

## Heterogeneous catalysts and process for reductive dechlorination of polychlorinated hydrocarbons\*

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**Abstract:** The utilization and decomposition of chlorinated wastes without formation of dioxins are challenges of great environmental importance. In this work, the catalytic reductive methods of chlorinated organics processing are described, focusing on catalyst development. Pd-containing catalysts are improved by modification of supports [use of ultra dispersed diamond (UDD) or double oxides] or by dilution of Pd by not-noble metals (Fe, Ni, Cu). Both ways are effective for the processing of 1,3,5-trichlorobenzene (TCB) as a model of polychlorinated organics. The reasons for improvement of catalysts are discussed. The best catalysts were effectively used for hydrodechlorination (HDC) of hexachlorobenzene (HCB).

**Keywords:** hydrodechlorination; reductive dechlorination; chlorinated organics; Pd catalysts; bimetallic catalysts; double oxides; ultra dispersed diamond.

### INTRODUCTION

Chlorinated organic substances have been used in industry, and some of them in abundance. A considerable quantity of chlorinated organic substances was accumulated in previous years as worked-out transformers and condenser oils; for instance, worked-out polychlorinated biphenyl (PCB) stocks in Russia are estimated at 180 000–200 000 tons [1]. Various methods were proposed for the utilization of polychlorinated organics, including incineration [2,3], oxidative decomposition, microbiological decomposition [4], electrochemical disposal [5], etc. Oxidative methods require high energy consumption because polychlorinated wastes are very stable to oxidation; the use of oxidative methods results in irreversible loss of hydrocarbon; in addition, the formation of dioxins is practically unavoidable, since catalytic dioxin formation may take place during the cooling of end-of-pipe gases. Ozonation [6] or supercritical water treatment [7] are energy-demanding methods. Biological methods are often slow and applicable only to a limited group of substances.

The most promising method is hydrodechlorination (HDC): it is suitable to a wide assortment of wastes, fast, often very selective, and never results in dioxin formation. Some reviews are devoted to the theoretical and applied aspects of this reaction [8–10]. Pd- and Pt-containing catalysts were found to be very active. Many different supports were tested with variable success. Carbon supports are the most

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stable to aggressive reaction medium, but their strength characteristics (e.g., attrition index) are often inadequate for industrial application. Some oxide supports of basic nature could also be applied. The development of new stable and active catalysts is still an important issue.

At present, two fundamental approaches to the design of HDC catalysts have been developed on the basis of a huge amount of experimental data. One approach deals with the preparation of catalysts that contain small metal particles. However, this method encountered the problem concerning the improvement of particle stability to agglomeration. Another way is to change the electronic state of metal in the catalytic active site. Recently, it has been shown that active sites for HDC have a bifunctional nature [11]. Activation of hydrogen proceeds on Pd(0) centers, and activation of chlorinated organics is effective on Pd( $\delta^+$ ). Furthermore, the activity of sites in HDC is best when the ratio Pd( $\delta^+$ )/Pd(0) is about 1.

In this work, Pd-containing catalysts were modified via three directions: (1) the use of a new carbon support—ultra dispersed diamond (UDD); (2) the modification of zirconia support through the addition of the second oxide; and (3) the addition of the second metal to Pd. Catalysts were tested in HDC of 1,3,5-trichlorobenzene (TCB), and some of them were used for HDC of real chlorinated waste, namely, hexachlorobenzene (HCB). The influence of different modification directions on the catalytic performance of catalysts in HDC reaction is discussed.

## EXPERIMENTAL

Carbon supports used in this work were activated charcoal granulated R4 (AC) purchased from VEB Laborchemie Apolda; UDD that was prepared by the detonation synthesis in the Russian Federal Nuclear Center—the All-Russian Research Institute of Experimental Physics (RFNC-VNIIEF); Pd/C catalyst by Fluka (cat. N 80982) was used for comparison. Catalysts on carbon supports were prepared by impregnation of supports with corresponding metal nitrates. Bimetallic catalysts were prepared by simultaneous impregnation of supports by two nitrates of corresponding metals. Metal precursors were decomposed by heating at 120 °C in air. Then, the metal was reduced by passing hydrogen at 280 °C for 3 h. Oxide supports were prepared from oxychlorides by coprecipitation at pH 9 and subsequent calcination. The temperature of crystallization was determined by differential thermal analysis (DTA). Oxide-supported Pd catalysts were prepared from PdCl<sub>2</sub> using a deposition–precipitation technique. In this case, the catalysts were reduced at 450 °C [the temperature was chosen on the basis of temperature-programmed reduction (TPR) data].

Catalytic tests were performed under multiphase conditions [12] at 50 °C. The reaction system consisted of a catalyst (100 mg), 0.8 mmol of a substrate as an isooctane solution (6 ml), 5 ml of 10 % KOH, 0.026 mmol of Aliquate 336; hydrogen was continuously bubbled through the reaction medium (2 ml/min). To prevent leaching of reaction components, a reactor was equipped with a back-flow condenser. Reaction conditions for all catalytic tests were the same.

Reaction products were analyzed by gas chromatography (GC) on Philips PU1100 (FID, DB-Wax, 30 m, and carrier gas—helium).

TPR was performed by heating of sample (100 mg) in 5 % H<sub>2</sub>/Ar at a flow rate of 30 ml/min and a heating rate of 13 °C/min. Hydrogen consumption was detected by a thermal conductivity detector.

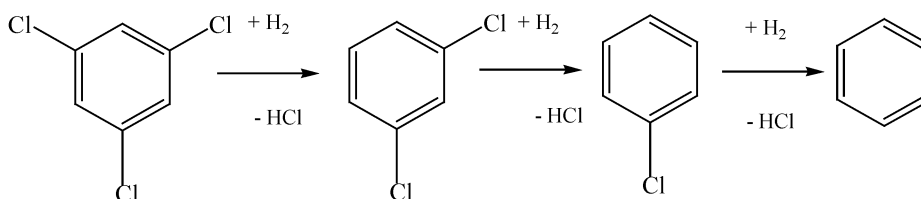
## RESULTS AND DISCUSSION

### UDD as the support for HDC catalysts

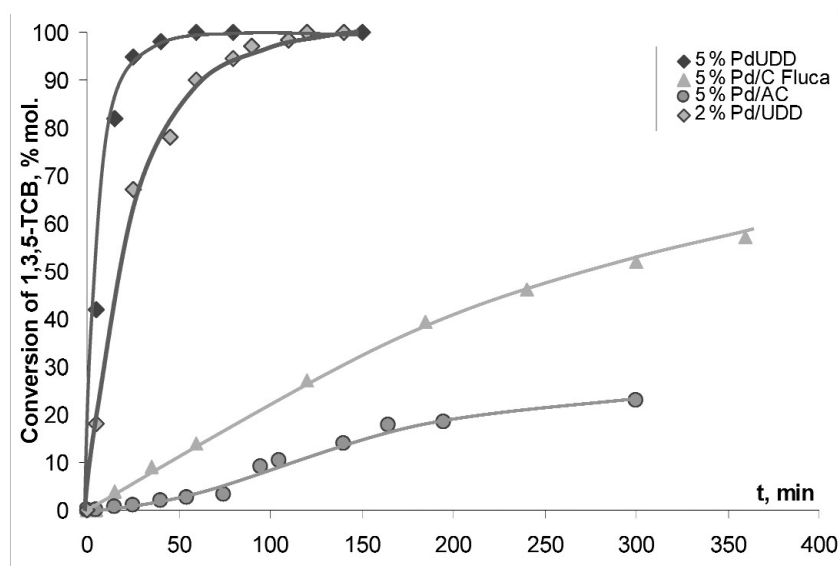
UDD may be produced cheaply and easily enough during the disposal of obsolete explosives by detonation [13]. Detonation of carbon-containing explosives with negative oxygen balance results in free carbon atoms release, coagulation, and rearrangement under high pressure and temperature conditions. The use of certain conditions (temperature, pressure, quenching time, etc.) makes it possible to obtain

UDD. UDD powders are very hard, chemically stable, and possess high specific surface area (about  $300 \text{ m}^2/\text{g}$ ) [14,15]. It was found that UDD and modified UDD have peculiar catalytic activity in CO oxidation [16].

In this work, 2 and 5 % Pd-containing catalysts supported on UDD and 5 % Pd on AC were prepared. A commercially available 5 % Pd/C catalyst by Fluka was used as well. Characteristics of supports and catalysts are shown in Table 1. Catalytic activity was tested in the multiphase HDC of TCB to benzene, as outlined by the scheme:



No traces of cyclohexane were found in reaction media. The curves of TCB conversion vs. time are presented in Fig. 1. UDD-supported catalysts (2 and 5 % Pd) are the most active among tested samples, in spite of a very high surface area of AC. The activity of Pd/C<sub>Fl</sub> has an average value between AC and UDD-supported catalysts, like the specific surface of this catalyst. 2 % Pd/UDD is slightly less active than 5 % Pd/UDD.



**Fig. 1** Conversion of TCB in the presence of Pd supported on carbon supports under multiphase conditions.

According to the textural data shown in Table 1, only UDD has a developed mesoporous structure. Pd/C<sub>Fl</sub> contains all types of pores, including mesopores. Transmission electron microscopy (TEM) images for the tested catalysts described in [17] demonstrate uniform distribution of Pd particles (average size 5 nm) on the UDD. The distribution of Pd particles on AC is broader (5–40 nm), and the texture contains mainly micropores. Thus, two main causes are responsible for the high catalytic activity of Pd/UDD as compared with Pd/AC and Pd/C<sub>Fl</sub>:

- Blocking of metal particles in micropores of carbon support. Such a type of metal blocking was suggested as the reason for a decreased catalytic activity in [18].
- Good distribution of small Pd particles on the surface of UDD.

Furthermore, considerable concentration of heteroatomic impurities (N, O) on the surface of UDD was found [19,20]. This fact could affect the distribution of Pd on the surface. On the other hand, the interaction of Pd with heteroatomic groups on the surface (e.g., carboxylic ones) could lead to the formation of partially positively charged species of Pd (i.e., electronic modification of Pd sites). The presence of Pd( $\delta^+$ ) may improve the performance of catalysts in HDC.

There is good reason to believe that all of the above listed reasons are valuable for good catalytic performance of UDD-supported catalysts.

**Table 1** Textural characteristics of carbon supports and corresponding Pd catalysts.

Samples	$S_{\text{BET}}$ , m <sup>2</sup> /g	Average pore size, Å	Pore volume, cm <sup>3</sup> /g		
			$V_{\text{micro}}$	$V_{\Sigma}$	$V_{\text{micro}}/V_{\Sigma}$ , %
UDD	260	128.1	0.008	0.84	0.92
5 % Pd/UDD	270	118.1	0.008	0.81	0.98
AC	1090	19.4	0.271	0.53	51.23
5 % Pd/AC	1025	19.2	0.252	0.49	51.01
5 % Pd/C <sub>FI</sub>	700	29.6	0.171	0.52	32.44

### Double oxide supports

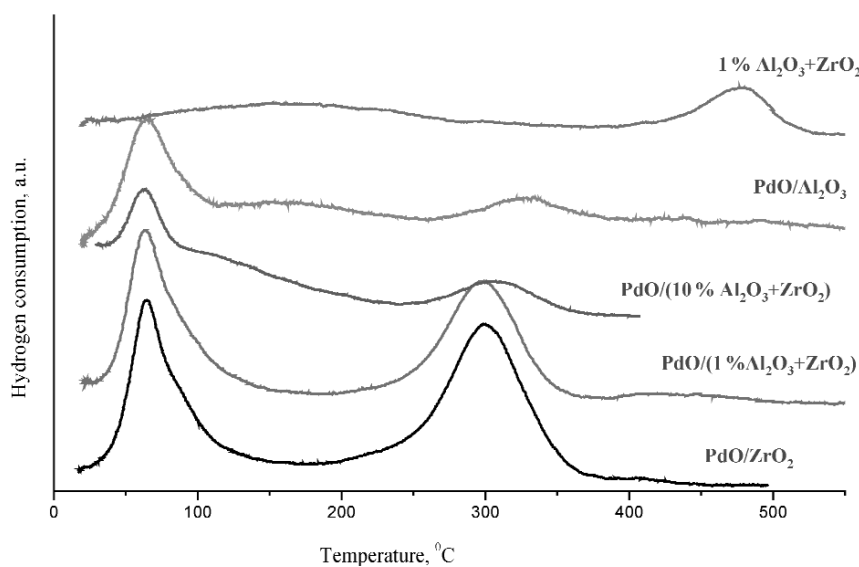
As mentioned in the introduction, good catalytic properties in HDC are related to formation of the Pd(0)-Pd( $\delta^+$ ) couple on the surface of supported catalysts, and the optimal Pd(0):Pd( $\delta^+$ ) ratio is about 1 [11]. Usually, only Pd(0) occurs in the catalyst after proper reduction. Pd(0) could be oxidized during interaction with R-Cl or HCl formed in HDC reaction. However, reductive reaction conditions provide continuous reduction of the metal in the course of reaction. Pd( $\delta^+$ ) can be obtained on the catalyst surface due to chemical interaction between Pd and support. For instance, intermetallic oxides Pd<sub>x</sub>Zr<sub>y</sub>O<sub>z</sub> are formed as a result of calcination of Pd that was supported on ZrO<sub>2</sub> by hydroxide deposition. The reduction of catalyst leads to formation of stable-phase Zr<sub>x</sub>Pd<sub>y</sub>OH<sub>z</sub>, which provides good proton mobility and could be repeatedly hydrogenated and dehydrogenated without degradation [21]. On the contrary, Zr<sub>x</sub>Pd<sub>y</sub>H<sub>z</sub> is metastable and disproportionates easily. Therefore, the presence of oxygen in the crystal lattice of oxide stabilizes intermetallic compounds formed during reduction and makes it possible to stabilize Pd( $\delta^+$ ) centers responsible for activation of chlorinated molecules.

In this work, ZrO<sub>2</sub> was used as a support because of its chemical stability under HDC conditions [22] combined with thermal and mechanic stability. Usually, a higher catalytic activity is achieved using tetragonal and cubic modifications of ZrO<sub>2</sub>, both of which have higher surface areas than the monoclinic form. However, these phases are metastable and transform into the monoclinic modification during heat treatment (calcination, reduction), which are necessary for catalyst preparation. Addition of the second oxide (Al<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, CaO, MgO) leads to stabilization of metastable ZrO<sub>2</sub> modifications [23,24]. In this work, three oxides were used as modifiers: Al<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, and Ga<sub>2</sub>O<sub>3</sub>. X-ray diffraction (XRD) studies showed that the addition of these oxides stabilizes the metastable phases of zirconia. The properties of the catalysts prepared are shown in Table 2. As it was presumed, the modified catalysts have a developed specific surface area. The XRD data confirm the prevalence of tetragonal and cubic phases of ZrO<sub>2</sub> in modified samples.

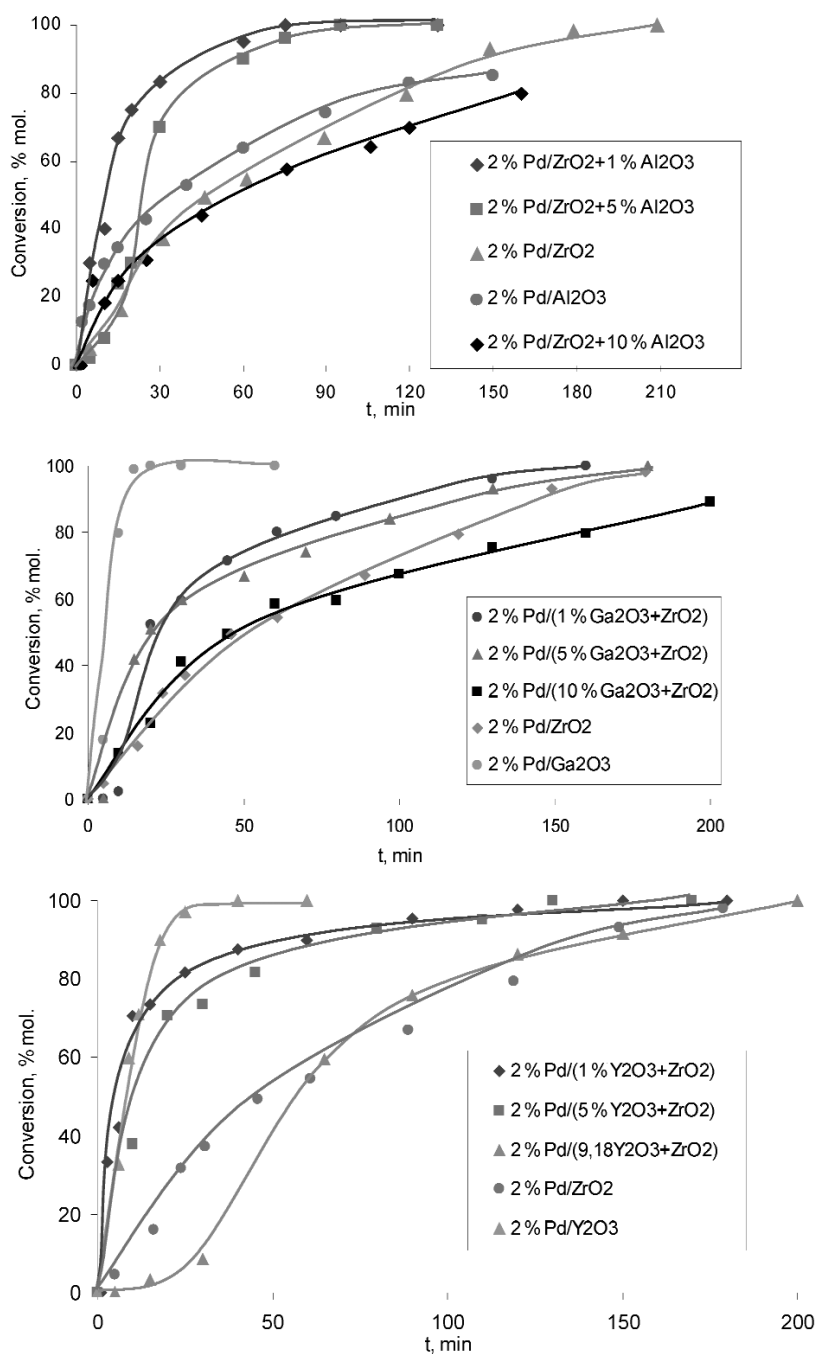
**Table 2** Composition and specific surface area for Pd supported on oxides supports (M: monoclinic; T: tetragonal; C: cubic; A: amorphous).

Catalyst	Content of second oxide, mol %	S <sub>BET</sub> , m <sup>2</sup> /g	Phase composition of support
2 % Pd/ZrO <sub>2</sub>	–	39	M
2 % Pd/Al <sub>2</sub> O <sub>3</sub>	–	130	A
2 % Pd/(xAl <sub>2</sub> O <sub>3</sub> + ZrO <sub>2</sub> )	x = 1	45	T
	x = 5	42	T + M
	x = 10	47	A
2 % Pd/Ga <sub>2</sub> O <sub>3</sub>	–	15	β-phase
2 % Pd/(yGa <sub>2</sub> O <sub>3</sub> + ZrO <sub>2</sub> )	y = 1	36	T
	y = 5	40	T
	y = 10	59	T
2 % Pd/Y <sub>2</sub> O <sub>3</sub>	–	4	α-phase
2 % Pd/(zY <sub>2</sub> O <sub>3</sub> + ZrO <sub>2</sub> )	z = 1	55	T + M
	z = 5	57	C
	z = 9	38	C

To study the nature of Pd active sites in the catalysts, the TPR analysis was performed for unreduced precursors of 2 % Pd/(xAl<sub>2</sub>O<sub>3</sub> + ZrO<sub>2</sub>) and 2 % Pd/ZrO<sub>2</sub> catalysts, as well as for (1 % Al<sub>2</sub>O<sub>3</sub> + ZrO<sub>2</sub>) support. After Pd deposition on the support, the samples were dried, calcinated, and then placed in a TPR cell. Pd in these samples occurs in the form of PdO. TPR profiles of such samples (Fig. 2) contain an additional peak at approximately 300 °C along with the peak of PdO reduction at approximately 80 °C. Reduction of zirconia proceeds at much higher temperatures (above 300 °C). Therefore, the appearance of this peak could be attributed to H<sub>2</sub> absorption by Pd<sub>x</sub>Zr<sub>y</sub>O<sub>z</sub> or its reduction. Thus, TPR data confirm the formation of two forms of Pd. The highest amount of hydrogen was consumed at high temperatures by PdO/ZrO<sub>2</sub> and PdO/(1 % Al<sub>2</sub>O<sub>3</sub> + ZrO<sub>2</sub>); in the latter system, the ratio between

**Fig. 2** TPR profiles for PdO/(xAl<sub>2</sub>O<sub>3</sub> + ZrO<sub>2</sub>) (2 % Pd).

two forms of Pd is near 1. The catalyst that was obtained by reduction of this system is the most active for TCB HDC (Fig. 3) in comparison with Pd on single zirconia and zirconia modified by larger amounts of alumina.



**Fig. 3** Conversion of TCB in the presence of 2% Pd/( $x$ Al<sub>2</sub>O<sub>3</sub> + ZrO<sub>2</sub>) (top), 2% Pd/( $x$ Ga<sub>2</sub>O<sub>3</sub> + ZrO<sub>2</sub>) (middle), and 2% Pd/( $x$ Y<sub>2</sub>O<sub>3</sub> + ZrO<sub>2</sub>) (bottom) under multiphase conditions.

As clearly seen from Fig. 3, 2 % Pd catalysts on zirconia modified by 1 and 5 % of  $Y_2O_3$ ,  $Ga_2O_3$ , and  $Al_2O_3$  are more active in the multiphase HDC of TCB than catalysts on unmodified  $ZrO_2$ . If the content of the second oxide is about 10 %, the activity of the catalysts is comparable with the activity of Pd supported on pure  $ZrO_2$ . Only in the case of alumina modifier, the conversion curve for 2 % Pd supported on pure modifier is situated below the conversion curves for modified samples. This finding could be connected with a low stability of alumina in HDC medium. On the other hand, 2 % Pd/ $Ga_2O_3$  is much more active than Pd on zirconia-gallia, and 2 % Pd/ $Y_2O_3$  is comparable in activity with the best catalyst on zirconia-yttria. A considerable difference was found in the stability of these pairs of catalysts. To compare stability under batch conditions, after the achievement of full conversion of substrate, additional amount of substrate as isooctane solution was loaded into the same batch. Up to 5 portions of substrate were loaded stepwise into the same batch. 2 % Pd/(1 %  $Ga_2O_3$  +  $ZrO_2$ ) does not lose activity during transformation of at least 5 portions of substrate (TCB) in the same batch. On the contrary, 2 % Pd/ $Ga_2O_3$  that is initially very active gradually loses activity when the number of substrate loadings is increased from 1 to 5. Similar results were obtained for 2 % Pd/ $Y_2O_3$  and 2 % Pd/(1 %  $Y_2O_3$  +  $ZrO_2$ ). Therefore, despite the high activity of 2 % Pd/ $Ga_2O_3$  and 2 % Pd/ $Y_2O_3$ , double oxide supported catalysts 2 % Pd/(1 %  $Ga_2O_3$  +  $ZrO_2$ ) and 2 % Pd/(1 %  $Y_2O_3$  +  $ZrO_2$ ) were much more stable. Due to high stability, the usage of double oxide supports is preferable.

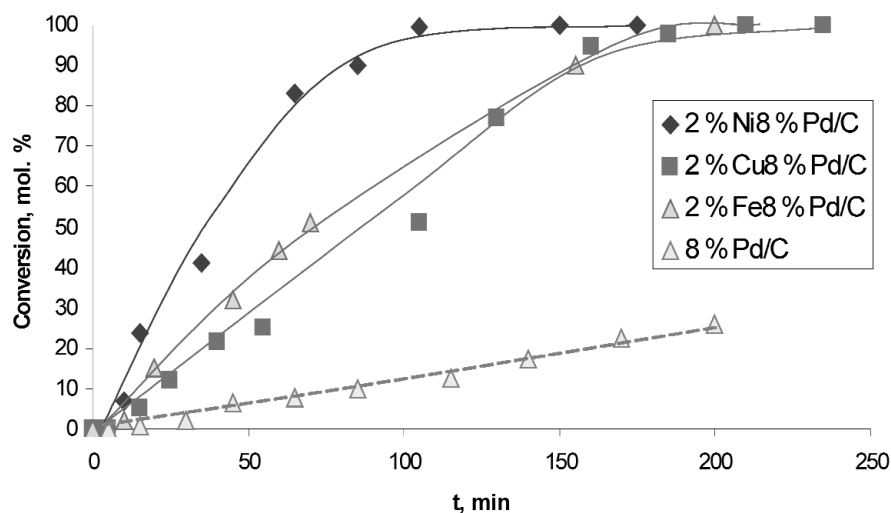
### Second metal addition

Another way to change the electronic state of Pd in the catalyst is the addition of a second metal. As shown earlier, the addition of Fe leads to significant improvement of carbon-supported Pd catalysts in HDC of 1,2-dichlorobenzene [24,25]. Addition of Fe to Pd causes (i) formation of a Pd-enriched Fe-Pd alloy that stimulates changes in electronic state of metals; and (ii) prevention of Pd poisoning due to chlorine elimination from the reaction mixture in the form of  $FeCl_3$ .

Alloy formation in the active component was found using magnetic measurements during TPR analysis [25]. Changes in the Pd electronic state in alloy were confirmed by X-ray photoelectron spectroscopy (XPS) analysis [26]. Such changes will surely affect the catalytic activity. In [27], the electronic modification of Pd by Cu in bimetallic catalyst is discussed; a difference in electronic state of pure and modified Pd was observed via the IR study using CO adsorption.

In this work, Pd modified by Fe, Ni, and Cu supported on AC was used. Total metal content in bimetallic catalysts was 10 mass %, at metal ratios of 2:8; 5:5, and 8:2 by mass. Pd/C catalysts containing the same Pd loading as in bimetallic catalyst were used for comparison. Cu/AC, Ni/AC, and Fe/AC are all tested and demonstrated no activity under the used conditions.

TCB conversion in the presence of bimetallic catalysts is presented in Fig. 4 and Table 3. The shapes of all kinetic curves are similar, and a comparison of different catalysts is possible on the basis of conversion value after equal reaction times. For this purpose, in Table 3 conversion of TCB on different bimetallic catalysts after 60 min of reaction is presented. As is clear from Table 3 and Fig. 4, all bimetallic catalysts are more active in the HDC of TCB under multiphase conditions than Pd/C with the same Pd loading. The activity of bimetallic catalysts containing the same second metal increases as the Pd content grows from 2 to 8 mass %. It is possible that one reason of Pd performance improvement is dilution of Pd by the second metal, which leads to more uniform Pd distribution than in pure Pd catalysts. Comparing the catalysts that have equal Pd:second metal ratio, but contain different second metals, it is clearly seen that the most active are Ni-containing catalysts. In the work [28], Ni-containing catalysts were the least active among tested double systems 3 %  $Pd_xMe_y/C$ , where  $Me = Pt, Fe, Ni$  and  $Co$ ,  $x = 95-5$ ,  $y = 5-95$ , and  $NaBH_4$  was used as reducing agent instead of  $H_2$  on the stage of catalysts reduction. Probably, the properties of the catalysts strongly depend on the preparation technique. For Fe- and Cu-containing catalysts, the increase of Pd:second metal ratio leads to a uniform increase of the conversion rate. For Ni-containing catalysts, the increase of Pd:Ni ratio above 1:1 leads to small changes in activity.



**Fig. 4** Conversion of TCB in the presence of 2 % M8 % Pd/C (M = Ni, Cu, Fe) under multiphase conditions.

**Table 3** Conversion of 1,3,5-TCB after 60 min of reaction for bimetallic Pd-containing catalysts supported on AC under multiphase conditions.

Metals	Conversion of 1,3,5-TCB		
	Pd:second metal, mass. content		
	2:8	5:5	8:2
Pd:Ni	38	75	80
Pd:Cu	14	30	43
Pd:Fe	12	18	33
Pd*	2	5	7

\*Conversion is observed in the presence of Pd/AC with corresponding Pd content (i.e., 2, 5, and 8 % mass).

Bimetallic catalysts were also used for the HDC of heavy molecule of HCB. For this purpose, the catalysts with a high Pd loading were chosen to shorten the reaction time. As illustrated by Fig. 5, in this case, all bimetallic catalysts are also more active in HCB HDC, than Pd/AC with the same Pd loading. But in this reaction, there is no significant difference between the catalytic performance of catalysts with different additives (Ni, Cu, Fe). Poisoning of bimetallic catalysts by chlorine probably makes all catalysts similar in activity. Formation of 6 mol of HCl as a result of 1 mol of HCB HDC instead of 3 mol in the case of TCB makes the reaction media more aggressive.

In addition, segregation of one metal on the surface of bimetallic cluster is important for catalysis [29]. XPS and magnetic measurements data described in [25] confirm the formation of Pd-enriched alloy in the Fe-Pd/C system and easiness of iron oxide chlorination in comparison with Pd. It is clear that in aggressive media, base metal chlorination proceeds first, protecting Pd active sites from the poisoning. There are considerations that the surface of alloy particle will be enriched by base metal under the influence of chlorinated hydrocarbons [30]; but initial enrichment by Pd discovered for our systems and multiphase conditions used in this work additionally protect active sites from deactivation.



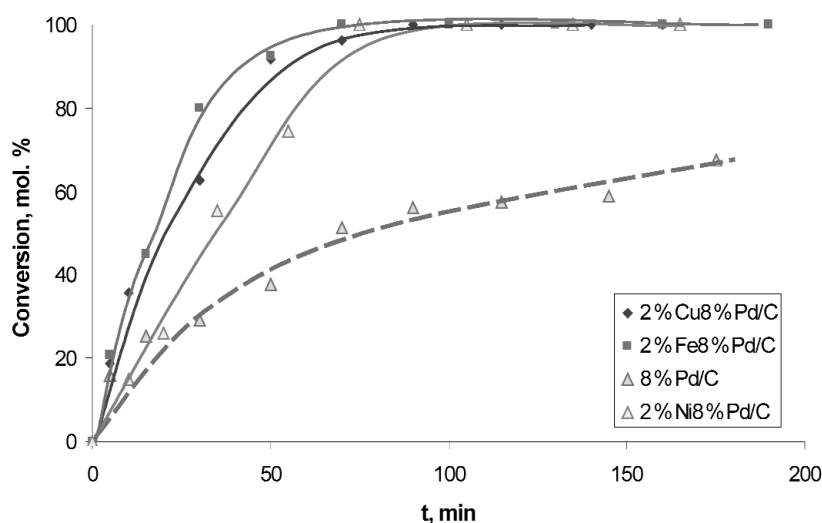


Fig. 5 Conversion of HCB in the presence of 2 % M8 % Pd/C (M = Ni, Cu, Fe) under multiphase conditions.

## CONCLUSIONS

HDC of polychlorinated substances on heterogeneous catalysts is a multiversion process that can be used for both processing of wastes and synthesis of target products. Pd-containing catalysts on UDD and double oxides and carbon-supported Pd-containing bimetallic catalysts demonstrate good performance as HDC catalysts. Both dilution of Pd by not-noble metal and modification of zirconia support by the second oxide lead to the formation of bifunctional Pd(0)-Pd( $\delta^+$ ) centers responsible for high catalytic activity of such modified catalysts in HDC reactions. The highest conversion rate for TCB transformations was achieved in the presence of 2 and 5 % Pd/UDD, 2 % Pd/Ga<sub>2</sub>O<sub>3</sub>, and 2 % Pd/Y<sub>2</sub>O<sub>3</sub>. Pd/UDD catalysts are also very stable and can be used repeatedly. As for oxide-supported Pd catalysts, double oxides (especially 1 and 5 % Y<sub>2</sub>O<sub>3</sub> + ZrO<sub>2</sub>) supported 2 % Pd catalysts are much more stable, with nearly the same activity as those supported on pure modifier oxide (e.g., 2 % Pd/Y<sub>2</sub>O<sub>3</sub>).

## ACKNOWLEDGMENTS

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