

# Dioxin '97, Indianapolis, Indiana, USA

## Catalytic Hydrodechlorination of Polychlorinated Aromatic Hydrocarbons

V. I. Simagina, V.A. Yakovlev, I.V. Stoyanova, V.A. Likhoboy, Borekov Institute of Catalysis, Pr. Acad. Lavrentieva, 5, Novosibirsk, 630090, Russia

### Abstract

Liquid phase dechlorination of chlorobenzene, hexachlorobenzene, polychlorinated biphenyls, on Me<sup>o</sup>/C (where Me<sup>o</sup> - Pd, Ni and bimetallic Pd-Ni; C - carbon material "Sibunit" with H<sub>2</sub> have been studied at 20-70°C and P<sub>H<sub>2</sub></sub>=1-50 atm. Catalysts were prepared via support impregnation by solution of metal salts, drying, thermal treatment with subsequent treatment by a reducing agent. As reducing agent was used NaBH<sub>4</sub>. According to the studies Pd/C and Ni-Pd/C showed the highest activity. These catalytic systems allowed to carry out effective dechlorination polychlorinated aromatic compounds at 70°C. Kinetic studies showed, that hydrodechlorination of these compounds to be consecutive reaction and under the conditions described may produce less-chlorinated compounds. In case of hydrodechlorination 1,2,4 trichlorobenzene the reaction path-way is: the three dichlorobenzene isomers and then, sequentially: chlorobenzene and benzene. Thus, the method allows selectivity remove halogen from the aromatic ring and providing the new methods for organic synthesis.

The catalytic systems (Pd/C and Ni-Pd) - H<sub>2</sub> allowed to carry out effective dechlorination of polychlorinated aromatic compounds (polychlorobiphenyls, hexachlorobenzene) to nonchlorinated products at 20-70°C and 1-50 atm H<sub>2</sub> in the ethanol-containing solution.

### Introduction

Design of new processes for the efficient removal of highly toxic chlorinated dibenzo-p-dioxins, polychlorinated aromatic hydrocarbons (polychlorinated biphenyls (PCB), hexachlorobenzene) attracts much interest nowadays, since these compounds represent a major environmental problem. Analysis of various methods of detoxification of organic chlorides leads to the conclusion that reductive methods are more ecologically favorable than oxidative ones<sup>1)</sup>. The fact the catalysis can play a major role in waste reduction. A recent 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<sup>2)</sup>. Noble metals are used commonly as hydrodechlorination catalysts in the liquid phase for organic synthesis<sup>3)</sup> and have been used for the same purpose in gas-phase work<sup>4)</sup>. Literature data have shown, successful dechlorination using Ni catalysts requires severe reaction conditions - high temperature and high hydrogen pressure. Pd, Pt, and Ru catalysts permitting successful dechlorination of polychloroaromatic compounds under mild conditions are not feasible for large-scale application because of their high price. Formerly we showed<sup>5)</sup> a possibility of dechlorination of chloroaromatic compounds, including dioxins, using a complex of compounds of transition metals (Ni, Pd, Ti, Fe, Cu) and hydrides of alkali and alkaline-earth

metals ( $\text{LiAlH}_4$ ,  $\text{MgH}_2$ ,  $\text{NaH}$ ,  $\text{NaH}(\text{LiAlH}_4)_{1/2}$ ) under mild conditions (20-70°C). However, such dechlorination requires inert atmosphere.

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

### Experimental Methods

Chlorobenzene and 1,2,4-trichlorobenzene (pure for analysis) were purified by vacuum distillation (to 99.5% purity). Hexachlorobenzene (chemical purity grade) 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 with subsequent treatment by a reducing agent. As reducing agent was used  $\text{NaBH}_4$ , were supported on a carbon material.. Then the samples were reduced by an ethanol solution of  $\text{NaBH}_4$  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, where X% shows the portion of the g-atoms of promoter (Pd) with respect to the total amount of nickel and promoter in the catalyst, and C is the carbon material.

As a support, the carbon material Sibunit described in<sup>5)</sup> was used. Surface area of carbon samples from adsorption of argon was 280 m<sup>2</sup>/g.

Hydrodechlorination was performed either in a thermostatic glass reactor or in a thermostatic autoclave provided with a magnetic stirrer under constant hydrogen pressure. In 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 excess NaOH required to bond HCl produced in the reaction. 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 using a LKhM-80 chromatograph (stainless-steel column of size 2 m x 3 mm, filled with 5% 8E 30 on chromaton N-AW-DMCS, flame-ionization detector, carrier gas - argon, 60 ml/min) and a LKB 2091 GAS CHROMATOGRAPH - MASS SPECTROMETER (glass capillary column of size 40 m x 0.3 mm, stationary phase SE-30).

### Results and Discussion

Table 1 lists the catalyst activities in chlorobenzene hydrodechlorination, which were characterized by the initial rate of benzene formation from chlorobenzene ( $W, \mu\text{mole} \cdot (\text{Me g-atom} \cdot \text{min})^{-1}$ , where Me is the transition metal). The process was carried out in the presence of

# Dioxin '97, Indianapolis, Indiana, USA

monometallic catalysts and their mixtures and bimetallic catalysts at 20°C and 70°C and 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 hydrodechlorination than the nickel catalyst and mixture of 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 hydrodechlorination. These assumptions require further verification.

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

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

№	Catalyst (Me)	W <sub>0</sub> (mole/(l·min·g-atom Me))	
		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. Degree of dechlorination (X) of 1,2,4-trichlorobenzene and hexachlorobenzene in the presence of mono- and bimetallic catalysts at 70°C and atmospheric hydrogen pressure.

№	Reactant (R)	Catalyst (Me)	Ratio R(C-Cl) <sup>a</sup> : Me	Solvent	Time (hours)	X (%)
1	C <sub>6</sub> Cl <sub>3</sub> H <sub>3</sub>	Ni/C	15:1	ethanol	6	10
2 <sup>b</sup>	C <sub>6</sub> Cl <sub>3</sub> H <sub>3</sub>	Ni/C + Pd/C	15:1	ethanol	6	37
3	C <sub>6</sub> Cl <sub>3</sub> H <sub>3</sub>	2%PdNi/C	15:1	ethanol	3	91
4	C <sub>6</sub> Cl <sub>6</sub>	Ni/C	30:1	eth.-tol. <sup>c</sup>	13	24
5 <sup>b</sup>	C <sub>6</sub> Cl <sub>6</sub>	Ni/C + Pd/C	30:1	eth.-tol. <sup>c</sup>	6,5	40
6	C <sub>6</sub> Cl <sub>6</sub>	2%PdNi/C	30:1	eth.-tol. <sup>c</sup>	6,5	89

a - on determining the ratio reactant:metal the reactant amount was estimated by the C-Cl fragment; b - molar ratio Ni:Pd = 98:2; c - as a solvent, the mixture 95% ethanol:toluene = 3:2 was used.

Table 2 presents the data on the degree of dechlorination (X) of 1,2,4-trichlorobenzene and hexachlorobenzene in the presence of mono- and bimetallic catalysts at atmospheric hydrogen pressure and 70°C. Parameter X was calculated as follows:

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

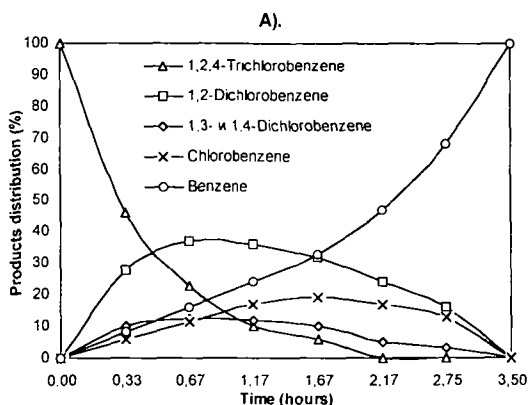
where  $C_i$  is the molar concentration of reactant containing  $i$  chlorine atoms in the molecule,  $j$  is the initial number of chlorine atoms in the molecule, and  $C^0$  is the initial concentration of dechlorinated compound.

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

Figure 1 shows the curves for distribution of the products of 1,2,4-trichlorobenzene hydrodechlorination in the presence of nickel (Ni/C) and bimetallic (2%PdNi/C) catalysts and of the mixture of nickel and palladium catalysts (Ni/C + Pd/C). As seen from the plots, dechlorination of 1,2,4-trichlorobenzene is a consecutive reaction. At the stage of formation of dichlorobenzene isomers 1,2-dichlorobenzene (1,2-DCB) is the main product in all three cases. In some instances the molar ratio 1,2-DCB : (1,3-DCB + 1,4-DCB) is 4:1. Thus, using the Pd-promoted nickel catalyst permits one not only to completely dechlorinate 1,2,4-trichlorobenzene in a short time under mild reaction conditions but also to selectively obtain the product of partial dechlorination - 1,2-dichlorobenzene.

Table 3 lists the results of hydrodechlorination of hexachlorobenzene and dielectric liquid (SOVTOL-10) in the presence of nickel and Pd-promoted nickel catalysts at a higher hydrogen pressure. The experimental data show that the promoted catalysts permit one either to obtain a high dechlorination degree ( $X$ ) in a shorter time (in the case of  $C_6Cl_6$ ) or to perform the process under milder reaction conditions (for SOVTOL-10) than on using the nickel catalysts.

As seen from the comparative analysis of experiments 4 and 5 (Table 3), the solvent nature significantly affects the hydrodechlorination efficiency. Heptane, as a component of the mixed solvent, is more efficient in hydrodechlorination of SOVTOL-10 than toluene. Toluene has the aromatic nature similar to polychlorobiphenyls. Therefore it is likely to compete with dechlorinated compound in adsorption on the graphite-like surface of carbon material Sibunit or on the metallic cluster of catalyst.



# Dioxin '97, Indianapolis, Indiana, USA

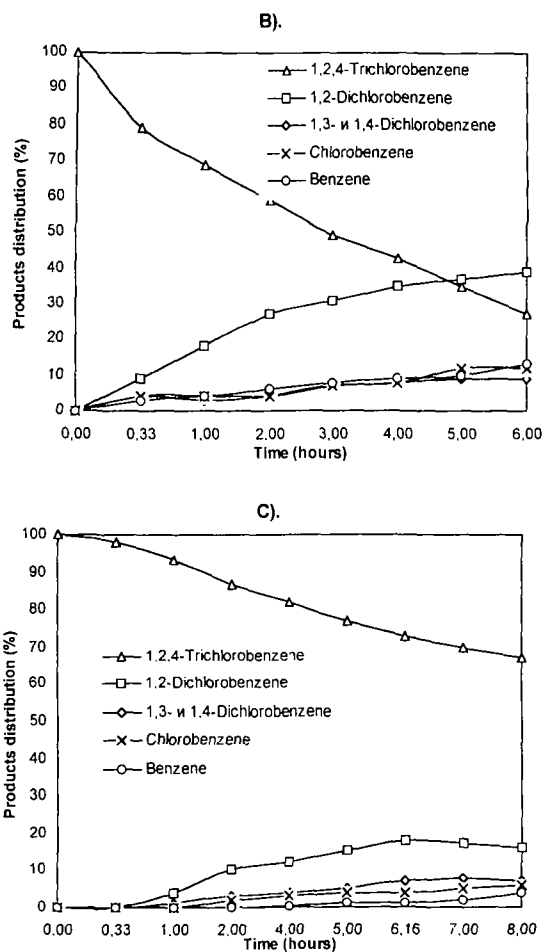


Fig. 1. Hydrodechlorination of 1,2,4-trichlorobenzene in ethanol (1 atm H<sub>2</sub>, 70°C) in the presence of: a) 2%PdNi/C, b) Ni/C + Pd/C, c) Ni/C.

Table 3. Degree of dechlorination (X) of hexachlorobenzene and dielectric liquid SOVTOL-10 in the presence of nickel and bimetallic Ni-Pd catalysts.

N <sup>o</sup>	Reactant (R)	Catalyst (Me)	Ratio R(C-Cl):Me	Temp (°C)	Solv. <sup>b</sup>	Press. H <sub>2</sub> ,(atm)	Time (hour)	X (%)
1	C <sub>6</sub> Cl <sub>6</sub>	Ni/C	30:1	50	eth.-tol.	20	7	87
2	C <sub>6</sub> Cl <sub>6</sub>	2%PdNi/C	30:1	50	eth.-tol.	20	5	89
3	C <sub>6</sub> Cl <sub>6</sub>	10%PdNi/C	30:1	50	eth.-tol.	20	4	88
4	SOVTOL-10	Ni/C	14:1	60	eth.-tol.	50	4	35 <sup>a</sup>
5	SOVTOL-10	Ni/C	14:1	60	eth.-hep.	50	4	50 <sup>a</sup>
6	SOVTOL-10	2%PdNi/C	26:1	50	eth.-hep.	20	3	90 <sup>a</sup>

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.

Data of chromatography-mass spectrometry show the main products of the hydrodechlorination of dielectric liquid SOVTOL-10 in the presence of 2%PdNi/C at 50°C and 20 atm H<sub>2</sub> (Table 3, No. 6) after 3 hours are biphenyl and benzene. Isomers of mono- and dichlorobiphenyl are also present in small amounts.

According to these results it could be possible to set up conditions on selective dehalogenation useful for synthetic purposes and detoxication methods of environmentally problematic compounds. This reaction allows polychlorinated aromatic to be reduced to the parent hydrocarbons without production of waste.

## Literature Cited

- (1) Kalnes, T. N., James, R.B. "Hydrodechlorination and Recycle of Organic Waste Streams". *Environ. Prog.*, 7(3), 1988, p. 185
- (2) Pinder A.R., *Synthesis*, (1980), p.425-452.
- (3) Kovenklioglu S., Cao Z., Shan D., Farrauto R.J., Balko E.N., *AIChE Journal*, 1992, 38, 7, 1003-1012.
- (4) Coq B., Ferrat G., Figueras F., *J.Catal.*, 1986,101, p.434-441.
- (5) Simagina V.I., Litvak V.V., Stoyanova I.V., Yakovlev V.A., Mastikhin V.M., Afanasekova I.A., Likholobov V.A., *Russian Chem. Bull.*, 1996, 45, 6, p.1321-1324