysis can play a major role in waste reduction. A resent study has shown that for organic wastes such as PCB dielectric liquids and halogenated petrochemical by-product, hydrodechlorination, recycle, and recovery are more attractive economically than direct incineration [3]. Transition metals (Ni, Pd, Pt, Ru), supported on to various materials (Al_2O_3 , SiO_2 , carbon), are used commonly as hydrodechlorination catalysts. Literature data have shown, successful dechlorination of polychlorinated compounds (polychlorobiphenyls, hexachlorobenzene) by using Ni catalysts requires severe reaction conditions - high temperature ($100-325^{\circ}C$) and high hydrogen pressure (50-100 atm) [4]. Pd, Pt, and Ru catalysts permitting successful dechlorination of polychloroaromatic compounds under milder conditions [5] are not feasible for large-scale application because of their high cost.

The aim of this study was getting and investigation of effective and inexpensive catalysts, permitting to carry out liquid-phase hydrodechlorination under mild reaction conditions. This problem was decided at employment of bimetalic catalysts consist of compounds of nickel and palladium (nickel - basic component), supported on carbon materials.

Material and Methods

Chlorobenzene was purified by vacuum distillation (to 99.5% purity). Hexachlorobenzene and dielectric liquid SOVTOL-10 (76 wt.% polychlorobiphenyls and 24 wt.% 1,2,4-trichlorobenzene) were used without purification. Using chromatograph - mass spectrometry it was determined that the mixture of polychlorobiphenyls contained 54 wt.% Cl and 46 wt.% (C+H).

Mono- and bimetallic catalysts were prepared as follows: via support impregnation by aqueous solutions of transition metal chlorides, drying. Then the

samples were reduced by an ethanol solution of NaBH_4 and washed with a water-ethanol mixture (ethanol:water = 1:1).

Nickel and palladium catalysts contained $1.7 \cdot 10^{-4}$ g-atom of the metal per 1 g of the catalyst (Ni/C or Pd/C). Promoted nickel catalysts contained $1.7 \cdot 10^{-4}$ g-atom of Me per 1 g of the catalyst, where Me = Ni + Pd. The promoted catalysts were designated as X%PdNi/C, in which the mole percentage of promoter (Pd) to amount of nickel and promoter in the catalyst was represented as X and carbon material - as C.

The hydrodechlorination was performed either in the thermostatic glass reactor or in the thermostatic autoclave provided with a magnetic stirrer under constant hydrogen pressure. In the standard experiments the fresh-prepared catalyst containing 0.1 mmole of metal was added to 0.5-3.0 mmoles (referred to the C-Cl fragment) of chloroaromatic compound dissolved in 10 ml of 95% ethanol or in 10 ml of the mixture of 95% ethanol and toluene or heptane (ethanol:toluene or heptane = 3:2). The ethanol solution contained NaOH excess required to bond HCl produced in the reaction. The resulting solution was vigorously stirred at the hydrogen pressure of 1, 20, or 50 atm. During the reaction the samples of the mixture were taken for GLC analysis. Undecane was used as an internal standard.

Qualitative and quantitative analyses of the reaction products were carried out by using a LKhM-80 chromatograph and a LKB 2091 GAS CHROMATOGRAPH - MASS SPECTROMETER. ^1H , ^{11}B NMR spectra were measured on Bruker CXP-300 NMR spectrometer. Electron microscopy data were obtained on a Jeol-100C instrument.

Results and Discussion

Table 1 lists the catalyst activities in chlorobenzene hydrodechlorination, which were characterized by the initial rate of benzene formation from chlorobenzene ($W_0/\text{mole} \cdot (\text{Me g-atom} \cdot \text{min})^{-1}$, where Me is the transition metal). The process was carried out in the presence of the monometallic catalysts and their mixtures and bimetallic catalysts at 20°C and 70°C and at atmospheric hydrogen pressure. Pd/C is most active among the studied catalysts. As follows from Table 1, the promoted catalyst exhibits the higher activity in the hydrodechlorination than the nickel catalyst and the mixture of the monometallic catalysts with the same content of corresponding transition metals as in the bimetallic catalyst. At 20°C and 70°C the activity of promoted nickel catalyst is, respectively, 13.3- and 3.3-fold higher than that of the mixture of palladium and nickel catalysts. Thus, by activity, the bimetallic catalyst shows a synergistic effect relative to the mixtures of palladium and nickel catalysts both at 20°C and 70°C. Apparently, when the bimetallic phase of the supported promoted catalyst forms, the promoter (Pd) either is incorporated into the nickel crystal lattice and increases the number of defects at the surface of bimetallic phase, or changes the electron state of the nickel phase of the catalyst, thus increasing the catalyst activity in the hydrodechlorination. These assumptions require further verification.

It has been shown that in the hydrodechlorination of the polychlorinated benzenes the bimetallic catalyst is more active than the nickel catalyst or mixture of monometallic catalysts.

perform the process under milder reaction conditions (for SOVTOL-10) than on using the nickel catalysts.

The catalyst Pd₂Ni₉₈/C was characterized with using ¹H, ¹¹B NMR solid state spectroscopy and electron microscopy. The obtained results could explain the high activity is attributable to high dispersed mettalic clusters (10-12 Å) and active site if the amorphous palladium-nickel-boron is also mettalic particle.

Thus, the conditions here reported for hydrodechlorination are characterized by a high reaction rate. Such high activity of Pd-promoted Ni catalysts may open the ways to new application. According to these results it could be possible to design catalysts and catalytical processes for hydrodechlorination by hydrogen of environmentally problematic compounds without production of any waste.

References

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As expected, the Pd-promoted nickel catalysts ensure the higher dechlorination degree (X) than the nickel catalysts or mixture of monometallic catalysts do under the same reaction conditions.

Table 1.

Activities of mono- and bimetallic catalysts (Ct) in hydrodechlorination of chlorobenzene (CB) in ethanol solution of NaOH at atmospheric hydrogen pressure (molar ratio Ct:CB = 1:5)

No	Catalyst (Ct)	W ₀ (mol/(L·min·g-atom Ct))	
		at 20 °C	at 70 °C
1	Ni/C	0,11	5,19
2	Ni/C + Pd/C	0,94	9,44
3	2%PdNi/C	12,5	25,0
4	Pd/C	29,3	62,3

Table 2.

Dechlorination degree (X) of hexachlorobenzene and dielectric liquid SOVTOL-10 in the presence of nickel and bimetallic Ni-Pd catalysts.

No	Substrate (S)	Catalyst (Ct)	Ratio S(C-Cl):Ct	Temp. (°C)	Solv. ^b	Press. H ₂ (atm)	Time (h)	X (%)
1	C ₆ Cl ₆	Ni/C	30:1	50	eth.-tol.	20	7	87
2	C ₆ Cl ₆	2%PdNi/C	30:1	50	eth.-tol.	20	5	89
3	C ₆ Cl ₆	10%PdNi/C	30:1	50	eth.-tol.	20	4	88
4	SOVTOL-10	Ni/C	14:1	60	eth.-tol.	50	4	35 ^a
5	SOVTOL-10	Ni/C	14:1	60	eth.-hep.	50	4	50 ^a
6	SOVTOL-10	2%PdNi/C	26:1	50	eth.-hep.	20	3	90 ^a

a - dechlorination degree (X) was determined as the ratio of the total number of removed chlorine atoms to the total initial number of chlorine atoms in SOVTOL-10; b - as a solvent, the mixture 95% ethanol:toluene = 3:2 was used.

Table 2 presents the data on the dechlorination degree of hexachlorobenzene and dielectric liquid (SOVTOL-10) in the presence of nickel and Pd-promoted nickel catalysts at a hydrogen pressure. Parameter X was calculated as follows:

$$X = 1 - \sum_{i=0}^j iC_i / jC^0$$

where C_i is the molar concentration of substratum containing *i* chlorine atoms in the molecule, *j* is the initial number of chlorine atoms in the molecule, and C⁰ is the initial concentration of the dechlorinated compound.

The experimental data show that the promoted catalysts permit one either to attain a high dechlorination degree (X) in a shorter time (in the case of C₆Cl₆) or to