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Pd–Fe/SiO_2 and Pd–Fe/Al_2O_3 catalysts for selective hydrodechlorination of 2,4-dichlorophenol into phenol

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ABSTRACT

The effect of iron introduction on the activity and selectivity of chemically precipitated supported palladium catalysts in the hydrodechlorination of 2,4-dichlorophenol in liquid phase at room temperature was studied. Bimetallic Pd–Fe catalysts supported on silica and alumina were characterized by using XPS, XRD, ToF-SIMS and TPR-H_2 techniques. The dispersion of active phase in catalytic systems was examined by XRD and chemisorption of CO gas. Bimetallic Pd–Fe/SiO_2 and Pd–Fe/Al_2O_3 catalysts containing 5 wt.% of Pd and 1–20 wt.% of Fe demonstrated high activity and high selectivity to phenol. However, Pd–Fe/Al_2O_3 catalysts with higher dispersion of the active phase were less active in the studied reaction than Pd–Fe/SiO_2 systems, but selectivity to phenol was comparable for both types of bimetallic catalysts. The stability of Pd–Fe/SiO_2 systems was higher than the bimetallic Pd–Fe/Al_2O_3 catalysts but selectivity to phenol decreases for that system systematically in each cycle of reaction, reaching only about 40% in the tenth cycle. It was also found that the addition of Fe to palladium catalysts limited the formation of cyclohexanone in the reaction medium.

1. Introduction

Chlorinated organic compounds (COCs) that were widely utilized in 20th century [1] currently constitute the main contamination components in nature. Because of the fact that they are resistant to biological factors, systematic increase of their concentration in the environment has been observed [2]. The presence of significant amounts of COCs in air, soil, and also in the tissues of living organisms may pose a threat to people's health and it may negatively influence the functioning of whole ecosystems.

Among the COCs, chlorophenols (CP's) are still regarded as useful industrial materials with a broad range of applications. Chlorophenols are used as intermediates for organic synthesis, pesticides, herbicides, biocides, dyes and wood preservatives [3,4]. Yet, these useful compounds are listed as priority pollutants by the United States Environmental Protection Agency [5,6], due to their high toxicity and resistance to decomposition. Due to the harmful activity of chlorophenols [7], effective methods for their decomposition need to be worked out. 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 [8,9]. The methods based on electrochemistry [10,11], photochemistry [12–14] and also on biotechnology [15–18] result in low conversion. On the other hand, the thermal methods, which include pyrolysis and hydrogenolysis, require high energy. Another approach used to eliminate those compounds from the environment is through catalytic hydrodechlorination (HDC) with hydrogen, which is attractive since it can be carried out at low temperature [19–21]. Among these techniques catalytic hydrodechlorination provides a promising non-destructive alternative technology whereby the chlorinated waste is converted into products with commercial value [19–33]. Phenol, obtained in the HDC process of 2,4-DCP over supported catalysts based on noble metals, is safer compound which may be used as a substrate in various industrial processes. Phenol is commercially used to make synthetic resins, dyes, pharmaceuticals, pesticides, synthetic tanning agents, perfumes, lubricating oils and solvents [34].

The catalytic hydrodechlorination of chlorophenols was conducted on supported mono- and bimetallic catalysts based on Pd [7,19–21,30,31,35–37], Pt [38–40] and Rh [7,32,39,41]. Among the

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studied supported bimetallic systems, those promoted with Ru [22], Rh [43–45], Bi [46,47] showed the best catalytic characteristics. In those publications, the influence of dispersion of active phase [48–50], the kind of support [36,37,42], addition of the second metal [42–45,51] and the role of natural water components like humic acid [52] and different kinds of ions [53] on the catalytic properties of supported systems in HDC of chlorophenols have been discussed.

Catalytic properties of nanoparticulate, bimetallic Pd/Fe have been also described in literature [37,54,55]. The authors of those publications have established the optimal composition of bimetallic systems and they have also studied the influences of reaction temperature, the pH of the reaction environment, and other natural factors, such as the presence of humic acids or saltiness of the water, on the catalytic properties in the process of HDC.

However, supported Pd–Fe catalysts have not been researched deeply in the hydrodechlorination reaction of polichlorophenols in the liquid phase, especially mutual interactions between palladium and iron in catalytic systems were not studied. Munoz et al. [56] used bimetallic Pd–Fe/γ-Al_2O_3 catalysts in degradation of chlorophenols by sequential combination of hydrodechlorination (HDC) and catalytic wet peroxide oxidation (CWPO). The Pd–Fe/γ-Al_2O_3 catalyst showed a high activity in both processes, however a decrease in activity was observed in each reaction HDC and CWPO cycle, which can be attributed to iron leaching and active site blockage by carbonaceous deposits. Complete dechlorination of chlorophenol and negligible ecotoxicity of final effluents were maintained upon successive applications in a four-cycles test with 2,4-DCP.

On the other hand, Golubina et al. [57] studied multiphase hydrodechlorination of 1,4-dichlorobenzene, hexachlorobenzene and 2,4,8-trichlorodibenzofurane over Pd/C and Pd–Fe/C catalysts. Metal-metal interaction and structure of bimetallic particles were studied by TPR and XPS techniques. Based on the obtained results, two aspects of the influence of iron addition were considered: (1) formation of Pd-enriched PdFe alloy, which resulted in an increase of catalytic activity of bimetallic catalysts in comparison with Pd/C; (2) formation of $FeCl_3$ under HDC reaction condition, which prevented complete chlorination of palladium, possibly leading to its deactivation.

In the present work the activity and the selectivity of chemically precipitated supported palladium catalysts modified with Fe in the hydrodechlorination of 2,4-dichlorophenol at room temperature were investigated. These systems were characterized by XRD, XPS, ToF-SIMS, AAS, TPR-H_2 and CO gas chemisorption techniques.

2. Materials and methods

2.1. Catalyst preparation

Palladium catalysts characterized with good resistance to chlorides deactivation are identified as the most efficient systems in HDC reaction [25,58]. What is more, metal dispersion has been identified as being critical [48]. Supported metal particle size can be modified by the synthesis method, the support used, metal loading, activation procedure and addition of second metal. In our studies we concentrated on the influence of iron addition on the activity and selectivity of 5%Pd/SiO_2 and 5%Pd/Al_2O_3. The incorporation of more than 5-wt.% of Pd into catalytic systems does not cause a significant increase in the activity of palladium catalysts and is not justified from an economical point of view [47].

Catalysts containing 5 wt.% of palladium were prepared by aqueous impregnation of alumina (Fluka, 143 m^2/g) and silica (Sigma–Aldrich, 291 m^2/g) from the solution of $PdCl_2$ (POCH, anhydrous, pure p.a.) which was acidified to pH about 5 with hydrochloric acid (CHEMPUR, 35–38%, pure p.a.). The water was evaporated at an elevated temperature ($T = 60\,^{\circ}C$) under vacuum. Monometallic catalysts were dried in air at 110 °C for 6 h, calcined at 500 °C for 4 h in an oxygen atmosphere (O_2, Air Products, 99,5%, at rate 20 mL/min), cooling in an argon to room temperature (Ar, Linde 5.0, at rate 20 mL/min), and then reduced in a hydrogen atmosphere (H_2, Air Products, Premium Plus, at rate 20 mL/min) for 2 h at 300 °C before catalytic measurements. The linear temperature increase rate was 20 °C/min between the thermal processing steps.

Bimetallic Pd–Fe/support catalysts containing 5 wt.% Pd and 1, 8, 20 wt.% Fe were obtained by coimpregnation of supports with water solution of $Fe(NO_3)_3{\cdot}9H_2O$ (POCH, pure p.a.) and $PdCl_2$ (POCH, anhydrous, pure p.a.) acidified to pH about 5 with hydrochloric acid (CHEMPUR, 35–38%, pure p.a.), according to the procedure described above.

2.2. Catalytic measurements

In our studies the reaction conditions were optimized for mono- and bimetallic catalysts. The mass-transfer limitations have been evaluated experimentally using the diagnostic criteria associated with varying hydrogen flow rate (0.05–0.5 L/min), stirring speed (50–750 rpm), catalyst concentration (0.5–2 g/L) and particle size (0.5–0.075 mm). All the HDC reactions of 2,4-DCP solution (0.4 L, 100 mg 2,4-DCP/L) were performed at the room temperature (20 °C) and at neutral pH ($pH = 7 \pm 0.1$). Experimental results have revealed the influence of mass transfer at the liquid/solid interface and intraparticle diffusion in limiting HDC rate. However, these effects were not observed when hydrogen flow was higher than 0.15 L/min, reaction mixture was stirred at least at 400 rpm, the catalysts concentration was higher than 0.75 g/L and particle sizes of catalysts were lower than 0.15 mm. For these reasons, all HDC reactions over mono- and bimetallic catalysts were performed under conditions described below in order to eliminate diffusion restriction.

The HDC of 2,4-dichlorophenol (2,4-DCP) solution (2,4-DCP concentration was 100 mg/L) was performed in a 400-mL thermostated glass reactor at the room temperature (20 °C). The hydrochloric acid formed during the HDC of 2,4-DCP was neutralized by the addition of an aqueous solution of sodium hydroxide (0.1 mol/L) to maintain constant $pH = 7 \pm 0.1$ in the reaction medium. The reaction was conducted with equal amount of catalyst ($m_{cat} = 0.4$ g) in each experiment. The mixture was stirred at 500 rpm and hydrogen was bubbled through at 0.2 L/min. Samples of the reaction medium were taken systematically, filtered and analyzed using high performance liquid chromatography (HPLC), coupled to a variable wavelength UV (210 nm) detector. The reaction products were separated on a Zorbax SB-C18 column (mobile phase MeOH/H_2O). In addition, further products of phenol hydrogenation were detected by gas chromatography (GC) (with FID detection; packed column 8% Carbowax 1540 on Chromosorb W).

For a group of selected catalysts (5%Pd/Al_2O_3, 5%Pd–8%Fe/Al_2O_3 and 5%Pd–8%Fe/SiO_2), the stability in the reaction of hydrodechlorination of 2,4-dichlorophenol was studied. Ten cycles of the 2,4-DCP (100 mg/L, 400 mL total volume) HDC reaction were performed on the same portion of catalyst ($m_{cat} = 0.4$ g). Each cycle of the reaction was conducted for 1.5 h at room temperature using H_2, flowing at 0.2 L/min. After this time, the product mixture was removed from above the catalyst, filtered and analyzed by HPLC, GC-FID and atomic absorption spectrometry (AAS). Over the course of the entire process, including particular catalytic cycles, the catalysts were not removed from the reactor. After the 10-th cycle of the reaction, the catalyst was quantitatively transferred into a weighing vessel, washed with deionized water, dried at 110 °C to constant weight, and weighed. The weight loss of the catalyst was less than 6 wt.%. These catalysts were analyzed by TOC technique to check if organic

Table 1
Activity and selectivity for hydrodechlorination of 2,4-dichlorophenol over Pd/support and Pd–Fe/support (support = Al_2O_3, SiO_2) catalysts after 1 h of reaction.

Catalyst	Chemisorption of CO [μmol/g_{kat}]	Dispersion [%]	TOF [h^{-1}]	$X_{2,4\text{-DCP}}$ [%]	S_{Ph} [%]	$S_{2\text{-CP}}$ [%]	$S_{4\text{-CP}}$ [%]	S_{CHO} [%]
5%Pd/Al_2O_3	109	23	3	94 (95)[a]	52 (54)[a]	19 (22)[a]	8 (1)[a]	21 (24)[a]
5%Pd–1%Fe/Al_2O_3	14	3	19	85	94	3	3	–
5%Pd–8%Fe/Al_2O_3	27	6	10	86 (92)[a]	97 (98)[a]	1 (1)[a]	2 (1)[a]	– –
5%Pd–20%Fe/Al_2O_3	13	3	21	92	96	1	3	–
5%Pd/SiO_2	34	7	11	97 (97)[a]	66 (59)[a]	6 (10)[a]	– –	28 (31)[a]
5%Pd–1%Fe/SiO_2	17	4	17	94	94	3	3	–
5%Pd–8%Fe/SiO_2	13	3	22	91 (92)[a]	98 (100)[a]	1 (0)[a]	1 (0)[a]	– (0)[a]
5%Pd–20%Fe/SiO_2	26	6	13	95	65	13	10	12

Activation of catalysts: drying in air at 110 °C, 6 h; oxidation in O_2 at 500 °C, 2 h; reduction in H_2 at 300 °C, 2 h.
Reaction conditions: T = 20 °C, m_{cat} = 0.4 g, $V_{2,4\text{-DCP}}$ = 0.4 L, $C_{0\ 2,4\text{-DCP}}$ = 100 mg/L, pH = 7, $V_{H_2} = 2.0$ L/min.

[a] Activity and selectivity to main reaction products for hydrodechlorination of 2,4-dichlorophenol over monometallic catalysts: 5%Pd/Al_2O_3 and 5%Pd/SiO_2 and bimetallic catalysts: 5%Pd–8%Fe/Al_2O_3 and 5%Pd–8%Fe/SiO_2 after 1.5 h of reaction.

carbon is present, which could indicate the decomposition of HDC products. The results of the conducted research do not show any amounts of organic carbon.

Alumina and silica used as a supports in studied mono- and bimetallic catalysts were inactive in HDC reaction performed in the same conditions.

2.3. X-ray photoelectron spectroscopy (XPS)

The bonding nature at the surface of Pd–Fe/SiO_2 catalysts was elucidated by X-ray photoelectron spectroscopy (XPS). Samples were prepared by pressing the catalytic powders onto 10 mm × 10 mm pieces of clean, UHV aluminum foil. These were placed into a Versaprobe 5000 (PHI, USA) spectrometer. Survey and high-resolution spectra were taken with a focused, monochromatic Al K-α source (E = 1486.6 eV; 100 μm spot size). A cold cathode electron flood gun and low-energy Ar^+ ions provided charge neutralization. The operating pressure was 2×10^{-6} Pa for Ar gas and the system base pressure was 5×10^{-8} Pa. To avoid ion-induced surface damage, surface sputtering was not used.

2.4. Powder X-ray diffraction (XRD)

Room temperature powder X-ray diffraction patterns were collected using a PANalytical X'Pert Pro MPD diffractometer. The X-ray source was a copper long fine focus X-ray diffraction tube operating at 40 kV and 30 mA. Data were collected in the range of $20 < 2\theta < 90°$, with an angular step of 0.0167° and 20 s of exposure time per step. A PANalytical X'Celerator detector, based on Real Time Multiple Strip technology was used to collect and record the diffraction spectra. Crystalline phases were identified by referencing the ICDD PDF-2 (ver. 2004) database.

2.5. Time-of-flight secondary mass spectrometry (ToF-SIMS)

The ToF-SIMS IV mass spectrometer was equipped with a Bi liquid metal ion gun and a high mass resolution time-of-flight mass analyzer. During the 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. 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 surface; ion images were obtained for a 500 μm × 500 μm surface area.

2.6. Chemisorption of CO measurements

Carbon monoxide chemisorption analysis was carried out in a Micromeritics ASAP 2020 apparatus. Samples were previously reduced in the same conditions in which the catalysts were prepared. After the reduction the samples were subsequently cooled to room temperature under He gas stream (30 sccm). The chemisorbed carbon monoxide was analyzed at room temperature using the adsorption-backsorption isotherm method.

2.7. Temperature-programmed reduction (TPR-H_2)

TPR measurements were carried out in a flow apparatus, which is described in Ref. [59]. The samples of fresh catalysts (about 0.3 g) were flushed with argon at room temperature for 0.5 h prior to the TPR measurements. After that, temperature programmed reduction measurements were carried out. TPR runs were performed in the temperature range 20–300 °C with a linear temperature increase rate of 20 °C/min using a hydrogen-argon (5 vol.% of H_2) mixture.

2.8. Total organic carbon (TOC)

The total carbon deposited on the catalysts was determined using a Shimadzu-TOC 5000 instrument with a solid sample module, where the carbon deposit is burnt at 900 °C in oxygen.

2.9. AAS analysis of the reaction mixture

The amounts of iron and palladium in the reaction mixture were determined by atomic absorption spectrometry (AAS) on GBC 923 plus spectrometer with the usage of flame atomization (air 10 sccm/min and acetylene 2 sccm/min). The absorption of reaction and standards solution was set for palladium and iron at wavelengths of 247.6 nm and 248.3 nm, respectively. The standard solutions (0.5; 1.0; 1.5; 2.0; 3.0; 4.0 mg/L) were prepared by the dilutions of Pd and Fe standard samples (CPI International) at 1000 mg/L concentration. The samples of reaction mixture (V = 5 mL) were mineralized with 5 mL HNO_3 (Baker Instra Analyzed) and 1 mL HCl (Baker Instra Analyzed) in the microwave reaction system Multiwave 3000 (Anton Paar) at 200 °C.

3. Results and discussion

The activity and selectivity of monometallic palladium and bimetallic Pd–Fe, supported on Al_2O_3, or SiO_2, catalytic systems in the hydrodechlorination of 2,4-dichlorophenol at room temperature in liquid phase were studied (Table 1). From the presented results, it can be concluded that supported palladium mono- and bimetallic catalysts show similar activity in the reaction of hydrodechlorination of 2,4-dichlorophenol. However, the selectivity to individual reaction products was completely different for each system. Monometallic supported catalysts (5%Pd/Al_2O_3 and 5%Pd/SiO_2) showed significantly lower selectivity to phenol. With

Table 2
Metal particle size of Pd/support and Pd–Fe/support (support = SiO_2, Al_2O_3) catalysts calculated from CO chemisorption measurements and on the basis of XRD studies according to the Scherrer equation.

Catalyst	Chemisorption of CO [μmol/g_{kat}]	Average size of the Pd crystallites [nm]	
		CO chemisorption	XRD analysis
5%Pd/Al_2O_3	109	5	7
5%Pd–1%Fe/Al_2O_3	14	38	25
5%Pd–8%Fe/Al_2O_3	27	20	18
5%Pd–20%Fe/Al_2O_3	13	39	30
5%Pd/SiO_2	34	15	8
5%Pd–1%Fe/SiO_2	17	31	28
5%Pd–8%Fe/SiO_2	13	41	31
5%Pd–20%Fe/SiO_2	26	19	10

these systems, further hydrogenation of phenol to cyclohexanone was found. Moreover, in the case of monometallic systems, significant amounts of 2-chlorophenol and 4-chlorophenol in the reaction mixture were observed. For bimetallic palladium–iron catalysts with higher amount of iron (≥20 wt.% Fe), supported on SiO_2, the selectivity to phenol was similar to the phenol selectivity for the 5%Pd/SiO_2 system. This behavior may be connected to the similar dispersion of the active phase in the 5%Pd–20%Fe/SiO_2 and 5%Pd/SiO_2 catalysts (Table 1).

On the basis of X-ray diffraction measurements, as well as from the chemisorption of CO, the average size of Pd crystallites for mono- and bimetallic systems was estimated (Table 2). It was observed that the addition of iron into supported palladium catalysts had a significant impact on the size of palladium crystallites (Fig. 1).

The increase in the average size of Pd crystallites in bimetallic catalysts, seems to cause an improvement in the selectivity to phenol (Tables 1 and 2). Yet, the 5%Pd–20%Fe/SiO_2 catalyst shows a lower selectivity to phenol when compared to bimetallic Pd–Fe/SiO_2 catalysts with a smaller amount of Fe. For that catalyst, cyclohexanone was detected in the reaction mixture, alongside phenol, 2-chlorophenol and 4-chlorophenol. The behavior of the bimetallic 5%Pd–20%Fe/SiO_2 catalyst was probably caused by differences in the dispersion of the active phase, which is similar to monometallic Pd/SiO_2 catalysts. Another reason for the behavior of the 5%Pd–20%Fe/SiO_2 catalysts, in comparison to other bimetallic catalysts with smaller amounts of iron, may be the differences in phase composition. XRD studies of bimetallic catalysts supported on alumina and silica show that in the case of using alumina as a support Fe_2O_3 was the main phase besides Fe_3O_4 (Table 3), while in the case of using silica only Fe_3O_4 phase formation was observed. Golubina et al. [57] on the basis of XPS investigations state the presence of Fe_2O_3 in the surface layer of bimetallic Pd–Fe/C catalysts even after reduction in H_2 at 500 °C. Thus, Pd–Fe/C catalysts gain the features of Pd/Fe_xO_y/C catalysts. In our studies, we found the presence of various forms of Fe_xO_y on the surface of palladium–iron catalysts supported on SiO_2 and Al_2O_3, especially in the 5%Pd–20%Fe/Al_2O_3 catalysts. That is why strong metal-oxide interaction becomes possible in such systems, and also spillover of hydrogen and heat adsorption changes for both substrate and hydrogen. This may also affect on the dispersion of the active phase, and consequently influence the selectivity.

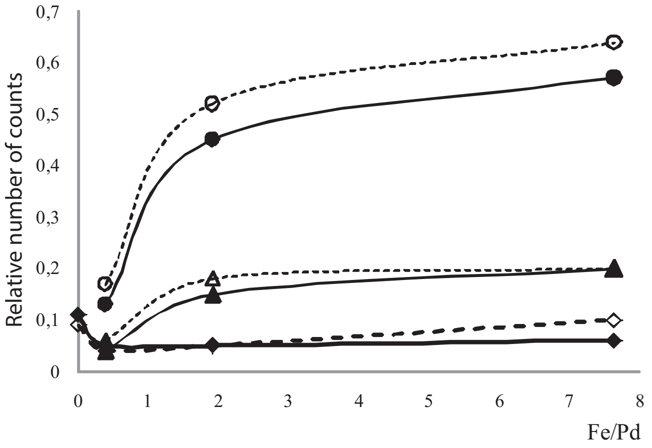


Fig. 1. The relative number of counts of secondary ions (◇ – $^{106}Pd^+$, ○ – Fe^+, △ – $FeOH^+$) as a function of the atomic ratio of Fe/Pd in Pd–Fe/Al_2O_3 (—) and Pd–Fe/SiO_2 (- - - -) catalysts.

Before the measurements of activity and selectivity, all the obtained catalysts were reduced in H_2 at temperature 300 °C. Therefore, establishing the phase composition of these systems was an important issue. Table 3 shows the phase composition of monometallic palladium and bimetallic Pd–Fe catalysts, supported on Al_2O_3 and SiO_2. For bimetallic systems with low percentage amounts of Fe (1–8 wt.% Fe), maxima ascribed to metallic phases of Pd and supports (Al_2O_3 and SiO_2) were present in X-ray diffractograms. For catalysts containing above 8-wt.% of iron, the phase of metallic Fe was detected by XRD, too. In the case of 5%Pd–20%Fe/Al_2O_3, 5%Pd–20%Fe/SiO_2 catalysts, iron oxides (Fe_2O_3 and Fe_3O_4) were additionally observed. The presence of Fe_3O_4 and Fe_2O_3 phases indicates the incomplete reduction of iron oxide during activation of the catalysts in an atmosphere of H_2 at 300 °C.

Additionally, the surface composition of Pd–Fe/Al_2O_3 and Pd–Fe/SiO_2 catalysts was studied by ToF-SIMS. On the basis of the secondary ion mass spectra of Pd–Fe/Al_2O_3, the ion intensities of Pd^+, Fe^+, $FeOH^+$ were estimated (Table 3). Fig. 1 shows the dependence between the intensities of ions: Pd^+, Fe^+, $FeOH^+$, and the composition of the studied Pd–Fe/Al_2O_3 catalysts. The intensity of the Pd^+ ions emission from the surface of the bimetallic catalysts did not depend on the amount of Fe introduced into the system. A proportional increase in the emission of secondary Fe^+ and $FeOH^+$ ions was observed with increased iron in the Pd–Fe/support systems. However, the simultaneous emission of iron and oxygen ions, confirms the incomplete reduction of Fe in the studied systems. In addition, ToF-SIMS did not detect the presence of any intermetallic compounds on the surface of palladium–iron catalysts.

To obtain a better understanding of the surface chemical states on the bimetallic catalysts, XPS studies were performed. The results obtained for 5%Pd–1%Fe/SiO_2 and 5%Pd–8%Fe/SiO_2 catalysts confirm the existence of various chemical states of palladium and iron on the surface of the analyzed systems (Figs. 2 and 3 and Table 4). The XPS results were fitted with proprietary software (Multipak) and the results were compared to the NIST database [60] and previously published data [61–67].

According to the literature, the electron binding energy of the Pd $3d_{5/2}$ peak, for metallic palladium, is in the range 334.6–335.6 eV [60–63]; while for metallic iron supported on SiO_2, the characteristic electron binding energy corresponds to the about 711.1 eV [60]. The shift of the peak maximum corresponding to Pd^0 toward higher binding energy, in the 335.3–336.5 eV range [63], indicates the presence of Pd–Fe intermetallic interactions. The presence of intermetallic PdFe alloy in the 5%Pd–8%Fe/SiO_2 catalyst is also supported by the shift in the binding energy of Fe $3d_{3/2}$ toward 711 eV [60,68]. On the other hand, it is well known that the binding energy of Fe $2p_{3/2}$ is about 709 eV for Fe^{2+} and 711 eV for Fe^{3+}. The occurrence of the Fe $2p_{3/2}$ peak at 710.7 may indicate that Fe_3O_4 is formed, and that both Fe^{2+} and Fe^{3+} oxidation states exist. Furthermore, on the surface of the tested system, the presence of palladium oxides (PdO and PdO_xPd), interaction between Pd and silica (Pd/SiO_x/Si), and palladium chloride ($PdCl_2$) was also revealed [64–67].

Table 3
Phase composition (XRD) and surface structure (ToF-SIMS) of Pd–Fe/support catalysts dried at 110 °C in air (6 h), oxidized at 500 °C in O_2(4 h) and reduced at 300 °C in H_2(2 h).

Catalyst	XRD analysis[a]						ToF-SIMS analysis[b]			
	Pd	Fe	Fe_3O_4	Fe_2O_3	Al_2O_3	SiO_2	Fe^+	$FeOH^+$	$^{106}Pd^+$	$^{108}Pd^+$
5%Pd/Al_2O_3	+	–	–	–	+		–	–	0.11	0.11
5%Pd–1%Fe/Al_2O_3	+	–	–	–	+		0.13	0.04	0.05	0.05
5%Pd–8%Fe/Al_2O_3	+	+	–	–	+		0.45	0.15	0.05	0.05
5%Pd–20%Fe/Al_2O_3	+	+	+	+	+		0.57	0.20	0.06	0.06
5%Pd/SiO_2	+	–	–	–		+	–	–	0.09	0.09
5%Pd–1%Fe/SiO_2	+	–	–	–		+	0.17	0.06	0.04	0.04
5%Pd–8%Fe/SiO_2	+	+	–	–		+	0.52	0.18	0.05	0.05
5%Pd–20%Fe/SiO_2	+	+	+	–		+	0.64	0.20	0.08	0.08

[a] Patterns obtained with CuK_α radiation, step scanned 20 s per step of 0.0167° of 2θ. Crystalline phases were identified by references to ICDD PDF-2 (ver.2004) database.
[b] Ion counts relative to the Al^+(Si^+) number of counts.

The catalytic samples, which underwent preliminary calcinations in O_2 at 500 °C, were treated with hydrogen in a TPR-$H_{2(1)}$ process (Fig. 4A). The calcined sample of the system containing 5%Pd/SiO_2 showed two low-temperature peaks located in the temperature range of 50–150 °C; first negative peak connected with hydrogen desorption from the β-hydride of palladium formed during the reduction of weakly bonded palladium oxide, and the second positive peak connected with the reduction of palladium oxide is more strongly bounded with the carrier. An addition of a small amount of iron (5%Pd–1%Fe/SiO_2) modified the intensity of the hydrogen evolution peak and the negative peak disappears, which suggests that β-PdH formation was inhibited. Lingaiah et al. [69] proved that the introduction of iron inhibits the formation of β-PdH phase that occurs in the monometallic palladium catalysts. This observation is consistent with previous studies made by Lietz et al. [70] and from our research on the catalytic properties of supported palladium systems promoted with Ag [71], Bi [46,47], In [72], Te [73] and Tl [74].

For the monometallic 8%Fe/SiO_2 system, a wide peak of hydrogen adsorption in the temperature range of 300–500 °C was observed. This is quite a natural situation considering that iron oxides do not easily reduce. Also, iron could create different forms of oxides in the first stages of contact between the sample and oxygen.

For the bimetallic 5%Pd–x%Fe/SiO_2 (x = 1; 8; 20%-wt.% Fe) catalysts the reduction process started practically at room temperature. The first maximum of the reduction rate at about 100 °C could probably be attributed to the reduction of palladium oxide. However, the slight shift of the H_2 adsorption maximum to a higher

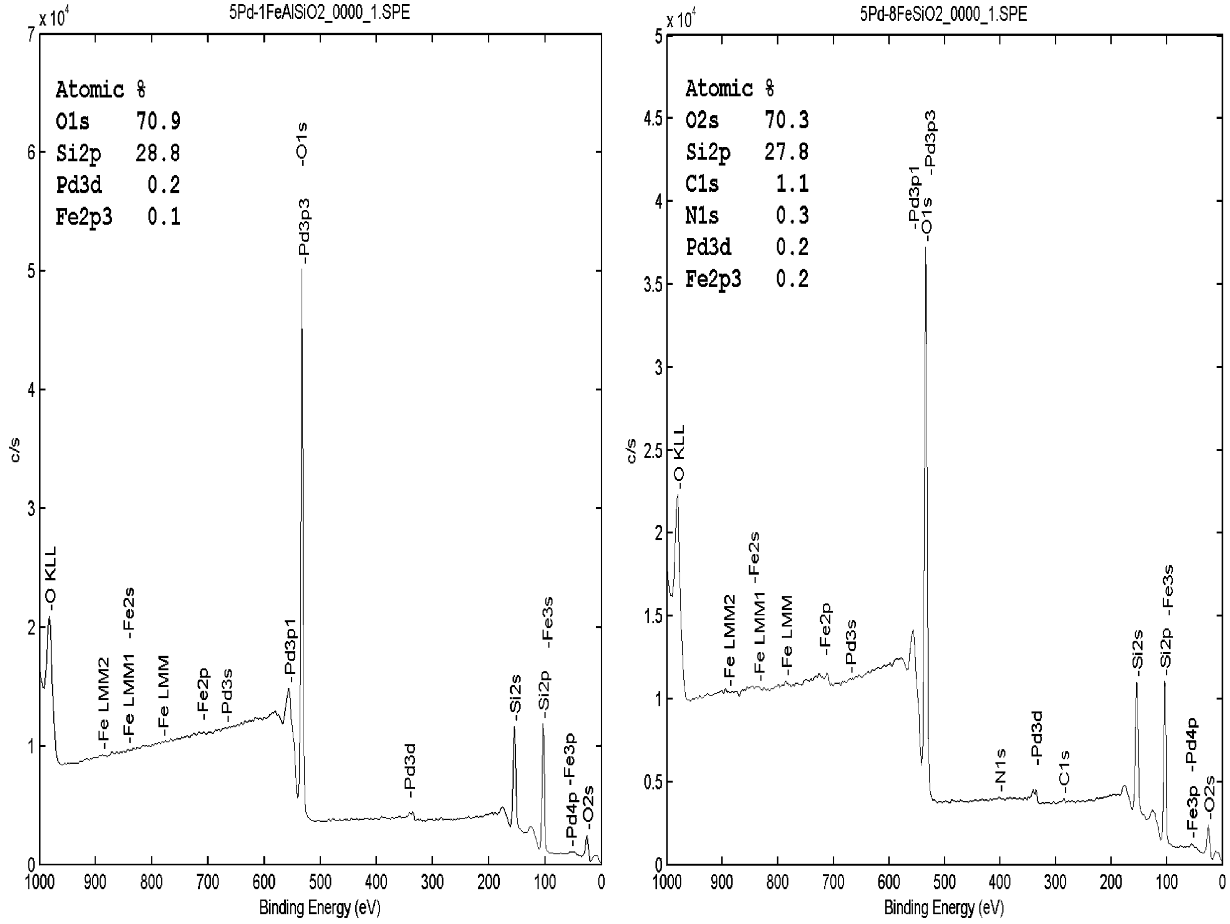


Fig. 2. Experimental spectra of 5%Pd–1%Fe/SiO_2 and 5%Pd–8%Fe/SiO_2 catalysts obtained for catalyst samples after oxidation at 500 °C in air and reduction at 300 °C in H_2 atmosphere.

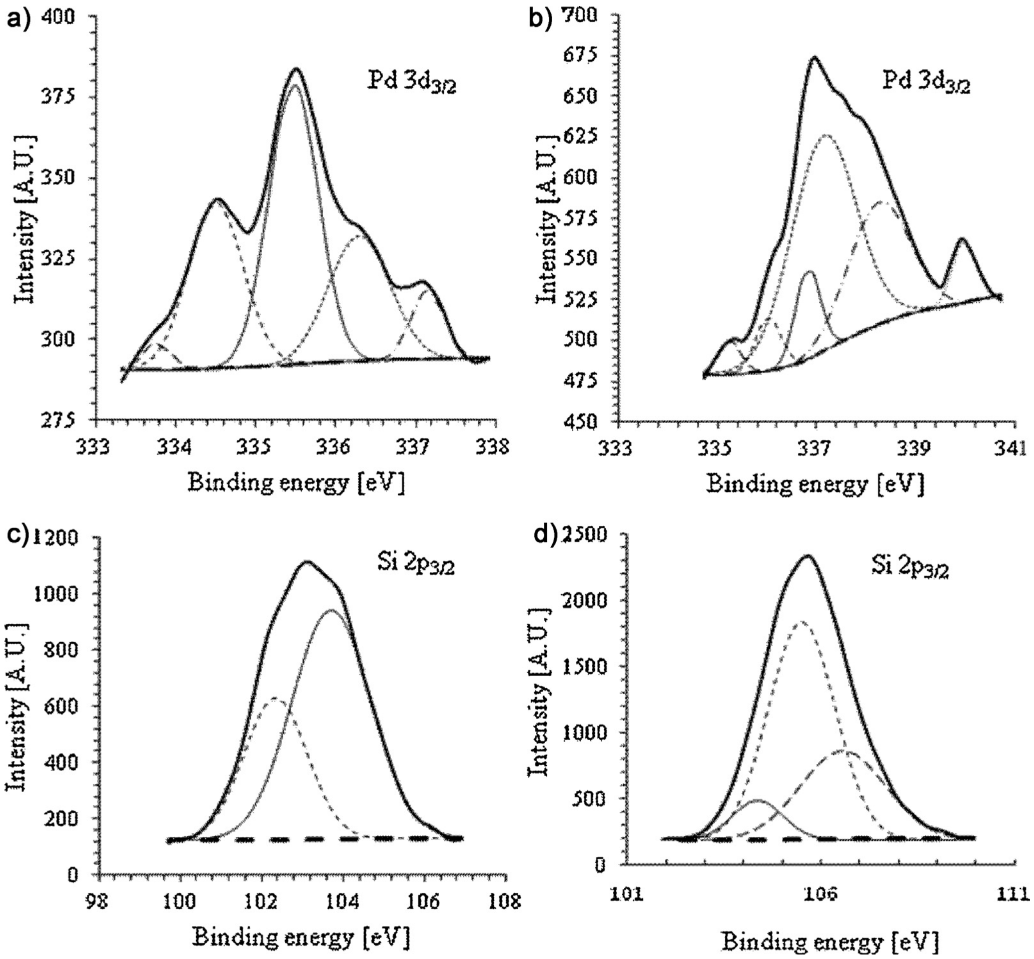


Fig. 3. Experimental Pd $3d_{3/2}$ and Si $2p_{3/2}$ spectra of (a) 5%Pd–1%Fe/SiO_2 and (b) 5%Pd–8%Fe/SiO_2 catalysts after oxidation at 500 °C in air and reduction at 300 °C in H_2 atmosphere.

temperature, in comparison to the 5%Pd/SiO_2 profile, could be attributed to the reduction of Pd_xFe_yO, which formed during the first contact of the bimetallic catalysts with oxygen, when the surface of catalyst is not totally stabilized. The presence of palladium on the surface of bimetallic Pd–Fe/SiO_2 catalysts probably facilitates the reduction of oxidized forms of iron. The next maxima in the reduction rate (present in the termograms) of bimetallic systems indicated the reduction of different iron oxides. The XRD studies revealed the presence of two different iron oxides (Fe_2O_3 and Fe_3O_4) in the catalytic systems with higher amount of iron (>8 wt.% Fe) under reduction in hydrogen atmosphere at 300 °C; this is in good agreement with TPR-H_2 measurements. Golubina et al. [57], demonstrated on the basis of XPS data the presence of Fe_2O_3 in the surface layer of supported bimetallic Pd–Fe catalysts, even after reduction by H_2 at 500 °C. This result is in accordance with other data [75] demonstrating that Fe^{3+} does not reduce in oxide-supported catalysts in the presence of noble metal even during H_2 treatment at about 500 °C. Because of the incomplete reduction of Fe_xO_y even at 500 °C, we decided to reduce our catalysts in lower temperature (at 300 °C) to avoid sintering of palladium on the surface.

Table 4
XPS data of Pd–Fe/SiO_2 catalysts after oxidation at 500 °C in air and reduction at 300 °C in H_2 atmosphere. Analysis of the spectra was performed based on the NIST [60] database and literature data [61–67].

Catalyst	5%Pd–1%Fe/SiO_2	5%Pd–8%Fe/SiO_2	Chemical state on the surface
Metal	Binding energy [eV]		
Pd $3d_{5/2}$	334.5	–	Pd
	335.5	335.3	Pd, PdFe
	336.3	336.8	PdO
	337.1	337.1	PdO
	–	338.2	$PdCl_2$
	–	340.0	PdO_xPd
Fe $2p_{3/2}$	–	710.7	Fe^{2+}/Fe^{3+} Fe/SiO_2, PdFe
Si $2p_{3/2}$	102.3	–	Pd/SiO_x/Si
	103.7	–	SiO_2, Fe/SiO_2
	–	104.0	SiO_2

The catalyst samples which underwent preliminary calcinations in O_2 at 500 °C and were treated with hydrogen in TPR-$H_{2(1)}$ process, were reoxidized at 500 °C for 2 h. Finally, TPR-$H_{2(2)}$ measurements were taken and their results are presented in Fig. 4B. The similar behavior of 5%Pd/SiO_2 and 8%Fe/SiO_2 catalysts in the TPR-$H_{2(1)}$ and TPR-$H_{2(2)}$ processes reveals the stationary state of the catalysts' surface composition under the activation step. After the catalyst reached the stationary state, its surface and texture did not change. This is probably why the obtained profiles in TPR-$H_{2(2)}$ are repeatable over successive cycles.

In the case of bimetallic Pd–Fe/SiO_2 catalysts, an additional maximum in the reduction curve at around 130 °C was built into the thermograms. Due to the lack of high-temperature maxima attributed to iron oxides reduction, it can be concluded that the surface of reoxidized bimetallic catalysts consists of Pd_xFe_yO phase,

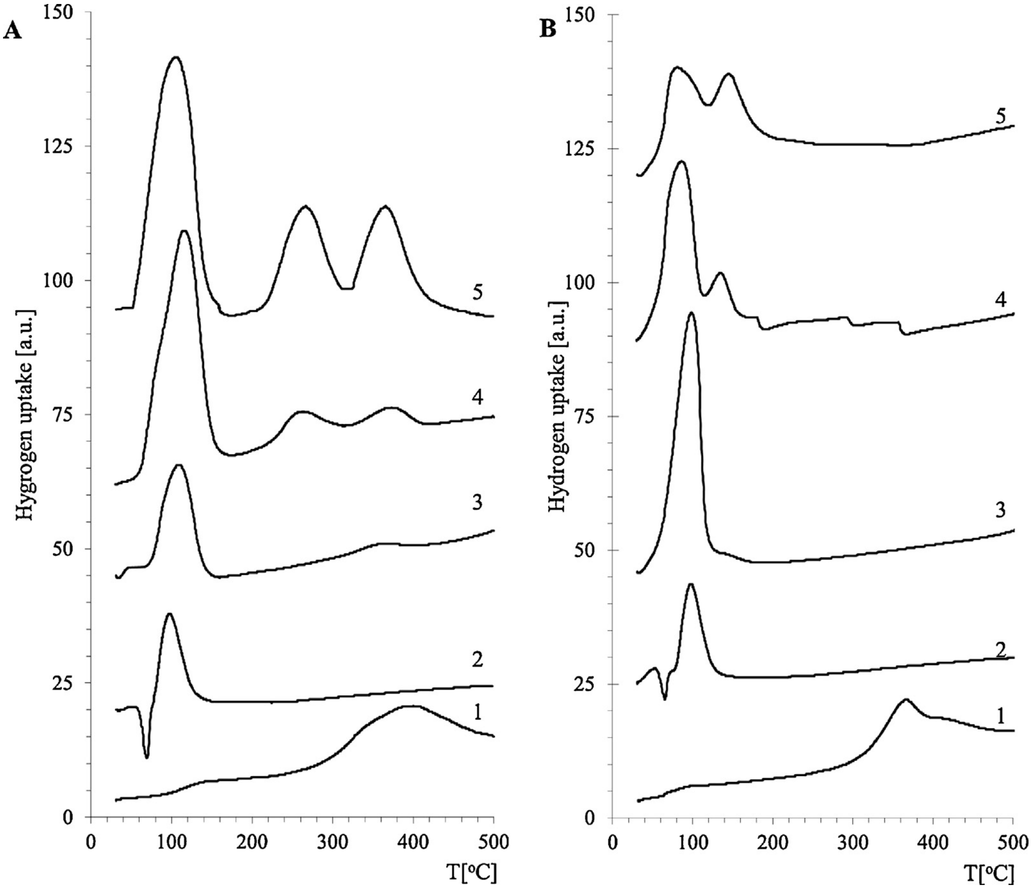


Fig. 4. Temperature programmed reduction (A) TPR-$H_{2(1)}$; (B) TPR-$H_{2(2)}$ of (1) 8%Fe/SiO_2; (2) 5%Pd/SiO_2; (3) 5%Pd–1%Fe/SiO_2; (4) 5%Pd–8%Fe/SiO_2; (5) 5%Pd–20%Fe/SiO_2 catalysts after drying in air at 110 °C, 6 h and oxidizing in O_2 at 500 °C, 4 h.

which is readily reduced with hydrogen at low temperature. However, it is also possible that the reduction of iron oxides catalyzed by palladium may also contribute to the formation of an additional low-temperature peak during temperature-programmed reduction of the reoxidized bimetallic Pd–Fe catalysts.

XRD and ToF-SIMS studies did not show the occurrence of strong interactions between Pd and Fe on the surface of Pd–Fe/SiO_2 and Pd–Fe/Al_2O_3 systems. However, XPS spectra and TPR-H_2 termograms may suggest some interactions between palladium and iron on the surface of silica, which most strongly occurred in systems with higher amounts of iron (>8 wt.% Fe).

Supported Pd and Pd–Fe catalysts are characterized by satisfactory stability in the studied reaction, which is an important property of the systems used in industrial practice. Table 5 shows the changes in the activity of 5%Pd/Al2O3, 5%Pd–8%Fe/Al_2O_3 and 5%Pd–8%Fe/SiO_2 catalysts after subsequent ten 1.5-h measuring cycles. In the course of overall process, including particular catalytic cycles, the catalysts were not removed from the reaction mixture.

In the case of the monometallic 5%Pd/Al_2O_3 catalyst, a gradual but systematic decrease in the activity, as well as in the selectivity to phenol and cyclohexanone, was observed in succeeding measuring cycles. On the other hand, after the tenth reaction cycle, the selectivity to 2-chlorophenol, when compared to the initial value, doubled. Thus, we can conclude that the hydrodechlorination of 2,4-dichlorophenol over the 5%Pd/Al_2O_3 catalyst in subsequent measuring cycles was retained on the first step of dechlorination, and 2-chlorophenol became the main product of the reaction.

For the bimetallic catalysts, the 5%Pd–8%Fe/Al_2O_3 showed a lower stability in the process of HDC of 2,4-DCP in comparison to the palladium–iron system deposited on SiO_2. The conversion of 2,4-DCP over the 5%Pd–8%Fe/Al_2O_3 catalyst after 15 h of work was approximately 70%. Better results were obtained for the 5%Pd–8%Fe/SiO_2 catalyst, which showed a high activity even after tenth reaction cycle. 5%Pd–8%Fe/Al_2O_3 and 5%Pd–8%Fe/SiO_2 catalysts showed a gradual but systematic decrease in the selectivity to phenol in the succeeding measuring cycles. The decrease in selectivity was greater for palladium–iron systems deposited on SiO_2.

The comparison of catalytic properties of 5%Pd–8%Fe/Al_2O_3 and 5%Pd/Al_2O_3 systems leads to the conclusion that in both cases the increase of concentration of 2-chlorophenol and 4-chlorophenol after subsequent measurement cycles can be observed. It might be also noticed that the concentration of 2-chlorophenol in the reaction mixture, in case of 5%Pd/Al_2O_3 catalyst, is high at the beginning of the reaction and that is goes up after subsequent measurement cycles. For 5%Pd–8%Fe/Al_2O_3 system, during first measurement cycles, the concentration of 2-chlorophenol is low and reaches a significant value, comparable with the monometallic system, only after the tenth measurement cycle. A similar dependence has been observed for 5%Pd–8%Fe/SiO_2 system. Consequently, it seems that such changes of properties may be caused by leaching of iron into the reaction mixture.

In order to check the stability of Pd–Fe/support catalysts in the process of HDC, AAS analysis of the reaction mixture for the presence of palladium and iron was conducted. Trace amounts of Pd were observed systematically in the reaction mixture; iron was not observed in the first cycle, but in subsequent cycles of reaction there were trace amounts present. The amount of both metals in the reaction mixture was very low, which confirmed the stability of the catalysts.

Table 5
Conversion and selectivity to main reaction products for hydrodechlorination of 2,4-DCP over 5%Pd/Al_2O_3, 5%Pd–8%Fe/Al_2O_3 and 5%Pd–8%Fe/SiO_2 catalysts after the following 1.5 h cycles of reaction.

Catalysts	Cycle of reaction	X [%]	S_{Ph} [%]	$S_{2\text{-}CP}$ [%]	$S_{4\text{-}CP}$ [%]	S_{CHO} [%]	AAS analysis of reaction mixture	
							Pd [mg/dm^3] (247.6 nm)	Fe [mg/dm^3] (248.3 nm)
5%Pd/Al_2O_3	1	95.4	53.6	21.7	0.6	24.1	0.04	–
	2	92.6	50.1	23.8	1.8	24.3		–
	3	92.0	47.4	30.8	2.5	19.3		–
	5	91.2	46.0	33.2	1.6	19.2	0.02	–
	7	89.5	43.2	37.4	2.0	17.4		–
	10	88.8	42.7	39.1	3.2	15.0	0.01	–
5%Pd–8%Fe/Al_2O_3	1	92.6	98.0	0.8	1.2	–	0.05	b.d.l.
	2	88.3	90.0	8.5	1.5	–	–	–
	3	87.1	88.1	10.1	1.8	–	–	–
	5	83.1	82.7	14.9	2.4	–	0.04	0.01
	7	75.4	71.7	26.3	2.0	–	–	–
	10	69.4	62.0	33.0	5.0	–	0.02	0.05
5%Pd–8%Fe/SiO_2	1	92.4	99.3	0.2	0.5	–	0.03	b.d.l.
	2	91.9	71.8	26.8	1.4	–	–	–
	3	89.9	56.1	42.2	1.7	–	–	–
	5	88.2	50.6	47.8	1.6	–	0.04	b.d.l.
	7	87.1	46.8	51.5	1.7	–	–	–
	10	81.8	40.8	55.0	4.2	–	0.01	0.08

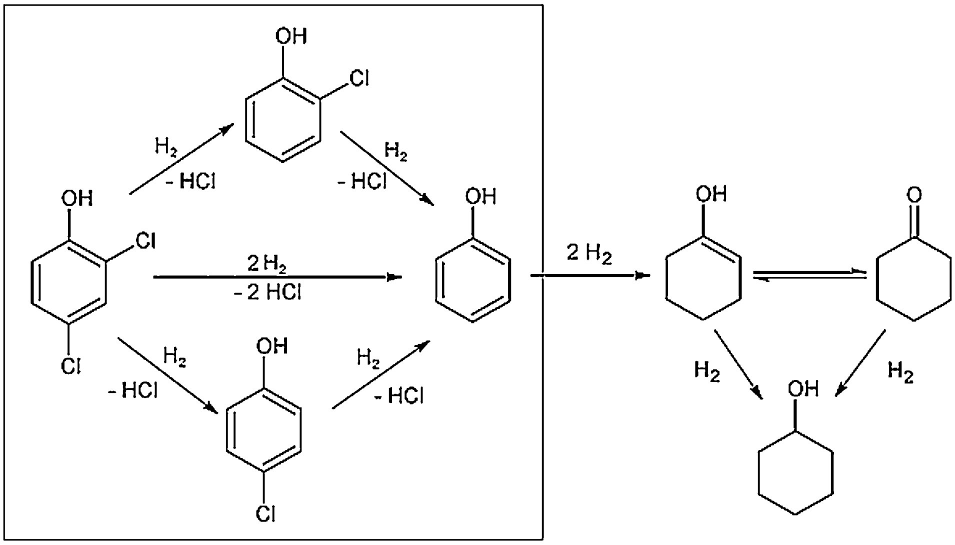
AAS measurments of reaction mixture after following reaction cycles over the same samples of catalysts (test of stability). b.d.l. – below detection limit; detection limits for: Pd – 0.01 mg/L, Fe – 0.005 mg/L.

Fresh as well as used 5%Pd–8%Fe/Al_2O_3 and 5%Pd–8%Fe/SiO_2 catalysts applied in the stability tests were analyzed to check if organic carbon is present, which could indicate the decomposition of HDC products. The results of the conducted research do not show any amounts of organic carbon, which further indicates the stability of catalysts in the studied reaction.

In the light of this research it might be assumed that due to a long contact of supported Pd–Fe catalysts with HCl, as a reaction product of HDC of 2,4-DCP in liquid phase, iron chloride is formed and the systems behave in a similar way to monometallic palladium systems. The confirmation of this hypothesis requires further research on the structure and it will be described in a further article.

4. Conclusions

Hydrodechlorination of 2,4-dichlorophenol process over palladium supported catalysts may occur according to the scheme:



The introduction of iron into palladium catalysts causes an increase in selectivity to phenol. Only phenol and small amounts of side products (2-chlorophenol and 4-chlorophenol) were detected in reaction mixture after the HDC of 2,4-DCP over Pd–Fe/support catalysts. It can be assumed, that the addition of iron into supported palladium systems prevented further reduction of phenol into cyclohexanone which occurred on the surface of monometallic palladium catalysts. The reason for this behavior of Pd–Fe/SiO_2 and Pd–Fe/Al_2O_3 catalysts in the HDC of 2,4-DCP is probably connected to bimetallic interactions on the surface of carriers. XPS and TPR-H_2 results indicate that some interactions between palladium and iron on the surface of tested catalysts do occur. However, XRD and ToF-SIMS studies of those bimetallic systems did not reveal the presence of intermetallic Pd_xFe_y phases.

It has been previously demonstrated [47,48,57] that the HDC of 2,4-DCP reaction over supported Pd catalysts is structurally sensitive. Activity, and especially selectivity to phenol, strongly depends on the dispersion of the active phase. Systems with low dispersion of palladium are more selective to phenol and cyclohexanone.

In conclusion, this investigation provides strong evidence of the efficiency of Pd–Fe/supported catalysts in the HDC of 2,4-DCP. Especially, bimetallic palladium–iron catalysts, containing up to 8 wt.%

of iron, supported on SiO_2 and Al_2O_3 seem to be interesting from practical point of view. However, it is still difficult to provide a clear explanation of the improved activity and selectivity of Pd–Fe over monometallic catalysts. This is due to the overlapping effects of active phase dispersion, surface structure, and chemical composition.

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