Liquid-Phase Dechlorination of Toxic Man-Made Products Using Nanodispersed Palladium Catalysts Sibunit

A. V. MEKHAEV[1], M. G. PERVOVA[1], O. P. TARAN[2], I. L. SIMAKOVA[2], V. N. PARMON[2], M. A. SAMORUKOVA[1], V. P. BOYARSKIY[3], T. E. ZHESKO[3], V. I. SALOUTIN[1] and YU. G. YATLUK[1]

[1]*Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, Ul. Akademicheskaya/S. Kovalevskoy 20/22, Yekaterinburg 620219 (Russia)*

E-mail: yatluk@ios.uran.ru

[2]*Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 5, Novosibirsk 630090 (Russia)*

[3]*Saint Petersburg State University, Universitetskaya Naberezhnaya 7/9, Saint Petersburg 199034 (Russia)*

Abstract

Studies concerning the liquid-phase catalytic reductive dechlorination of toxic man-made products using catalysts M/Sibunit (M = Ni, Pt, Pd) were performed. It has been demonstrated that the most pronounced activity is exhibited by catalysts based on palladium.

Key words: reductive dechlorination, polychlorbiphenyl (PCB), herbicides, metal-carbon catalysts, Sibunit

INTRODUCTION

The most widespread (and most hazardous) modern ecotoxicants are presented by polychlorinated biphenyls (PCBs) and 2,2,2-trichloro-1,1-bis(*p*-chlorophenyl) ethane (DDT). Owing to the fact that they exhibit a number of unique biological, chemical and physical properties, they found wide application in industry and agriculture. However, because of the fact that the mentioned compounds are highly toxic and chemically stable, they are considered to be persistent organic pollutants and so they are forbidden to use by the World Health Organization. In addition, PCBs are the precursors of polychlorobenzodioxines and polychlorodibenzofurans, whose toxicity level is much greater than the value inherent in PCBs themselves [1]. Therefore, the utilization of both PCBs and DDT represents an urgent task.

A great number of methods were investigated concerning the neutralization of PCBs and DDT [2] such as pyrolysis, oxidation methods, dechlorination, photolysis, radiolysis, electrochemical and biotechnological methods, *etc*. In recent years, the method of reductive dechlorination (hydrodechlorination) has received wide recognition. This is connected, first and foremost, with the potentialities of applying new types of catalysts prepared using modern materials and technologies (including nanomaterials and nanotechnology).

For the reductive dechlorination of PCBs, as a rule, palladium containing catalysts on inert carriers (mainly carbon, Al_2O_3 and SiO_2) [3–8] are typically used.

Previously, our studies demonstrated the possibility of using metal-carbon compositions as catalysts for reductive dechlorination [9]. Owing to the achievements of modern science and technology it is possible to produce reliable novel porous carbon materials suitable for use as carriers for catalysts. The Boreskov Institute of Catalysis of the SB RAS developed a porous graphite-like material Sibunit [10] that exhibits high strength, thermal stability, re-

sistance against repeated regeneration, as well as mesoporous structure, which makes it a promising support for a catalyst of liquid-phase processes [11].

The aim of this work consisted in comparative studies concerning the catalytic properties of nanodispersed metal catalysts (metal: Ni, Pt, Pd) based on the Sibunit in the reductive dechlorination and hydrogenation of ecotoxicants for further using the products of their processing as raw materials in various industrial fields.

EXPERIMENTAL

Obtaining Me/Sibunit catalysts

Metal/Sibunit catalysts were obtained basing on the samples of a graphite-like carbon material from the Sibunit series using the following methods.

The 5 % Ni/Sibunit catalyst was prepared on the basis of commercial Sibunit-4 (Institute of Hydrocarbons Processing, SB RAS, Omsk) *via* impregnation according to water-absorbing capacity, using $Ni(NO_3)_2$ as a precursor of the active component. The characteristics Sibunit-4 are as it follows: the total water-determined pore volume is equal to 0.52 cm^3/g, the specific surface area (S_{sp}) being equal to 390 m^2/g, the average pore diameter determined *via* BET (D_{BET}) amounting to 6.6 nm. After impregnation, the catalyst was dried in a flow of argon at the temperature of 160 °C (the temperature increase rate being of 2 °C/min) within 3 h and then it was reduced in a flow of hydrogen at 400 °C (at 2 °C/min) during 4 h.

The 5 % Pt/Sibunit catalyst was prepared *via* cation adsorption from H_2PdCl_4 solution as described in [12], using mesoporous Sibunit ($S_{sp} = 390$ m^2/g, $D_{BET} = 7$ nm) as a carrier. The reduction of the platinum precursor adsorbed was carried out in a flow of hydrogen (30 mL/min) at 150 °C during 1 h and then within 1 h at 250 °C, the temperature increasing rate from 150 to 250 °C equal to 5 °C/min.

The 2 % Pd/Sibunit catalyst was prepared *via* homogeneous precipitation in the presence of a carrier (mesoporous Sibunit, $S_{sp} = 390$ m^2/g, $D_{BET} = 7$ nm) using H_2PdCl_4 solution as a precursor, as well as and Na_2CO_3 solution as a precipitator, according to the technique described in [13]. Metal reduction was carried out in a flow of hydrogen (20 mL/min), with a gradual rise in temperature up to 100 °C during 3 h. A sample of the catalyst was filtered, washed with a great amount of distilled water until a negative reaction for Cl$^-$ and then air-dried at a room temperature.

The 5 % Pd/Sibunit catalyst was prepared using a similar method, with a corresponding increase in the amount of H_2PdCl_4.

The 10 % Pd/Sibunit catalyst was prepared using the technique described above, using the 5 % Pd/Sibunit catalyst as a carrier.

Textural and morphological properties of the catalysts prepared were studied using low temperature (77 K) nitrogen adsorption (Micromeritics ASAP 2400), high resolution transmission electron microscopy (JEOL JEM-2010 TEM with 200 kV accelerating voltage) and pulse CO chemisorption [14, 15] (Table 1).

TABLE 1

Textural and morphological characteristics of catalysts

Samples	Fraction, mm	S_{sp}, m^2/g	V_{por}, cm^3/g	Mean diameter of active metal nanoparticles, nm		
				$<d_l>$	$<d_{v/s}>$	$<d_{CO}>$
5 % Ni/Sibunit	0.25−0.5	390	0.52	−	−	−
5 % Pt/Sibunit	0.04−0.09	395	0.74	4.5± 2.9	5.8	10.0
2 % Pd/Sibunit	0.04−0.09	383	0.61	3.0±1.0	3.1	4.4
5 % Pd/Sibunit	0.04−0.09	350	0.88	2.6±0.5	2.8	8.8
10 % Pd/Sibunit	0.04−0.09	316	0.55	−	−	81

Note. $<d_l>$ is midlinear particle diameter; $<d_l> = \Sigma d_i/N$, where d_i is diameter of nanosized metal particles in the catalyst; N is total number of particles; $<d_{v/s}>$ is volume-surface average particle diameter of the surface; $<d_{v/s}> = \Sigma d_i^3/\Sigma d_i^2$; $<d_{CO}>$ is average particle diameter determined from the data of pulse CO adsorption.

Dechlorination of polychlorinated biphenyls

To a reactor equipped with a reflux condenser were placed 10 mL of ethanol, 0.2 g of catalyst, 0.2 g of PCB (0.61 mmol), 0.1424 g of NaOH (3.05 mmol) under hydrogen bubbling (30−40 mL/min) and magnetic stirring, during 5 h. The catalyst was separated *via* centrifugation. The reaction mixture was neutralized with dilute hydrochloric acid. To the an emulsion formed was added K_2CO_3, on the basis of 1.0 g of potassium carbonate for 1.0 mL of the liquid, to hold it during 1 day. The upper layer was separated and analyzed using GC.

In the same manner we performed the dechlorination of DDT.

The dechlorination of hydrolyzed polychlorbiphenyl (PCB−OH) and triclosan were performed in aqueous NaOH solution. After the neutralization, the reaction mixture was extracted twice with methylene chloride. The extract was dried and analyzed by GC.

For the analysis of carbonylated PCB by GC we performed the reaction of esterification. To a reactor was placed 50 mg of carbonylated PCB, then were added 1.0 mL of ethanol and 0.05 mL of concentrated H_2SO_4. The reaction mixture was heated and maintained at 100 °C within 30−40 min. After cooling, to the reaction mixture was added 10 mL of water and 2 mL of toluene. After this, we analyzed the toluene extract of the esters of carbonylated PCBs.

The dechlorination of Sovtol mixture carbonylation was performed according to the method of PCB dechlorination. The catalyst used was separated *via* centrifugation, after that the solution was neutralized with excess of 0.5 M HCl solution and evaporated to obtain dry solid. The solid obtained was extracted with chloroform (continuous hot extraction). Chloroform was evaporated; the resulting mixture was analyzed by GC with pre-esterification via the above mentioned method.

Analysis of dechlorination products

For the quantitative estimation (using internal normalization) we analyzed dechlorination products using a Shimadzu GC 2010 gas chromatograph with a flame ionization detector (GC-FID), ZB-5 silica capillary column 30 m long and 0.25 mm in diameter, the film thickness was 0.25 μm (polymethylsiloxane, 5 % phenyl groups). The initial temperature of the column was equal to 40 °C (hold for 3 min), then it was heated at a rate of 10 °C/min, with the final column temperature amounting to 290 °C The evaporator temperature was equal to 280 °C, the detector temperature being of 320 °C.

In order to identify the products of dechlorination we used an Agilent GC 7890A MS 5975C gas chromatography/mass spectrometer with a quadrupole mass spectrometric detector (GC-MSD) at electron acceleration energy of 70 eV. We used silica capillary column HP-5MS, 30 m long, 0.25 mm in diameter, with film thickness equal to 0.25 μm. The carrier gas was helium, with flow splitting 1 : 50, the flow rate through the column being equal to 1.0 cm^3/min. The initial column temperature was equal to 40 °C (hold for 3 min), programming the heating at a rate of 10 °C/min up to 290 °C (holding for 20 min), the evaporator temperature equal to 250 °C, the source temperature being equal to 230 °C, the quadrupole temperature amounting to 150 °C, the evaporator temperature being of 280 °C.

^{1}H NMR spectra were registered on a Bruker Avance DRX-400 spectrometer (Bruker Bio-Spin) with the operating frequency of 400 MHz in dimethyl sulphoxide (DMSO).

RESULTS AND DISCUSSION

The M/Sibunit catalysts prepared were studied using a complex of physical and chemical methods. Textural and morphological characteristics inherent in the catalyst are presented in Table 1. The texture investigation by low temperature nitrogen adsorption demonstrated that the application of the active metal onto the carrier does not result in a significant decrease of the specific surface area of the carrier, except for sample 10 % Pd/Sibunit. Average particle size of platinum and palladium nanoparticles were determined basing on TEM and pulse CO chemisorption data. The differences observed in the average size of the metal particles (see Table 1) could be caused by blocking the metal surface and, consequently, either by decreasing the surface available for CO adsorption, or

by the presence of very large metal particles (alongside with small ones) those not always could be revealed using the TEM. In our case, most likely, there is an effect of the presence of large platinum and palladium agglomerates formed as a result of sintering. The micrographs of the 10 % Pd/Sibunit catalyst demonstrate large agglomerates of up to 70 nm alongside with small particles (up to 5 nm), which did not allow us to estimate the average size of palladium particles. Particle size for the mentioned catalyst determined from data on CO chemisorption (see Table 1, sample 10 % Pd/Sibunit) indicate the that some part of the active metal is inaccessible for CO adsorption, and thus for the processes of hydrodechlorination.

The catalytic activity of the systems prepared was investigated for the reductive dechlorination reaction of polychlorinated biphenyls in the liquid phase at a room temperature:
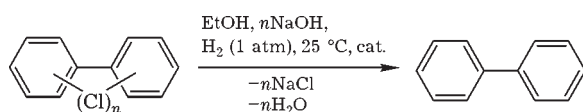
First of all, we performed a comparative analysis of the catalytic activity of the samples containing different metals. According to the GC data, the presence of 5 % Ni/Sibunit and 5 % Pt/Sibunit samples after 6 h resulted in revealing only initial PCBs in the reaction mixture. The reaction catalyzed by the system 5 % Pd/Sibunit, resulted in the formation is biphenyl as the main product. This fact indicates that there is a high catalytic activity of Pd-containing system observed with respect to the reaction of hydrodechlorination under these experimental conditions. For this reason, all the further investigations were performed using palladium catalysts.

For Pd/Sibunit catalysts, we studied the catalytic activity depending on the metal content in the sample. The accumulation level of biphenyl depending on time is demonstrated in Fig. 1. It can be seen that the samples containing 5 and 10 % of palladium are to a considerable extent more active than the sample with the
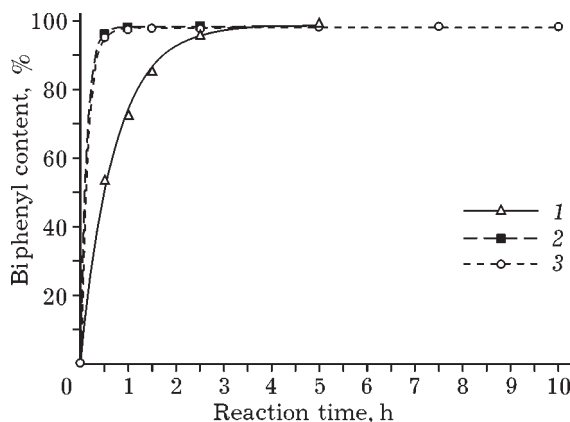
Fig. 1. Content of biphenyl in the reaction mixture depending on the hydrodechlorination reaction time carried out on Pd/Sibunit catalysts with different content of Pd, %: 2 (*1*), 5 (*2*), 10 (*3*).

palladium content equal to 2 %. When 2 % Pd/Sibunit catalyst sample was used, the reaction duration of 30 min results in the biphenyl content in the mixture to amount to 53 %, whereas in the case of 5 % Pd/Sibunit and 10 % Pd/Sibunit catalyst samples used this value was already equal to 95 %. However, in the case of further performing the reaction with the 2 % Pd/Sibunit sample the biphenyl content amounted up to 95 % after 2.5 h.

The conversion level of biphenyl with the using of 5 and 10 % Pd/Sibunit catalyst samples are the same, but the use of the former is preferable because of lower palladium content, and, consequently, its lower cost. In addition, as it was demonstrated in studying the catalysts by the methods TEM and CO chemisorption, a part of the surface of palladium in the 10 % Pd/Sibunit catalyst is not accessible for chemical reactions. With a 10-fold decrease in the content of the 5 % Pd/Sibunit catalyst the conversion level of biphenyl reaches only 63 % in 5 h.

Data concerning a particular composition of the reaction mixtures of partially dechlorinated PCBs (the reaction time amounting to 1 h) in the presence of palladium catalysts containing different amounts of the active component are presented in Table 2.
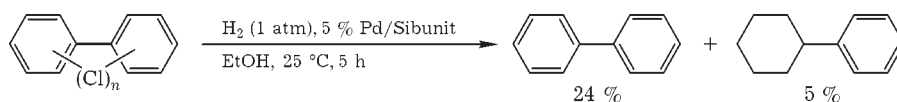
Scheme 1.

TABLE 2

Composition of incomplete dechlorination mixtures of polychlorinated biphenyls in the presence of palladium catalysts containing different amounts of the active component (according to GC data)

Catalysts	Content, %					
	Biphenyl	Monochloro-biphenyls	Dichloro-biphenyls	Trichloro-biphenyls	Tetrachloro-biphenyls	Pentachloro-biphenyls
2 % Pd/Sibunit	72.1	11.5	13.1	1.2	0.4	0.3
5 % Pd/Sibunit	97.7	1.2	0.5	0.6	–	–
10 % Pd/Sibunit	97.3	0.5	0.3	1.9	–	–

The reductive dechlorination of PCB without using sodium hydroxide results in the hydrogenation of one benzene ring of the biphenyl to form phenylcyclohexane (Scheme 1).

A low content of biphenyl in the reaction mixture indicates a low dechlorination level. With increasing the temperature of the reaction up to 75 °C, the reaction mixture exhibits the presence of 24 % of phenylcyclohexane and 9 % of biphenyl. In this case the dechlorination level remains low, as it is in the first case. When the reaction is carried out on heating, however in the presence of alkali, there is only 53 % of the biphenyl in the products found alongside with chlorinated biphenyls; no hydrogenation of the benzene ring is observed in this case. Consequently, the presence of alkali is necessary for the dechlorination reaction to be efficient, but it inhibits the reaction of benzene ring hydrogenation. An increase in temperature decelerates the dechlorination, but promotes the hydrogenation of biphenyl to yield phenylcyclohexane.

Thus, for the conversion of PCB into phenylcyclohexane it should be hydrodechlorinated in an alkaline medium in the presence of the palladium catalyst with further hydrogenation in the neutral medium with the same catalyst. In the reaction of biphenyl hydrogenation we tested also a platinum catalyst. However, hydrogenation products were not revealed in the reaction mixture.

The stability of 5 % Pd/Sibunit catalyst with respect to deactivation under these experimental conditions we evaluated *via* repeated using the catalyst. It is seen (Fig. 2) that with repeated using the catalyst its activity decreases, but an increase in the reaction time up to 5 h provides biphenyl content to be of about 95 % in

all the cases. The catalyst deactivation could be caused by the sorption of chloride ions (formed in the course of the reaction) on the surface of fine palladium particles, which makes the adsorption of the substrate difficult and, therefore, makes difficult its further transformations [16, 17]. However, in order to confirm this assumption, a separate study is required.

After PCB solutions in ethyl alcohol held with the catalyst within 1 day, the initially colourless solution becomes yellow. The investigation with the use of GC technique revealed the presence of acetaldehyde, its diethyl acetal, aldol and crotonaldehyde in such solutions as alcohol impurities. Basing on this fact it was suggested that ethanol can be directly used as a reducing agent for PCB.

Indeed, in the course of the process of PCB dechlorination when heated in alcoholic solution of sodium hydroxide on the 5 % Pd/Sibunit catalyst in the absence of free hydrogen
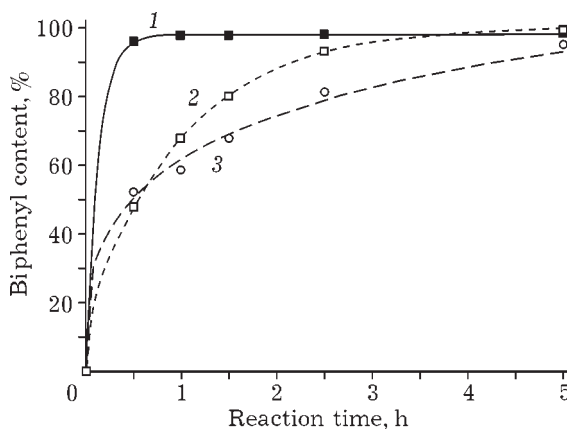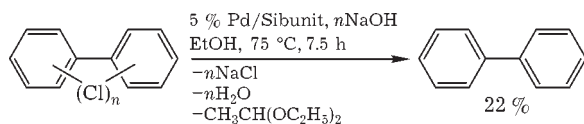

Fig. 2. Content of biphenyl in the reaction mixture depending on the hydrodechlorination reaction time in the presence of 5 % Pd/Sibunit catalyst for its single (*1*), double (*2*) and triple (*3*) use.

we revealed 22 % of biphenyl and partially dechlorinated PCBs in the reaction mixture:

The results obtained are in agreement with the data available from the literature [18, 19]. Thus, the authors of [18] successfully dechlorinated chlorobenzene using methanol as a reducing agent on Pd/C catalyst. The authors of [19] observed an increase in the rate of chlorobenzene hydrodechlorination at 50 °C in the presence of isopropanol as a solvent in the two-phase system aqueous KOH/organic solvent. Later, the authors of [20] explained this fact by isopropanol participation in the reaction as a reducing agent.

Technical-grade mixtures Sovtol contain 64, 75, 90 % of pentachlorobiphenyls (Sovtol-1, Sovtol-2, Sovtol-10, respectively), the second component of the Sovtol represents 1,2,4-trichlorobenzene. We performed reductive dechlorination directly for mixture Sovtol-2 in the presence of 5 % Pd/Sibunit catalyst. We demonstrated that trichlorobenzene is converted into benzene and pentachlorobiphenyls are converted into the hydrogenation of PCB the mixture of biphenyl and phenylcyclohexane, just as it was for the hydrogenation of PCB.

For the purpose of PCBs processing of into valuable products, a special method was earlier developed consisting in the hydrolysis of

polychlorinated chlorophenylphenols in DMSO [9]. No dechlorination of hydrolyzed PCB was observed for 5 % Pd/Sibunit catalyst sample. However, after pre-processing the hydrolyzed mixture by a portion of a catalyst that absorbs the impurities of sulphur compounds the dechlorination occurs with the conversion level of 28 % to result in forming a mixture of *o*-, *m*- and *p*-phenylphenols at a ratio of 67 : 7 : 26, respectively (Scheme 2).

The reason for this behaviour consists in the poisoning of the catalyst by trace amounts of DMSO those could not be detected using GC.

A not less hazardous ecotoxicant DDT under these experimental conditions undergoes complete dechlorination, too (Scheme 3). This results in the removal of not only aromatic chlorine, but also aliphatic chlorine to form 93 % of 1,1-diphenylethane as the main product. The product obtained can be used as a heat carrier. The formation of 1,1,4,4-tetraphenylbutane (4 %) as a by-product dimerization of 1,1-diphenylethane was an unexpected result.

At the present time, as an antibacterial agent one uses an active broad-spectrum biocide triclosan (5-chloro-2-(2,4-dichlorophenoxy) phenol). This compound exhibits anti-inflammatory properties and can influence upon gram-positive and gram-negative microorganisms. Under the action of light and water triclosan is transformed into toxic dioxin. It is proved that triclosan can cause mutation of microorganisms [21]. In contrast to the PCBs the problem of utilizing triclosan is not so urgent, but, judging from the literature,
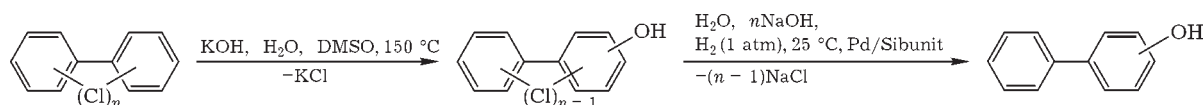
Scheme 2.
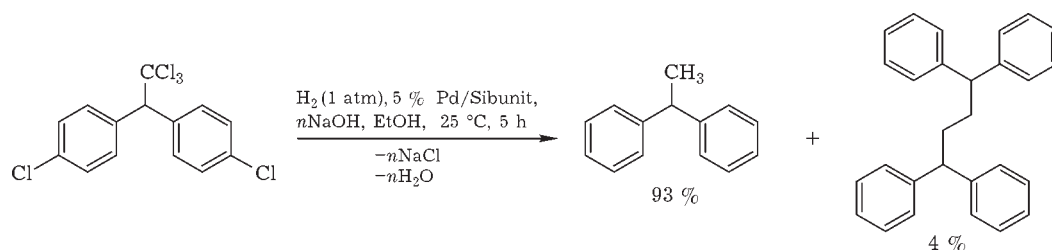
Scheme 3.
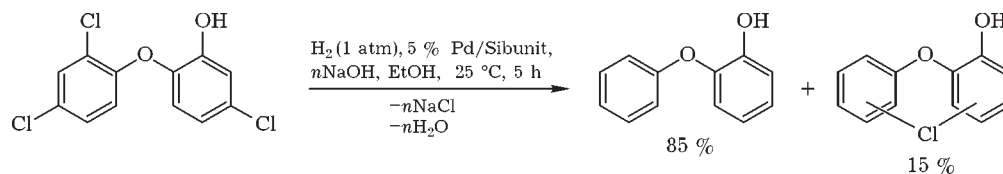
Scheme 4.

TABLE 3

Composition of mixtures obtained from carbonylizing the Sovtol mixture on 5 % Pd/Sibunit catalyst

Sovtol components	Carbonylation product	Yield, %
B-Cl$_3$	B (COOH)$_1$ Cl$_2$	3.1
	B (COOH)$_2$ Cl$_1$	4.5
	B (COOH)$_3$ Cl$_0$	2.8
BPh-Cl$_4$	BPh (COOH)$_0$ Cl$_4$	2.1
	BPh (COOH)$_1$ Cl$_3$	10.5
	BPh (COOH)$_2$ Cl$_2$	1.8
	BPh (COOH)$_3$ Cl$_1$	0.9
	BPh (COOH)$_4$ Cl$_0$	1.0
BPh-Cl$_5$	BPh (COOH)$_0$ Cl$_5$	3.2
	BPh (COOH)$_1$ Cl$_4$	21.2
	BPh (COOH)$_2$ Cl$_3$	20.6
	BPh (COOH)$_3$ Cl$_2$	6.7
	BPh (COOH)$_4$ Cl$_1$	0.5
	BPh (COOH)$_5$ Cl$_0$	0.7
BPh-Cl$_6$	BPh (COOH)$_0$ Cl$_6$	–
	BPh (COOH)$_1$ Cl$_5$	5.1
	BPh (COOH)$_2$ Cl$_4$	7.4
	BPh (COOH)$_3$ Cl$_3$	2.4
	BPh (COOH)$_4$ Cl$_2$	0.9
Total		95

Note. Here and in Table 4: B – benzene, BPh – biphenyl.

TABLE 4

Composition of mixtures resulting from the subsequent hydrodechlorination of the Sovtol»mixture carbonylation products on 5 % Pd/Sibunit catalyst in alcohol and water solutions

Products	Yield, %	
	Solvent	
	Ethanol	Water
B-(COOH)$_1$	8.7	1.1
B-(COOH)$_2$	8.4	6.8
BPh	2.6	0
BPh-(COOH)$_1$	17.5	30.3
BPh-(COOH)$_2$	17.3	21.7
BPh-(COOH)$_3$	4.1	3.6
Total	59	64

Note. For design. see Table 3.

it could be relevant in the course of time. We investigated the possibility of triclosan dechlorination under the same conditions in the presence of 5 % Pd/Sibunit catalyst (Scheme 4).

The reaction resulted in obtaining o-phenoxyphenol (the conversion level equal to 85 %); the substance also represents a biocide with the efficiency an order of magnitude lower than the efficiency of triclosan [22]. However, this compound is not capable of hazardous conversion.

In addition to the above proposed method for processing PCBs into valuable products such as a mixture of phenylphenols (raw material for the production of phenylphenol formaldehyde resins [23]), a method known consisting in the carbonylation of Sovtol to produce a mixture of chlorinated aromatic carboxylic acids [24]:

$$ArHal + CO + K_2CO_3 \xrightarrow[\text{R = H, Alk}]{^-Co(CO)_4 / R} ArCOOK + KHal + CO_2$$
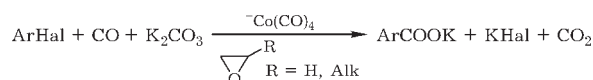
Data concerning the composition of products obtained *via* the carbonylation of Sovtol mixture and the subsequent dechlorination are presented in Tables 3 and 4. It can be seen (see Table 4), that the conversion level for carbonylated PCBs into carboxylic acid is approximately the same at around 60 % both in ethyl alcohol and in water. The ratio between carboxylic acids in this case varies. To all appearance, polycarboxylic acids under dechlorination could be partially decarboxylated.

CONCLUSION

The studies performed demonstrate that the Pd/Sibunit system represents an active catalyst in the reaction of PCBs, DDT, and triclosan reductive dechlorination. The use of such a catalyst allows one to carry out hydrodechlorination in the liquid phase, in the presence of alkali, at a room temperature and hydrogen pressure amounting to 1 atm. In this case, af-

ter 30 min of the reaction course, a 95 % conversion level can be reached. With the use of the catalyst during three cycles, its activity somewhat decreases, however an increase in the reaction time up to 2−3 h allows achieving the same conversion rate as fresh catalyst. This indicates the stability of the catalyst system under these experimental conditions, which, of course, represents one of the major advantages of the catalyst. Under varied experimental conditions (the absence of sodium hydroxide and high temperature) the rate of the dechlorination decreases to a considerable extent, whereas the rate of the hydrogenation process demonstrate a considerable increase, which allows adjusting the regioselectivity of the process in a simple manner. The combination of the two processes such as the reductive dechlorination of PCBs and the hydrogenation of one benzene ring of the resulting biphenyl opens the possibility of PCB conversion directly to obtain phenylcyclohexane, the main component of modern heat-transfer agents. The dechlorination of DDT results in the formation of 1,1-diphenylethane, the compound that can be used as a component of modern heat-transfer agents [25].

REFERENCES

1 Klyuev N. A., Kurlyandskiy B. A., Revich B. A., Filatov B. N., Dioksiny v Rossii, Moscow, 2001.
2 Zanaveskin L. N., Averyanov V. A., *Usp. Khim.*, 67, 8 (1998) 788.
3 Noma Y., Ohno M., Sakai S.-I., *Fresenius Environ. Bull.*, 12, 3 (2003) 302.
4 Rodriguez J. G., Lafuente A., *Tetrahedron Lett.*, 43, 52 (2002) 9581.
5 Lorenc-Grabowska E., Yperman J., Gryglewicz G., Hoste S., Carieer R., *Fuel*, 85, 3 (2006) 374.
6 Kume A., Monguchi Y., Hattori K., Nagase H., Sajiki H., *Appl. Catal. Sect. B: Environ.*, 81, 3−4 (2008) 274.
7 Aresta M., Dibenedetto A., Fragale C., Gianoccaro P., Pastore C., Zammiello D., Ferragina C., *Chemosphere*, 70, 6 (2008) 1052.
8 Munakata N., Reinhard M., Palladium Catalysis for the Treatment of Contaminated Waters: A Review, in: Physicochemical Groundwater Remediation, in J. A. Smith, S. E. Burns (Eds.), Kluwer Academic/Plenum Publishers, New York, 2001, pp. 45−71.
9 Mekhaev A. V., Chupakhin O. N., Uymin M. A., Ermakov A. E., Pervova M. G., Gorbunova T. I., Mysik A. A., Saloutin V. I., Yatluk Yu. G., *Izv. RAN. Ser. Khim.*, 6 (2009) 1284.
10 Ermakov Y. I., Surovkin V. F., Plaksin G. V., Semikolenov V. A., Likholobov V. A., Chuvilin A. L., Bogdanov S. V., *React. Kinet. Catal. Lett.*, 33 (1987) 435.
11 Simakova I. L., Semikolenov V. A., *Kinetika i Kataliz*, 32, 4 (1991) 989.
12 Kholodovich A. N., Simonov P. A., Kvon R. I., Bukhtiyarov A. V., Zaikovskii V. I., Chesalov Yu. A., Romanenko A. V., *Kinetika i Kataliz*, 49, 6 (2008) 936.
13 Simakova O. A., Simonov P. A., Romanenko A. V., Simakova I. L., *React. Kinet. Catal. Lett.*, 95, 1 (2008) 3.
14 Anderson J. R., Structure of Metallic Catalysts, Academic Press, London, 1975.
15 Sarcany J., Gonzalez R. D., *J. Catal.*, 76 (1982) 75.
16 Xia Chuanhai, Xu Jie, Wu Wenzhong, Liang Xinmiao, *Catal. Commun.*, 5 (2004) 383.
17 Heck K. N., Nutt M. O., Alvarez P., Wong M. S., *J. Catal.*, 267 (2009) 97.
18 RU Pat. No. 2072340, 1997.
19 Simagina V. I., Tayban E. S., Grayfer E. D., Gentsler A. G., Komova O. V., Netskina O. V., *Pure Appl. Chem.*, 81, 11 (2009) 2107.
20 Simagina V. I., Kosinov N. A., Tayban E. S., Netskina O. V., Komova O. V., Gentsler A. G., VIII Int. Conf. "Mechanisms of Catalytic Reactions" (Proceedings), Novosibirsk, 2009, vol. II, p. 106.
21 Suller M. T. E., Russell A. D., *J. Antimicrob. Chemotherapy*, 46 (2000) 11.
22 Sivaraman S., Sullivan T. J., Johnson F., Novichenok P., Cui G., Simmerling C., Tonge P. J., *J. Med. Chem.*, 47 (2004) 509.
23 US Pat. No. 2093481, 1937.
24 RU Pat. No. 2215729, 2003.
25 US Pat. No. 6022488, 2000.