Bi modified Pd/support (SiO$_2$, Al$_2$O$_3$) catalysts for hydrodechlorination of 2,4-dichlorophenol

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ABSTRACT

The influence of bismuth addition on the activity and selectivity of home-made supported palladium catalysts in the reaction of hydrodechlorination of 2,4-dichlorophenol to phenol was studied. Bimetallic Pd–Bi/Al$_2$O$_3$ and Pd–Bi/SiO$_2$ catalysts, containing 5 wt.% of Pd and 1–5 wt.% of Bi, are characterized by high conversion of 2,4-dichlorophenol, which reaches about 100% at the end of the reaction run. However, the catalysts 5%Pd–8%Bi/SiO$_2$ and 5%Pd–8%Bi/Al$_2$O$_3$ show considerably lower conversion (respectively, about 25% and 60%), but they are characterized by the highest selectivity towards phenol (respectively, about 95% and 60%). The stability of the chosen bimetallic catalyst 5%Pd–1%Bi/Al$_2$O$_3$ is higher than that of the monometallic palladium catalyst. The XRD and ToF-SIMS studies proved the presence of intermetallic compounds BiPd and Bi$_2$Pd, which probably modify the catalytic properties of Pd–Bi/support catalysts in hydrodechlorination of 2,4-dichlorophenol.

1. Introduction

Chlorophenols belong to an important group of organic compounds. They are commonly used as chemical feedstocks in the manufacture of pesticides, herbicides, biocides, wood preservatives, pharmaceuticals and dyes. The wide application of chlorophenols in different branches of chemical industry may be the reason for their easy penetration to the natural environment. The presence of a great amount of chlorophenols in air, water and soil poses a serious risk to human health and it negatively influences all ecosystem functions. These compounds have toxic, mutagenic and possibly carcinogenic properties and they are characterized by high stability.

From the environmental point of view, the development of an efficient method of elimination of chlorophenols is necessary. Several techniques were investigated for the treatment of waste streams containing toxic chlorinated organic contaminants. The widely used chemical method of incineration often leads to the formation of highly toxic by-products such as dioxins [1,2]. The methods based on electrochemistry [3,4], photochemistry [5,6] and also on biotechnology [7–10] result in low conversion. On the other hand, the thermal methods, which include pyrolysis and hydrogenolysis, require high energy. Catalytic hydrodechlorination (HDC) is now viewed as a promising emerging technology [11–14].

Although the study of catalytic HDC of chlorophenols was initiated in the 1960s, the first literature reported the destruction of chlorophenol in the liquid phase in 1992 [13]. The authors of this work describe a catalytic process of destruction of chlorinated phenols at 35 °C using supported monometallic palladium catalyst, where hydrogen was used as a reducing agent. The only organic product of hydrodechlorination reaction was phenol.

A lot of research about hydrodechlorination of chlorophenols in liquid phase with the usage of supported palladium catalysts has been conducted in recent years [14–27]. The papers show that activity and selectivity of studied catalysts depend on dispersion, the amount of active phase, methods of preparation, the type of support used, temperature of reaction, etc.

Recently, in many carbon–halogen bond hydrogenolysis processes the research on palladium bimetallic systems characterized by higher activity and stability than in the case of monometallic systems has started. However, the influence of the addition of a second metal to Pd/support systems on catalytic properties in the reaction of hydrodechlorination of 2,4-dichlorophenol in the liquid phase has not been studied thoroughly yet.

The data gathered in the literature [28] concern mainly hydrodechlorination of organohalogen compounds in the gas phase, which is conducted at relatively high temperatures (above 200 °C). The influence of the addition of such metals as Fe [29–31], Re [32,33], Ag [30,34], Au [35], Co [30], K [36] and La, Bi, Sb, Sn, Ba and Zn [37,38] to palladium catalysts on their activity and selectivity in gas-phase hydrodechlorination of CFCs has been studied.

The changes in catalytic properties of bimetallic systems were explained by different effects. Malinowski et al. [35] reported

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the increase in selectivity towards CH_2F_2 in the gas-phase hydrodechlorination of CCl_2F_2 over Pd–Au/MgF$_2$ catalysts which showed two Pd–Au solid solutions [35]. Coq et al. [30] studied the behavior of palladium when alloyed with Fe, Co or K in hydrodechlorination of the same compound. They found that the addition of those metals causes the maintenance of a constant value of selectivity to CH_2F_2, so it improves the stability of those systems in the studied process. The presence of Fe, Co or K prevents the diffusion of halide species into the bulk palladium, which is the reason for lowering the selectivity value in the process over Pd/Graphite catalyst. Shekar et al. [37,38] studied Bi–Pd/FCCA catalysts in the reaction of gas-phase hydrodechlorination of CCl_2F_2 in the temperature range 200–320 °C and stated that the addition of bismuth to palladium catalysts improves not only the thermal stability but also the selectivity towards CH_2F_2. In the case of Bi–Pd/FCCA catalysts, the presence of intermetallic compounds BiPd$_3$ type was observed. These compounds can modify the catalytic properties of bimetallic catalysts.

On the basis of the facts presented above, two main aspects need to be pointed out to understand the effect of adding a second metal to palladium catalysts: the degree of interaction between both metals and the distribution of metal components on the catalyst. These issues will be thoroughly studied in our work for Pd–Bi/support systems. In the case of these bimetallic catalysts the formation of intermetallic compounds BiPd and Bi$_2$Pd [39,40], which probably modify the catalytic properties in studied reaction was observed in our earlier studies.

In this work, we present the results of activity and selectivity of monometallic palladium supported catalysts and bimetallic systems modified with Bi in hydrodechlorination of 2,4-dichlorophenol. The catalysts were characterized by X-ray diffraction (XRD), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and temperature-programmed reduction (TPR). The main focus will be put on mutual interactions between palladium and bismuth and their influence on catalytic properties of Pd–Bi/support systems.

2. Experimental

2.1. Catalyst preparation

Catalysts containing 5 wt.% of palladium supported on silica (Aldrich, 250 m^2/g) and alumina (Fluka Typ 507C, 143 m^2/g) were prepared from water solution of PdCl$_2$ (aq., POCh Gliwice) by aqueous impregnation. The water was evaporated at an increased temperature (353 K) under vacuum. The catalysts were dried in air at 110 °C for 6 h, calcined at 500 °C for 4 h in oxygen atmosphere and then reduced in hydrogen atmosphere for 2 h at 300 °C.

Bimetallic Pd–Bi/support (SiO$_2$, Al$_2$O$_3$) catalysts containing 5 wt.% Pd and 1, 3, 5, 8 wt.% Bi were obtained from monometallic palladium catalysts by repeated impregnation of these systems with water solution of Bi(NO$_3$)$_3$·5H$_2$O (aq., POCh Gliwice) according to the procedure described above.

2.2. Catalytic measurements

The catalysts were activated in the flow reactor in hydrogen atmosphere at 300 °C directly before the measurements of activity. Having put the catalyst in the reactor in water, it was saturated with hydrogen for 0.5 h before introducing 2,4-dichlorophenol to the system. It was done to ensure complete palladium reduction.

The hydrodechlorination of 2,4-dichlorophenol solution (100 mg/dm^3) was performed in a thermostated glass reactor of 400 ml equipped with a stirrer, a hydrogen supply system, a burette containing NaOH (0.01 mol/dm^3) and a pH electrode. The reaction was conducted at room temperature, pH = 7 and for the steady amount of catalyst (m_{cat} = 0.4 g). The solution NaOH with assumed concentration was introduced to the system manually from the burette. The mixture was stirred at 1300 rpm and hydrogen was bubbled through at 0.300 dm^3/min. No pressure control was required as the total operating pressure in the system was equal to atmospheric pressure. A further increase in the speed of stirring and the speed of hydrogen flow did not cause further changes in activity. The choice of the stirring speed and hydrogen flow rate served to minimize transport limitations.

Samples of the reaction medium were taken systematically, filtered and analyzed using a liquid chromatograph coupled with a variable wavelength UV detector Varian 9050. The analytical wavelength was 210 nm. The reaction products were separated on a Zorbax SB-C18 column 250 mm × 4.6 mm ID, using water solution of MeOH as a mobile phase. For the selected catalysts, the reaction products were detected by GC (Hewlett Packard 5890 with FID detection; packed column 8% Carbowax 1540 on Chromosorb W, 1500 mm × 8 mm ID) for the full analysis of the mixture of phenol/cyclohexanone/cyclohexanol.

Catalytic results are expressed as conversion (X, %) and selectivities (S, %). Those parameters were defined as:

$$X = \left[1 - \left(\frac{C_{2,4DCP}}{C_{02,4DCP}}\right)\right] \times 100\%$$

$$S = \left[\frac{C_P}{C_{02,4DCP} - C_{2,4DCP}}\right] \times 100\%$$

where $C_{02,4DCP}$ is a molar concentration of 2,4-dichlorophenol at the beginning of the hydrodechlorination process, $C_{2,4DCP}$ is a molar concentration of 2,4-dichlorophenol after time t, C_P is a molar concentration of phenol after time t. The tests of catalytic activity were conducted for each catalyst three times and the presented results constitute arithmetical mean of these three measurements.

2.3. Characterization of catalysts

2.3.1. Powder X-ray diffraction (XRD)

Room temperature powder X-ray diffraction patterns were collected using a PANalytical X'Pert Pro MPD diffractometer. A copper long fine focus X-ray diffraction tube operating at 40 kV and 30 mA was the X-ray source. Divergent optics were used in a Bragg–Brentano (flat-plate sample) geometry, with fixed divergence (1/2°) and antiscatter (1°) slits. Incident and receiving 0.04 rad Soller slits were used to limit axial divergence, and a nickel filter on the receiving side was used to eliminate CuK$_\beta$ radiation. Data were collected in the range 20–90° 2θ with step 0.0167° and exposition per step of 20 s. A PANalytical X'Celerator detector based on Real Time Multiple Strip technology capable of measuring the intensities simultaneously in the 2θ range of 2.122° was used. Crystalline phases were identified by referring to ICDD PDF-2 (ver. 2004) data base.

2.3.2. Time of fly secondary mass spectrometry (ToF-SIMS)

The secondary ions mass spectra were recorded with a TOF-SIMS IV mass spectrometer manufactured by Ion-Tof GmbH, Muenster, Germany. The instrument was equipped with Bi liquid metal ion gun and high mass resolution time-of-flight mass analyzer. During the measurement, the analyzed area was irradiated with the pulses of 25 keV Bi$_3^+$ ions at 10 kHz repetition rate and an average ion current 0.6 pA. The analysis time was 30 s for both positive and negative secondary ions giving an ion dose below the static limit of 1×10^{13} ions/cm^2. Secondary ion mass spectra were recorded from an approximately 100 μm × 100 μm area of the spot surface, ion images were obtained for 500 μm × 500 μm surface area.

The catalyst samples were prepared by pressing pellets.
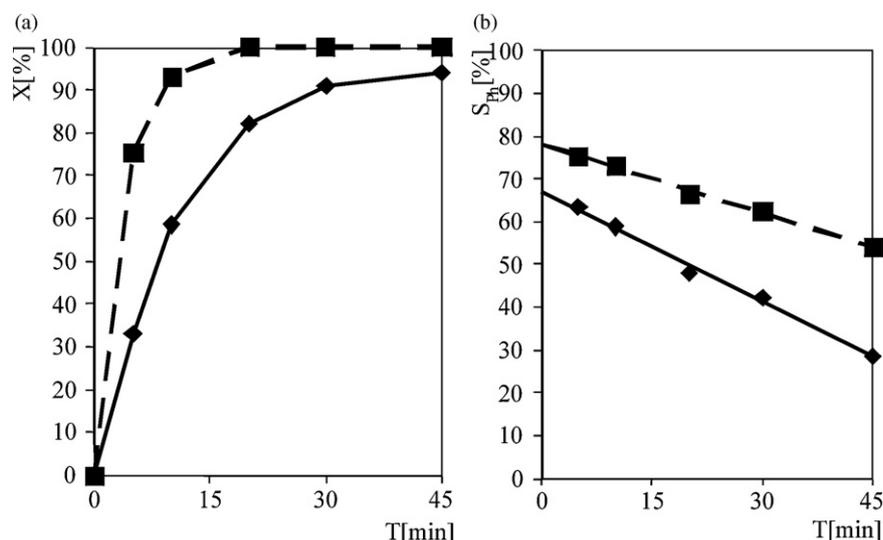
Fig. 1. (a) Conversion of 2,4-dichlorophenol and (b) selectivity towards phenol as a function of time of hydrodechlorination in liquid phase over ♦−5%Pd/Al$_2$O$_3$ and ■−5%Pd/SiO$_2$ catalysts. Reaction was conducted at room temperature for the steady amount of catalyst (m_{cat} = 0.4 g). 400 ml solution of 2,4-dichlorophenol (0.04 g) in water was used. Reaction mixture was stirred at 1300 rpm and hydrogen was bubbled through at 0.300 dm^3/min.

2.3.3. Temperature-programmed reduction (TPR) measurements.

The measurements were carried out in AMI-1 (Altamira) apparatus. The catalyst samples (0,05 g), prior to the TPR measurements were calcined at 500 °C for 2 h in the mixture of oxygen–argon (10 vol.% of O$_2$) at a flow rate of 30 cm^3/min. TPR runs were performed in the temperature range: TPR(1): 20–300 °C; TPR(2): 20–300 °C; TPR(3): 20–650 °C, using a mixture of hydrogen–argon (10 vol.% of H$_2$) at a flow rate of 30 cm^3/min and a linear temperature growth of 10 °C min^{-1}.

2.3.4. CO sorption measurements

The measurements of CO sorption were carried out with the use of an impulse method at room temperature applying argon as carrier gas. The catalyst samples prior the sorption step were oxidized at 500 °C for 4 h using O$_2$ and reduced at 300 °C for 2 h using H$_2$. After this operation the samples of catalysts were cooled in argon to room temperature. The volume of dosed carbon monoxide equals 0.57 cm^3.

3. Results and discussion

In the process of hydrodechlorination of 2,4-dichlorophenol in the liquid phase, supported palladium catalysts are characterized by good activity [14–27]. In the open literature, the influence of many factors such as the kind of support, type of salt, method of catalysts preparation and amount of active phase on the catalytic activity in this process have been considered. The role of palladium dispersion in the hydrodechlorination process in the liquid phase has been investigated only in few papers [41–46]. However, the presented results are not only scant but also incon-

clusive. In our study of hydrodechlorination of 2,4-dichlorophenol in the liquid phase we observed the influence of palladium dispersion on both activity and selectivity in the studied reaction (Fig. 1.)

The conversion of 2,4-dichlorophenol for 5%Pd/SiO$_2$ catalysts is higher than for 5%Pd/Al$_2$O$_3$ systems. For the former catalyst almost complete conversion of 2,4-dichlorophenol was observed after 20 min. The physicochemical characteristics of the palladium catalysts in question are presented in Table 1. According to expectations, the dispersion of palladium supported on silica is smaller than for palladium supported on alumina. This fact confirms the influence of the dispersion of the active phase on the catalytic activity, which was also observed by Gomez-Quero et al. [41].

The dispersion of palladium has also an impact on selectivity. For the systems with lower dispersion, higher selectivity towards phenol is observed. On the other hand, for the systems with higher dispersion (5%Pd/Al$_2$O$_3$), the concentration of phenol decreases considerably and the reaction proceeds to the formation of cyckohexanone and cyclohexanol (Fig. 2 and Table 2).

In order to prove the hypothesis the reaction of hydrodechlorination of 2,4-dichlorophenol proceeds with better yield of phenol on bigger crystallites, the samples of 5%Pd/Al$_2$O$_3$ catalyst were reduced in hydrogen at the temperature of 300, 500 and 700 °C. After that, the samples underwent catalytic tests (Fig. 3) and XRD studies (Fig. 4).

The catalysts which were reduced at 700 °C were characterized by bigger crystallites (Fig. 4) and showed higher activity and selectivity towards phenol than the systems reduced at a lower temperature (300 and 500 °C).

Table 1
Specific surface area and diameter of the Pd crystallites estimated for monometallic 5%Pd/support and bimetallic 5%Pd–X%Bi/support catalysts.

Catalysts	Activation procedure	Specific surface area S_{Pd} (m^2/g$_{cat}$)[a]	Diameter of the Pd crystallites (nm)[b]
5%Pd/Al$_2$O$_3$	O$_2$, 500 °C, 2h/H$_2$, 300 °C, 2h	4.61	7
5%Pd–3%Bi/Al$_2$O$_3$	O$_2$, 500 °C, 2h/H$_2$, 300 °C, 2h	6.95	–
5%Pd/SiO$_2$	O$_2$, 500 °C, 2h/H$_2$, 300 °C, 2h	0.28	47
5%Pd–1%Bi/SiO$_2$	O$_2$, 500 °C, 2h/H$_2$, 300 °C, 2h	0.45	21
5%Pd–3%Bi/SiO$_2$	O$_2$, 500 °C, 2h/H$_2$, 300 °C, 2h	0.54	8
5%Pd–8%Bi/SiO$_2$	O$_2$, 500 °C, 2h/H$_2$, 300 °C, 2h	0.52	8

[a] Specific surface area determined on the basis of CO chemisorption, with the assumption that 0.84×10^{15} of CO particles takes up the surface of 1 cm^2 Pd [47].
[b] Diameter of the Pd crystallites estimated from XRD analysis, using the Scherrer equation.
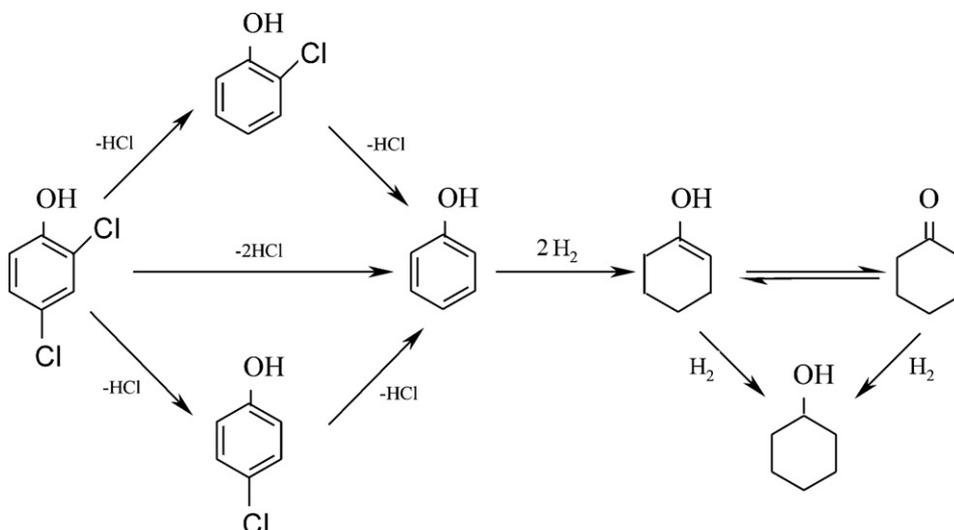
Fig. 2. Scheme of the reaction of hydrodechlorination of 2,4-dichlorophenol.

Table 2
Initial specific rate of reaction and selectivities towards phenol, 2-chlorophenol and 4-chlorophenol for the chosen catalytic systems.

Catalyst	$R^a \times 10^{-6}$ (mol min^{-1} m^{-2})	$X_{2,4\text{-dichlorophenol}}$ (%)		S_{phenol} (%)		$S_{2\text{-chlorophenol}}$ (%)		$S_{4\text{-chlorophenol}}$ (%)	
		t_{20}	t_{45}	t_{20}	t_{45}	t_{20}	t_{45}	t_{20}	t_{45}
5%Pd/Al$_2$O$_3$	1.24	82.08	93.90	48.16	28.71	0.84	–	8.21	–
5%Pd–1%Bi/Al$_2$O$_3$	–	98.59	100	56.03	37.36	3,91		18,67	–
5%Pd–3%Bi/Al$_2$O$_3$	0.88	94.97	100	64.69	40.71	–	–	–	–
5%Pd–8%Bi/Al$_2$O$_3$	–	33.12	63.24	78.61	56.16	–	–	–	–
5%Pd/SiO$_2$	20.54	100	100	66.51	53.99	0.10	–	5.62	–
5%Pd–1%Bi/SiO$_2$	13.67	92.00	100	79.06	68.99	1.57	–	12.25	–
5%Pd–3%Bi/SiO$_2$	10.46	92.26	100	94.44	85.09	–	–	–	–
5%Pd–5%Bi/SiO$_2$	–	89.19	98.49	85.30	77.72	–	–	–	–
5%Pd–8%Bi/SiO$_2$	0.48	4.29	23.29	99.98	95.09	–	–	–	–

^{a} R—initial specific rate calculated after the first 20 min of reaction.

An addition of bismuth to supported palladium catalysts leads to the change of both activity and selectivity in the studied reaction of hydrodechlorination of 2,4-dichlorophenol in the liquid phase (Table 2). The introduction of bismuth to 5%Pd/support (SiO$_2$, Al$_2$O$_3$) catalysts in the amount of up to 5% wt. practically causes only a slight change in the activity, however, a significant decrease in the activity after the introduction of high amounts of bismuth (8-wt.% Bi) is observed. Additionally, bimetallic Pd–Bi/SiO$_2$ catalysts
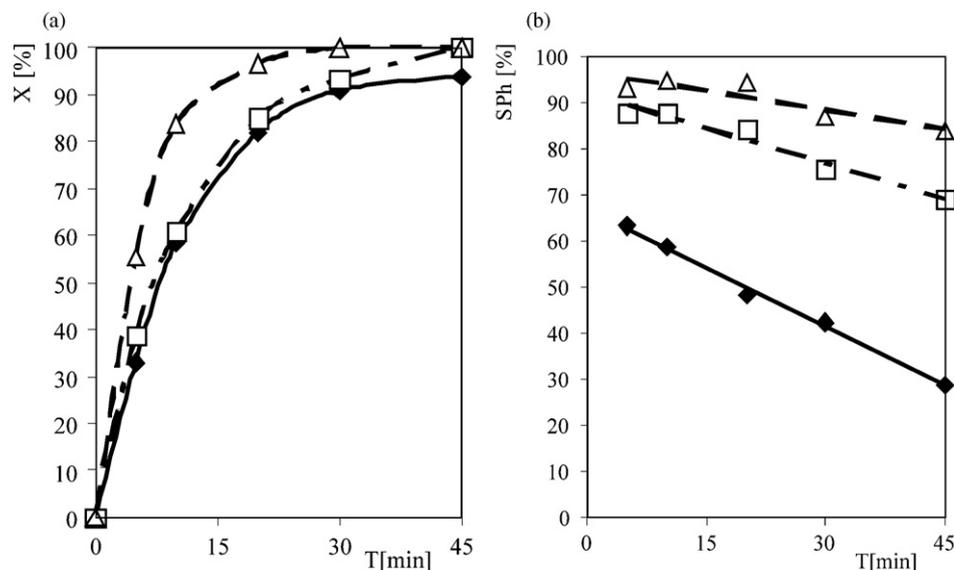
Fig. 3. (a) Conversion of 2,4-dichlorophenol and (b) selectivity towards phenol as a function of time of hydrodechlorination in liquid phase over 5%Pd/Al$_2$O$_3$ catalysts reduced at ◆—300 °C, □—500 °C and △—700 °C. Reaction was conducted at room temperature for the steady amount of catalyst ($m_{cat} = 0.4$ g). 400 ml solution of 2,4-dichlorophenol (0.04 g) in water was used. Reaction mixture was stirred at 1300 rpm and hydrogen was bubbled through at 0.300 dm^3/min.
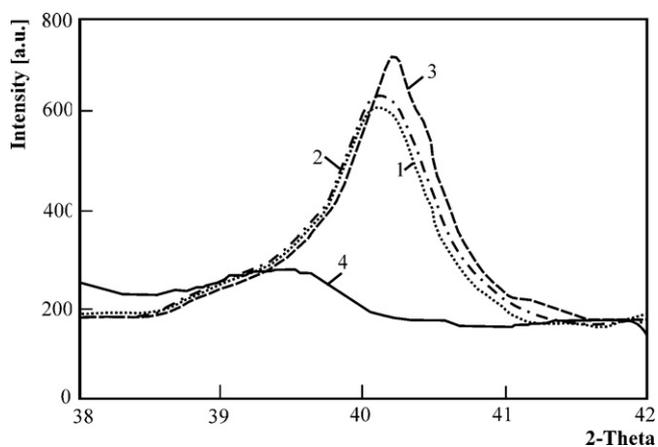
Fig. 4. XRD patterns for 5%Pd/Al$_2$O$_3$ catalysts reduced at 1–300 °C, 2–500 °C and 3–700 °C. Diffractogram 4 was detected for pure support Al$_2$O$_3$. Patterns obtained with CuK$_\alpha$ radiation, step scanned 20 s per step of 0.0167° of 2θ.

are characterized by higher selectivity towards phenol in comparison with monometallic systems. Studies of CO sorption performed at room temperature and XRD studies show an increase in the dispersion of palladium after the introduction of bismuth (Table 1). For the monometallic and bimetallic systems the increase in the dispersion resulted in the decrease in the selectivity to phenol. However, comparing the selectivity to phenol for monometallic palladium catalyst supported on silica with the selectivity of bimetallic catalysts on the same support, one can see that despite the increase in the dispersion of palladium after introducing bismuth to the systems, the selectivity of these systems is higher (Table 2). Strong metal–promotor interactions (SMPI) leading to the formation of intermetallic compounds could probably be responsible for such behavior of these bimetallic systems.

The studies of Pd–Bi/C catalysts in oxidation of glucose performed by Wenkin et al. [48] show the presence of two binary alloys with the compositions of BiPd and BiPd$_3$. Small amounts of Pd metal and Bi$_2$O$_3$ oxide were simultaneously detected, and another phase which most probably corresponds to Bi$_2$Pd$_5$ was present. The same authors [49,50] performed catalytic oxidation of glucose over pure intermetallics Bi$_2$Pd, BiPd and BiPd$_3$. They noticed that catalytic behavior of those phases was very different.

Also, our studies performed for Pd–Bi/SiO$_2$ catalysts in oxidation of glucose and lactose show the presence of intermetallic compounds BiPd and Bi$_2$Pd, which determine the catalytic properties of these systems [39,40].

Therefore, we assume that the selectivity of palladium–bismuth catalysts in the reaction of hydrodechlorination of 2,4-dichlorophenol in the liquid phase is probably connected with the presence of intermetallic compounds on the surface.

The surface structure of Pd–Bi/SiO$_2$ and Pd–Bi/Al$_2$O$_3$ was analyzed using ToF-SIMS and XRD techniques.

The results of the XRD study of Pd–Bi/SiO$_2$ and Pd–Bi/Al$_2$O$_3$ reduced catalysts are presented in Table 3. The conducted XRD studies show that in the case of Pd–Bi/SiO$_2$ catalysts the pres-

Table 3
The results of XRD analysis of reduced Pd–Bi/support catalysts. Crystalline phases were identified by references to ICDD PDF-2 (ver. 2004) data base.

Catalysts	Pd	Bi	BiPd (C)	BiPd(Sob)	Bi$_2$Pd
5%Pd–1%Bi/SiO$_2$	+	−	+	+	−
5%Pd–3%Bi/SiO$_2$	+	−	+	+	−
5%Pd–8%Bi/SiO$_2$	+	−	+	+	+
5%Pd–1%Bi/Al$_2$O$_3$	+	−	−	−	−
5%Pd–5%Bi/Al$_2$O$_3$	+	−	−	−	−
5%Pd–8%Bi/Al$_2$O$_3$	+	−	−	−	−

ence of BiPd and Pi$_2$Pd intermetallic compounds is observed. BiPd intermetallic compounds are observed for all the studied systems and Bi$_2$Pd compounds are detected only for catalysts with higher amounts of bismuth (5%Pd–8%Bi/SiO$_2$). However, in the case of Pd–Bi/Al$_2$O$_3$ catalysts, intermetallic BiPd and Bi$_2$Pd compounds were not detected by XRD measurements.

On the basis of the XRD studies, it was stated that bimetallic systems supported on alumina and silica significantly differed from each other as regards the degree of crystallinity. A low degree of crystallinity of these systems supported on Al$_2$O$_3$ impeded the identification of metallic phases in the case of these catalysts.

To get a better understanding of the nature of interactions between palladium and bismuth on the surface of alumina and silica, the samples of bimetallic catalysts were characterized by ToF-SIMS. This technique made it possible to observe the changes of catalyst surface, which are invisible for XRD, for example, the application of ToF-SIMS allowed us to observe the presence of intermetallic Bi$_x$Pd$_y$ compounds for bimetallic catalysts supported on alumina.

Fig. 5 shows an ionic view of microarea of palladium catalyst supported on alumina and modified with bismuth after oxidation in oxygen atmosphere for 4 h at 500 °C and reduction in hydrogen atmosphere for 2 h at 300 °C. The brightness of particular places in the images corresponds to the intensity of secondary ions emission.

On the basis of images of bimetallic palladium–bismuth catalysts, it is visible that Pd and Bi atoms are distributed homogenously on the surface of alumina. The obtained images of those catalysts show that the secondary ions BiPd$^+$ and BiPdO$^+$ are emitted from the surface, which demonstrated strong interactions between those metals. Slightly different images were obtained for palladium–bismuth systems supported on silica. In the case of this carrier, both metals were not located homogenously on the surface, forming explicit clusters with increased emission of both Pd$^+$ and Bi$^+$ ions and BiPd$^+$ and Bi$_2$Pd$^+$ ions [39,40]. What is more, the intensity of emission of BiPd$^+$ and Bi$_2$Pd$^+$ ions is about 10 times higher for the systems supported on alumina than it was observed for the catalysts supported on silica (Fig. 6). Emission of those ions from the surface of catalysts Pd–Bi/Al$_2$O$_3$ and Pd–Bi/SiO$_2$ proves the occurrence of BiPd and Bi$_2$Pd phases in these systems, which was shown using XRD only for silica supported catalysts.

In the light of performed studies, it can be assumed that the presence of intermetallic compounds of Bi$_x$Pd$_y$ on the surface of Pd–Bi/support catalysts may have an influence on their activity and selectivity in the reaction in question. For the catalysts containing small amounts of bismuth 5%Pd–1%Bi/support and 5%Pd–3%Bi/support, the formation of mainly BiPd-type intermetallic compounds is observed (Table 3). These catalysts are characterized by high activity and selectivity towards phenol (Table 2). However, in the catalysts containing higher amounts of bismuth (>5% weight), we observed the presence of both Bi$_2$Pd-type and BiPd-type intermetallic compounds. Despite high selectivity towards phenol, these catalysts showed surprisingly low activity in the studied reaction.

Similarly, temperature-programmed reduction studies prove an existence of strong interactions between Pd and Bi in Pd–Bi/Al$_2$O$_3$ systems.

Fig. 7 presents TPR$_1$ spectra obtained for 5%Pd/Al$_2$O$_3$, 3%Bi/Al$_2$O$_3$, 5%Pd–3%Bi/Al$_2$O$_3$, 5%Pd–8%Bi/Al$_2$O$_3$ systems after calcination in O$_2$ at 500 °C for 2 h. The calcined samples of the system containing 5%Pd/Al$_2$O$_3$ show two low temperature peaks located in the temperature range of 25–150 °C. This seems to be connected with the formation of two different forms of palladium oxide in the first stage of contact between the samples and oxygen. For 5%Pd–3%Bi/Al$_2$O$_3$ catalyst two maxima of the reduction rate are observed, which are probably connected with the reduction of different oxide forms. An introduction of bismuth in the amount of
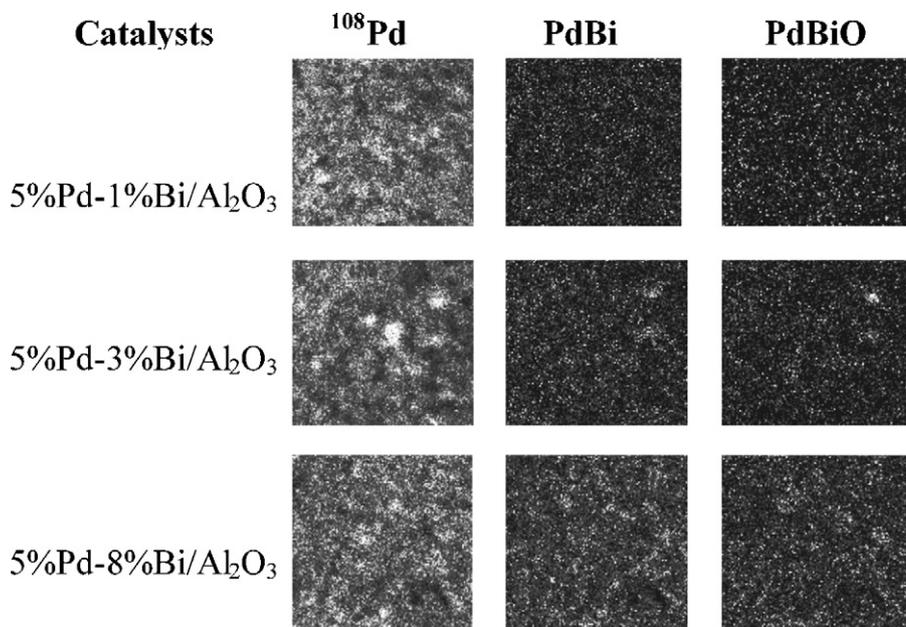
Fig. 5. Positive secondary ions ToF-SIMS image of Pd–Bi/Al$_2$O$_3$ catalysts surfaces after single oxidation–reduction cycle. The analyzed area of the surface 500 μm × 500 μm. During measurement the analyzed area was irradiated with pulses of 25 keV Bi$_3^+$ ions at 10 kHz repetition rate and an average ion current 0.6 pA. Secondary ions emitted from the bombarded surface were mass separated and counted in time-of-flight (ToF) analyzer.

8 wt.% to 5%Pd/Al$_2$O$_3$ catalyst causes the disappearance of the first peak connected with hydrogen adsorption.

More interesting results have been obtained from the successive measurement cycles. The catalyst samples which underwent preliminary calcination in O$_2$ at 500 °C and were treated with hydrogen in TPR$_1$ process were reoxidized at 500 °C for 2 h and reduced in TPR$_2$ up to 300 °C. Finally, after the reoxidation step, TPR$_3$ mea-

surements were taken up to the temperature of 650 °C and their results are presented in Fig. 8. The TPR$_2$ and TPR$_3$ images are practically the same, which proves that the surface of the systems is stabilized during the initial reduction process (TPR$_1$).

In the case of catalysts 5%Pd/Al$_2$O$_3$ and 5%Pd–1%Bi/Al$_2$O$_3$, instead of hydrogen adsorption peaks only desorption peaks were observed. It leads to the conclusion that the total reduction of all
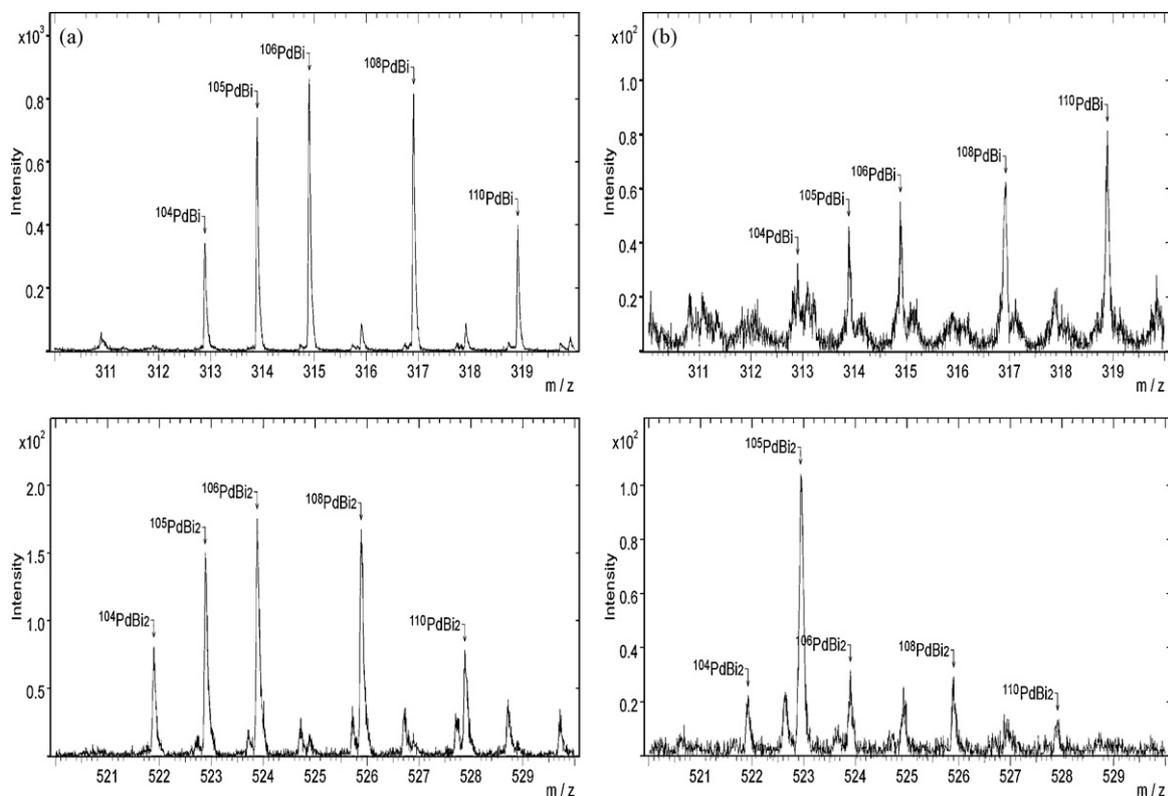
Fig. 6. The ToF-SIMS (+) spectra of (a) 5%Pd–8%Bi/Al$_2$O$_3$ and (b) 5%Pd–8%Bi/SiO$_2$ catalysts after oxidation at 500 °C in O$_2$ and reduction at 300 °C in H$_2$. The analysis time was 30 s for positive secondary ions giving an ion dose below the static limit of 1×10^{13} ions/cm^2.

Table 4
Stability of 5%Pd/Al$_2$O$_3$ and 5%Pd–1%Bi/Al$_2$O$_3$ in the reaction of 2,4-dichlorophenol hydrodechlorination.

Catalyst	$X_{2,4\text{-dichlorophenol}}$ (%)											
	1st cycle			3rd cycle			5th cycle			7th cycle		
	t_5	t_{20}	t_{45}	t_5	t_{20}	t_{45}	t_5	t_{20}	t_{45}	t_5	t_{20}	t_{45}
5%Pd/Al$_2$O$_3$	33.02	82.08	93.90	14.47	63.16	90.80	7.06	47.54	77.05	4.50	32.41	57.39
5%Pd–1%Bi/Al$_2$O$_3$	70.33	98.59	100	50.01	94.11	100	45.98	80.47	100	18.72	73.36	97.08

oxide forms took place at room temperature. Moreover, Pd has the ability to form hydride phases under normal conditions. The desorption peaks observed for 5%Pd/Al$_2$O$_3$ and for bimetallic systems in the TPR$_3$ process at a temperature of around 80 °C probably correspond to β-PdH decomposition. Similar patterns are obtained for supported palladium catalysts promoted with Cu, Sn, Pb and Ag [51–53]. However, upon the incorporation of a second metal the suppression of β-PdH phase was postulated for the supported bimetallic catalyst. The introduction of bismuth into supported palladium catalysts did not lead to the disappearance of the desorption peak suggesting that the β-PdH formation was not inhibited.

Moreover, the appearance of two reduction peaks at the temperature of about 180 and 300 °C for the 5%Pd–3%Bi/Al$_2$O$_3$ and 5%Pd–8%Bi/Al$_2$O$_3$ catalysts might indicate the formation of a mixed oxide in those bimetallic systems. The existence of this form could lead to the formation of intermetallic compounds in the reduction atmosphere. For those systems the formation of BiPd and Bi$_2$Pd phases was indicated by ToF-SIMS study.

In Table 4 the stability of mono- and bimetallic systems in the reaction of hydrodechlorination of 2,4-dichlorophenol in an aqueous phase was shown. The stability of catalysts was estimated on the basis of activity changes during seven 45-min-long measurement cycles. The process of reduction was conducted for the steady amount of catalyst ($m_{cat} = 0.4$ g) without its removal
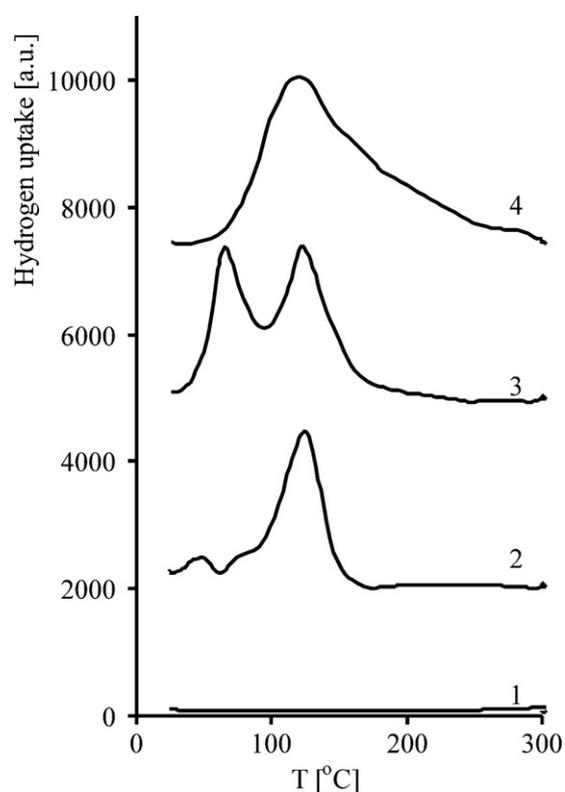
Fig. 8. Temperature-programmed reduction (TPR$_3$) of (1) 3%Bi/Al$_2$O$_3$; (2) 5%Pd/Al$_2$O$_3$; (3) 5%Pd–1%Bi/Al$_2$O$_3$; (4) 5%Pd–3%Bi/Al$_2$O$_3$ and (5) 5%Pd–8%Bi/Al$_2$O$_3$ catalysts. Samples which underwent preliminary calcination in O$_2$ at 500 °C and were treated with hydrogen in TPR$_1$ and TPR$_2$ processes, and reoxidized each time at 500 °C for 2 h.

from the reaction mixture in the subsequent cycles. After each 45-min-long measurement cycle, a new portion of 2,4-dichlorophenol ($m_{2,4\text{-dichlopophenol}} = 0.04$ g) was introduced to the reaction mixture.

In the case of monometallic catalyst 5%Pd/Al$_2$O$_3$, a systematical decrease in its activity was observed in each measurement cycle. In the 7th measurement cycle, the conversion of 2,4-dichlorophenol falls to the value of about 50%. This phenomenon is not observed for the bimetallic system 5%Pd–1%Bi/Al$_2$O$_3$. In this case, even in the 7th measurement cycle, the conversion of 2,4-dichlorophenol is practically complete. Therefore, the addition of bismuth to palladium catalysts, which lead to the formation of intermetallic BiPd compounds, causes a significant improvement of their stability in the process.

4. Conclusions

Bimetallic Pd–Bi/Al$_2$O$_3$ and Pd–Bi/SiO$_2$ catalysts, containing 5 wt.% of Pd and 1–5 wt.% of Bi, are characterized by high activity in the hydrodechlorination of 2,4-dichlorophenol. However, systems containing a larger amount of bismuth (5%Pd–8%Bi/Al$_2$O$_3$, 5%Pd–8%Bi/SiO$_2$) show poorer activity in the studied reaction. The addition of bismuth into supported palladium leads to the improvement of selectivity towards phenol and stability in the studied process.

The ToF-SIMS and XRD measurements of bimetallic Pd–Bi/support (SiO$_2$, Al$_2$O$_3$) catalysts showed the presence of

Fig. 7. Temperature-programmed reduction (TPR$_1$) of (1) 3%Bi/Al$_2$O$_3$; (2) 5%Pd/Al$_2$O$_3$; (3) 5%Pd–3%Bi/Al$_2$O$_3$ and (4) 5%Pd–8%Bi/Al$_2$O$_3$ catalysts. Samples which underwent preliminary calcination in O$_2$ at 500 °C.

intermetallic compounds on their surfaces. The presence of BiPd-type compounds was observed independently of the carrier used. However, additionally the creation of Bi_2Pd compound on the surface was observed for the systems containing high amounts of bismuth. At the same time, these catalysts were characterized by low conversion of 2,4-dichlorophenol in the studied process. Therefore, the presence of intermetallic Bi_2Pd compound on the surface of Pd–Bi/support systems may be responsible for low activity of these catalysts in the reaction of hydrodechlorination of 2,4-dichlorophenol.

The high activity, selectivity and stability of Pd–Bi/support systems containing up to 5 wt.% of bismuth constitute a premiss to their possible application in the chemical industry.

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