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Research Article

Synthesis, Characterization, and Catalytic Activity of Palladium-polyvinylpyrrolidone Complex in Oxidation of Octene-1

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Abstract

The metal complex catalysis with participation of unsaturated hydrocarbons gains great interest because of ecological aspect and a possibility of re-using of the catalyst. It has a number of advantages in comparison with a heterogeneous catalysis, such as high activity and selectivity, low temperatures of reaction and pressure. A palladium-polyvinylpyrrolidone complex was synthesized and characterized by potentiometry, conductometry, mass-, and IR-spectroscopy. The complex was tested for catalytic activity in reaction of octene-1 oxidation by inorganic oxidizers (KIO_4, $NaBrO_3$, $Na_2S_2O_8$, $K_2S_2O_8$) in dimethylsulfoxide or dimethylformamide under mild conditions. The reaction product was octanone-2, obtained in good yield (80-98 %) and characterized by gas chromatography and mass spectrometry. The catalysts can be easily recycled five consecutive runs without significant loss of catalytic efficiency. The use of different surface analysis techniques, such as: Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray spectroscopy (EDX), led to a better understanding of the polymer promoting effect.

Keywords: Polyvinylpyrrolidone; Palladium; Catalyst; Octanone-2; Oxidation

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1. Introduction

While homogeneous catalysts play very important role in organic synthesis because of well-defined catalytic sites with controllable properties such as reactivity and selectivity [1], industrial applications largely favor heterogeneous catalysts because of facile product separation and catalyst recycling [2,3]. Increasing research activity is therefore devoted to the combination of these advantages by linking catalytically active metal complexes to solid organic or inorganic supports [4,5]. Such materials combine properties of the homogeneous and heterogeneous catalysts and display high activity and selectivity as well as facile catalyst separation from the reaction products. Creation of new effi-

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cient catalysts requires a physical and chemical research of structure, a structure of the complexes which are formed at interaction of metal ions with polymeric ligands. The obtained results are of self-contained interest to coordination chemistry, and in applied aspect promote perfecting of sorption methods of concentrating, creation of the high performance heterogeneous metal-complex systems applied as catalysts in various reactions, such as: hydrogenation, oxidation of olefins [6-10].

This work focuses on synthesis and characterization of a palladium-polyvinylpyrrolidone complex from palladium(II) chloride and a water-soluble polyvinylpyrrolidone (PVP, 40 kDa). Thermodynamic characteristics of PVP, its complexing process with palladium(II) ions, a structure of a complex and the influence of external factors, such as: pH, ionic strength of solution, temperature on stability of a complex, have been investigated. The obtained complex was tested for catalytic activity in oxidation reactions of octene-1 by various inorganic oxidizers (potassium periodate (KIO_4), sodium bromate ($NaBrO_3$), sodium and potassium peroxodisulphates ($Na_2S_2O_8$, $K_2S_2O_8$) in dimethylsulfoxide (DMSO) or dimethylformamide (DMF) under mild conditions (70 °C, P_{N2} = 1 atm) as depicted in Scheme 1. The yield of final product was determined by a gas chromatographic method. The final product of reaction is octanone-2 (or *n*-hexylmethylketone). The catalyst stability under reaction conditions was checked and the structure of used catalyst was studied.

2. Materials and Method

2.1 Materials

Palladium chloride (content of metal 59.32 %), polyvinylpyrrolidone (molecular mass 40000, AppliChem, Germany), sodium hydroxide, sodium chloride, hydrochloric acid, dimethylsulfoxide (DMSO), dimethylformamide (DMF) (AppliChem, Germany), distilled water, inorganic salts, KIO_4, $NaBrO_3$, $Na_2S_2O_8$, $K_2S_2O_8$ (Aldrich), were used without purification.

2.2 Synthesis of the $PdCl_2$-PVP Complex

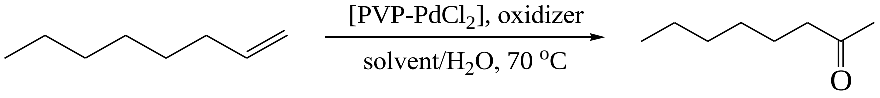
Synthesis of the $PdCl_2$-PVP complex was carried out as follows. The complex $H_2[PdCl_4]$ was synthesized according to the literature [11]. Palladium(II) chloride (1.0 g, 5.6 mmol) was added to a solution of 30 mL water and 1.0 mL concentrated HCl contained in a 100-mL round-bottomed flask. The resulting mixture was heated under reflux until all the palladium(II) chloride was dissolved. The dark reddish-brown solution of $H_2[PdCl_4]$ was then allowed to cool to room temperature. Then in a glass dish 20 mL of $H_2[PdCl_4]$ (0.5 mmol) was placed and mixed with 20 mL of an aqueous solution of PVP (0.167 g, 1.5 mmol). The mixture was stirred within 10-20 minutes at ambient temperature in order to allow for complete linking of the Pd(II) ions to the polymer. All volatile components were removed in aspirator vacuum and the complex was dried and stored in air at ambient temperature. Yield: 0.25 g (97 %).

2.3 Measurements

Potentiometric measurements were conducted on ionomer pX-150MI with using silver chloride and glass electrodes. Conductometric studies were performed on a device ConductivityMeter 13701/93 (PHYWE, Germany) under thermostated conditions. All experiments have been carried out under temperature control with an accuracy of ±0.2 °C. The GC analysis was carried out on Shimadzu GC-17A and Varian 3900 devices in the programmed mode from 70 to 280 °C with heat rate 5 °C/min with use of a capillary column of CS-Chromatography Service of Type FS-OV-1-CB-0.25. Mass spectra were recorded on the Varian Saturn 2100T device. IR spectra of Pd-PVP complex were recorded on the FTIR-4100 type A JASCO device. The surface analysis techniques were performed on the device of the JSM-6490LA scanning electron microscopy (SEM) with an energy dispersive X-ray (EDX) detector for the elemental analysis (JEOL, Japan). Gas chromatograms as well as IR-, mass spectra of the separated fractions, SEM and EDX images were taken in analytical laboratories at the Technical University of Kaiserslautern (TUK, Germany).

2.4 Typical Reaction Procedure

Oxidation of octene-1 by inorganic oxidizers was carried out on temperature-controlled la-



Scheme 1. Oxidation reaction of octene-1 by various inorganic oxidizers

boratory setup with intensively stirred up glass gradientless temperature-controlled reactor "a catalytic duck", supplied by potentiometric device and connected to the gas burette filled with nitrogen. The laboratory setup for testing the $Pd(PVP)_3Cl_2$ catalyst for octene-1 oxidation is shown in Figure 1. Laboratory experiments were made as follows. The reactor with a total volume of 150 mL was charged with the catalyst (0.029 g, 0.057 mmol) under a nitrogen atmosphere. Reactor and gas burette were preheated to 70 °C and an initial redox potential of solution (φ,V) was measured at this temperature, determined by redox-potential φ_{Pd}. The certain temperature was kept due to the water system passing through the glass reactor and connected to heating devices which looks like cooling machine. Then in nitrogen current an oxidizer (3 mmol) and aqueous solvent (8 mL, 4:1 by volume) were placed, in the last turn octene-1 (1 mmol) was added, and an electric motor was switched on.

During the catalytic reaction the redox potential in the reaction solution, was monitored with a platinum working electrode and a calomel half-cell as a reference electrode dipped in solution and connected to a potentiometer pH-340, whose readings were recorded in regular intervals and recalculated to potential difference values with regard to the normal hydrogen electrode. Temperature was maintained with an accuracy ±0.5 °C by means of the thermostat. After the experimental runs the reaction solutions were merged and analyzed on a gas chromatograph.

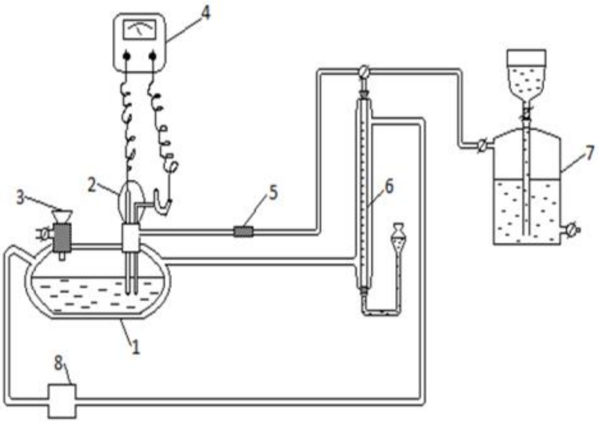


Figure 1. Laboratory setup for testing the catalyst: (1) reactor "a catalytic duck"; (2) platinum electrode in couple with a saturated calomel half-cell; (3) device for sample drawing of reactionary solution; (4) potentiometer pH-340; (5) calcium chloride tube; (6) temperature-controlled burette; (7) gasometer; (8) thermostat

2.5 GC-MS Sample Preparation

Samples for the GC and a mass spectroscopy were prepared according to the literature procedure [12]. The reaction mixture was cooled to ambient temperature. Then it was transferred to a separatory funnel and diluted with brine (10-15 mL). The aqueous layer was extracted with ethyl acetate (3 × 5 mL). The combined organic phases were washed with H_2O (3 × 10 mL) and brine (25 mL) and then dried over $MgSO_4$. After filtration and concentration under reduced pressure, the crude material was purified by flash chromatography and the product containing fractions were combined and concentrated under reduced pressure.

3. Results and Discussion

3.1 Infrared Spectroscopy

The nature of the modifying effect of PVP on ions Pd(II) and a possible molecular structure of the PVP-$PdCl_2$ complex before experiment were studied by IR-spectroscopy. The IR spectra of PVP and PVP-$PdCl_2$ complex are given in Figure 2. The characteristic peak of C=O bond in PVP becomes asymmetric after addition of the $PdCl_2$ complex that testifies to the strong coupling between PVP and Pd(II) in the PVP-$PdCl_2$ complex. IR spectra of PVP and PVP-$PdCl_2$ complex contain bands at 3454 and 3407 cm^{-1} characteristic for PVP. The carbonyl group in PVP is characterized by peak at 1652 cm^{-1}, widened because of double bond C=N in a lactam ring. This band is shifted to 1634 cm^{-1} in the PVP-$PdCl_2$ complex. Differences between the IR spectra of PVP and PVP-$PdCl_2$ complex suggest strong donor-acceptor interaction be-

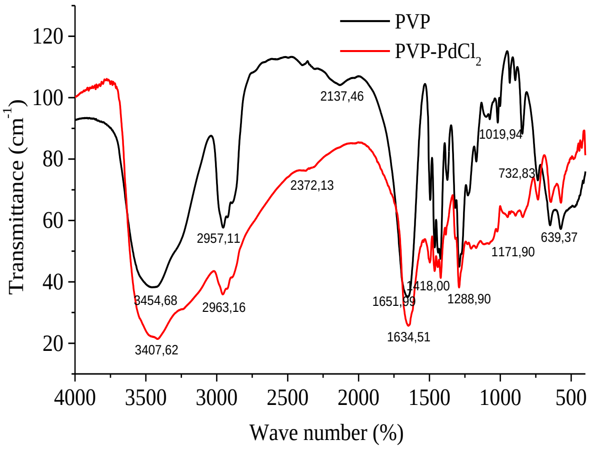


Figure 2. IR spectra of PVP and PVP-$PdCl_2$ complex before experiment

tween the oxygen atoms of the PVP ligand and Pd(II) ions.

3.2 Potentiometric and Conductometric Titration

Interaction between polyvinylpyrrolidone and Pd^{2+} ions was investigated by potentiometric and conductometric methods, which allowed to establish the structure, concentration and stability constants of the polymer/metal complex. Figures 3a,b show the results of potentiometric and conductometric titrations of polymer solutions with Pd(II) ions. Titration curves allowed to find optimum molar ratio of the reacting components k (k=[Me^{2+}]/[PVP]). For the PVP-Me^{2+} system an optimum molar ratio of components is k = 0.35 that demonstrates formation of complex particles with composition M:L = 1:3, i.e. one ion of metal complex contacts with three mono-links of a polymeric ligand. It can be seen from the Figure 3a, interaction of reagents is followed by pH decrease of medium that is probably caused by formation of a mixed double bond of a polyligand with palladium ions.

The structure of a complex polymer-Me^{2+} is confirmed on the basis of dependence of a specific conductivity on a ratio of initial components. From the Figure 3b it is visible that an electrical conductivity of solutions with increase in molar maintenance of metal ions passes through an inflection point at Pd^{2+}–PVP ratio of 1:3. It is known that when using $PdCl_2$ or $K_2[PdCl_4]$ as starting compounds in solution the chloroaquacomplexes of structure $[PdCl_{4-n}(H_2O)_n]_{(n-2)}^{-}$ (where n = 0-3) are formed [13,14]. The common scheme of reagents interaction is shown in Figure 4.

3.3 Stability of a Palladium-Polymer Complex

For a determination of the stability of a palladium-polymer complex a modification of the

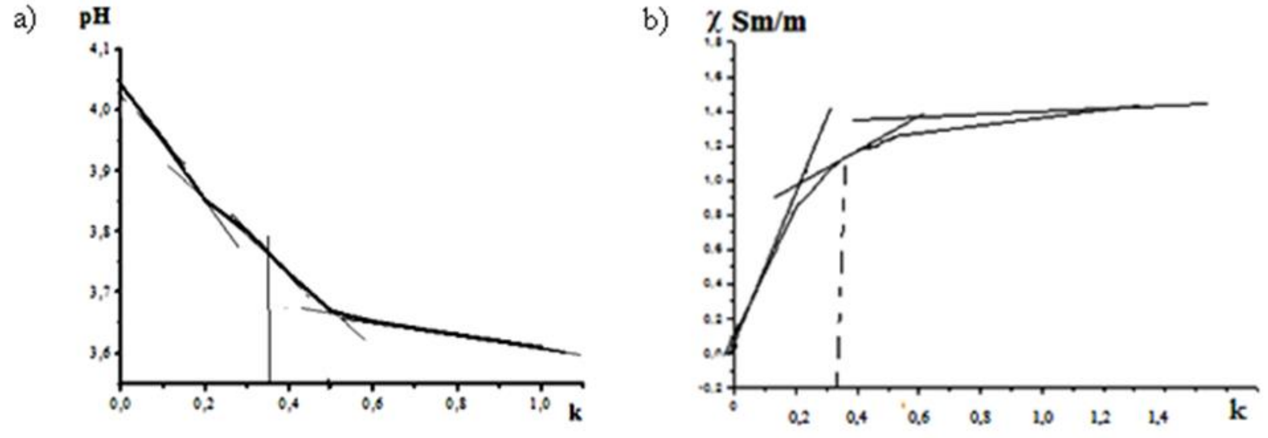


Figure 3. Curves of potentiometric (a) and conductometric (b) titration of polymer (10^{-2} M) with palladium salt $H_2[PdCl_4]$ (10^{-2} M) (where k – optimum molar ratio of the reacting components [Pd^{2+}]/[PVP], χ – specific electrical conductivity of solution in Sm/m)

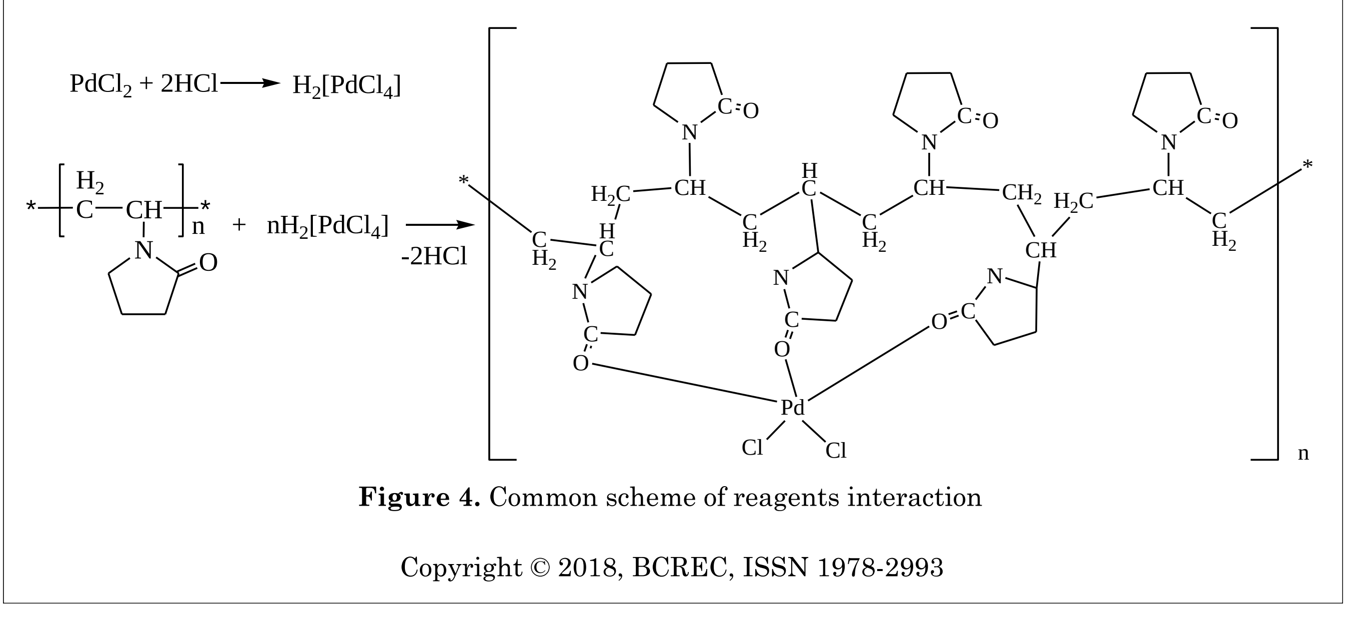


Figure 4. Common scheme of reagents interaction

method of Bjerrum was used [15]. For this purpose the polymeric ligand was titrated by sodium hydroxide in absence and in the presence of palladium ions in the temperature range 25-70 °C at different values of the ionic strength of the solution (0.1; 0.5; 1.0 mol/L). Sodium chloride was used to create the ionic strength of the solution. With increase in ionic strength of the solution the PVP-Pd^{2+} complex stability decreases. It should be noted that increase in temperature did not exert a uniform effect on the complex under investigation: in the temperature range from 25 to 45 °C the complex stability increased and was found to decrease at higher temperatures up to 70 °C. In the Figure 5 the curve of potentiometric titration of PVP solution by an aqueous solution of sodium hydroxide in the absence and in the presence of a metal ion at 25 °C and *I* = 0.1 mol/L is presented. It is necessary to notice that curves of potentiometric titration at other values of temperature and ionic strength of solution have a similar appearance. Titration curve in the presence of metal ions as it is visible from the Figure 5, is in more acidic area, than in their absence that can demonstrate existence of a complexing process between a polymeric ligand

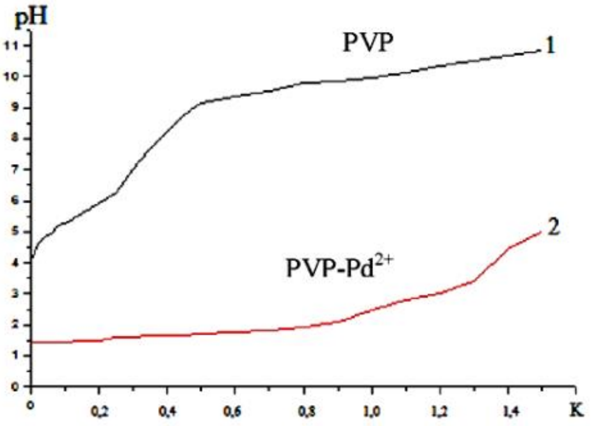


Figure 5. Curves of potentiometric titration of aqueous solutions of a polyelectrolyte of PVP (10^{-2} M) (1) and PVP-Pd^{2+} (10^{-2} M) (2) by sodium hydroxide (10^{-2} M) and *I* = 0.1 mol/L at 25 °C

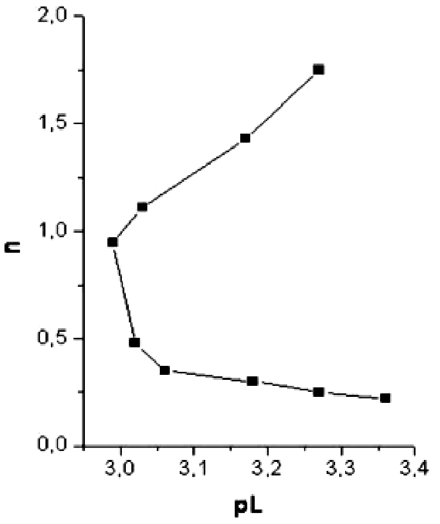


Figure 6. Function of PVP-Pd^{2+} complex formation at 25 °C and I = 0.1 mol/L (where n – Bjerrum's formation functions or average coordination number of a metal ion, pL or -lg[L] – concentration of the free ligands calculated on Henserson-Hasselbach equation pH = pKα + mlg[L]/[LH⁺], where m - the empirical coefficient considering interlink interaction of a polymeric chain)

Table 1. Values of Bjerrum's formation functions of the PVP-Pd^{2+} complex at 25 °C and I = 0.1 mol/L

pH	$[LH^+]\times10^4$ (mol L^{-1}) [a]	$[L]\times10^5$ (mol L^{-1}) [b]	$[L_C]\times10^3$ (mol L^{-1}) [c]	pL[d]	n [e]
4.07	2.48	0.01	3.08	6.89	2.99
4.19	6.01	0.04	2.73	6.39	2.65
4.30	9.49	0.09	2.38	6.09	2.31
4.45	13.00	0.15	2.03	5.83	1.97
4.60	16.40	0.26	1.69	5.59	1.64
4.75	19.80	0.44	1.35	5.36	1.31
4.95	23.20	0.78	1.00	5.11	0.97
5.10	26.60	1.20	0.66	4.92	0.31

[a] [L] – concentration of the free ligands which are not involved in a complexing process;
[b] [LH^+] – concentration of the protonated ligand groups;
[c] $[L]_C$ – concentration of the ligand groups connected in a complex;
[d] pL or -lg[L] – concentration of the free ligands calculated on Henserson-Hasselbach equation pH = pK_α + mlg[L]/[LH^+], where m - the empirical coefficient considering interlink interaction of a polymeric chain;
[e] n – Bjerrum's formation functions or average coordination number of a metal ion.

and metal ion. According to literary data [16,17], the more shift of titration curves of polymer-metal ion systems of relatively pure polymer, then higher stability of the formed polymer-metal complexes. Apparently from the Figure 5 (curve 2), at the initial stage there is a neutralization of protons by hydroxyl ions, the subsequent increase of pH solution is caused by excess of sodium hydroxide. Hydrolytic equilibriums in solutions of palladium(II) chloride, had been investigated in works [18,19] (Equations 1-4):

$$PdCl^{2-}_4 + H_2O \leftrightarrow PdCl_3OH^{2-} + H^+ + Cl^- \quad (1)$$

$$PdCl_3OH^{2-} + H_2O \leftrightarrow PdCl_2(OH)^{2-}_2 + H^+ + Cl^- \quad (2)$$

$$PdCl_2(OH)^{2-}_2 + H_2O \leftrightarrow PdCl(OH)^{2-}_3 + H^+ + Cl^- \quad (3)$$

$$PdCl(OH)^{2-}_3 + H_2O \leftrightarrow Pd(OH)^{2-}_4 + H^+ + Cl^- \quad (4)$$

The values of Bjerrum's formation functions (n) of the PVP-Pd^{2+} complex at 25 °C and I = 0.1 mol/L were specified in Table 1. It can be seen from Table 1, the palladium ion forms three coordination bonds with oxygen atoms of PVP (n = 2.99). The formed polymer-metal complex decomposes at pH = 5.1 (n = 0.31). The stability constants found on curves of complexes formation in the coordinates n – pL at 25 °C and I = 0.1 mol/L were presented in Figure 6 (at other values of T and I they were found in the same way). At half values of Bjerrum's formation function (n) graduated and full concentration constants of stability of complexes were calculated. The obtained values of concentration and thermodynamic constants of stability of the studied complex are presented in Table 2. With increase in ionic strength of solution the stability of the PVP-Pd^{2+} complex drops. Possibly, this is explained by screening of the coordination and active functional groups of polymer by small ions of electrolyte that it leads to decrease in their availability to metal ions. Increase in temperature renders on ambiguous influence on the studied process: in the temperature range 25-45 °C the stability of a complex rises, and it falls in the temperature range 45-70 °C.

Table 2. Constants values of the polymer-metal PVP-Pd^{2+} complex stability in an aqueous solution

T (°C)	I (mol L⁻¹) [a]	lgβ [b]
25	0	11.40
	0.1	11.60
	0.5	9.60
	1	9.60
45	0	25.62
	0.1	28.00
	0.5	13.10
	1	16.40
70	0	14.85
	0.1	14.60
	0.5	12.60
	1	11.00

[a] I – ionic strength of solution (mol/L);
[b] β - constant of complexes stability.

3.4 Thermodynamic Characteristics of a Complexing Process

In this work thermodynamic characteristics of a complexing process were calculated (Δ_rG^0, Δ_rH^0, ΔrS^0) and presented in Table 3. At the same time the classical equations of chemical thermodynamics in relation to systems with participation of polymeric compounds were used. It can be seen from the Table 3, that the reaction of $H_2[PdCl_4]$ solution with PVP in the temperature range 25-70 °C is characterized by negative values of Gibbs's energy that demonstrates course of the studied process in the direction of PVP-Pd^{2+} complex formation. Positive value of change of an enthalpy (Δ_rH^0) in the temperature range 25-45 °C testifies to the endothermic nature of polycomplex formation

Table 3. Thermodynamic characteristics of formation process of the PVP-Pd^{2+} complex in an aqueous solution

T (°C)	lgβ^0 [a]	-Δ_rG^0 (kJ mol⁻¹) [b]	Δ_rH^0 (kJ mol⁻¹) [c]	Δ_rS^0 (J mol⁻¹ K⁻¹) [d]
25	11.40	65.04	1288.4	4541.7
45	25.62	155.96		
70	14.85	97.50	-898.5	-2335.3

[a] β^0 – reference thermodynamic constant of complexes stability;
[b] Δ_rG^0 – Gibbs's energy change of reaction;
[c] Δ_rH^0 – enthalpy change of reaction (heat effect);
[d] Δ_rS^0 – entropy change of reaction.

therefore with temperature increase the equilibrium constant (stability) of the studied process raises according to the equation of Vant-Hoff's isobar, owing to the shift of a chemical equilibrium towards of reaction [20]. At temperatures raising from 45 to 70 °C the complex formation is exothermic, therefore the stability constant of the Pd^{2+}–polymer complex decreases with temperature rise. Changes of entropy values of the ligand groups of PVP and a palladium ion, replacement of solvent molecules and formation of the chelate structures are connected to destruction of solvent molecules [21,22]. The size of an entropy change during the studied reaction has sign-variable character: in the temperature range 25-45 °C has positive value that is probably caused by chloride ions separation, replacement of water molecules, as a result of destruction of hydrated forms of the functional groups of polymer. In the temperature range 45-70 °C, owing to the shift of a chemical equilibrium towards initial reagents, the specified processes happen to a lesser extent that brings system to more ordered state what testifies to negative value Δ_rS^0. The interpretation of the experimental data arrives at a formulation of a Pd^{2+}–PVP complex with one Pd^{2+} ion coordinated to three pyrrolidone units of the PVP polymer, which stability depends on ionic strength of solution and temperature.

3.5 Scanning Eelectron Microscopy Characterization

To study of a surface of fresh $Pd(PVP)_3Cl_2$ complex SEM technique was used and images are presented in the Figure 7. According to microscopic pictures it is visible that the formation of metal–polymer complex with some macroporous structure take place.

3.6 Catalytic Tests

The PVP-Pd^{2+} complex was tested as a catalyst in octene-1 oxidation by various inorganic

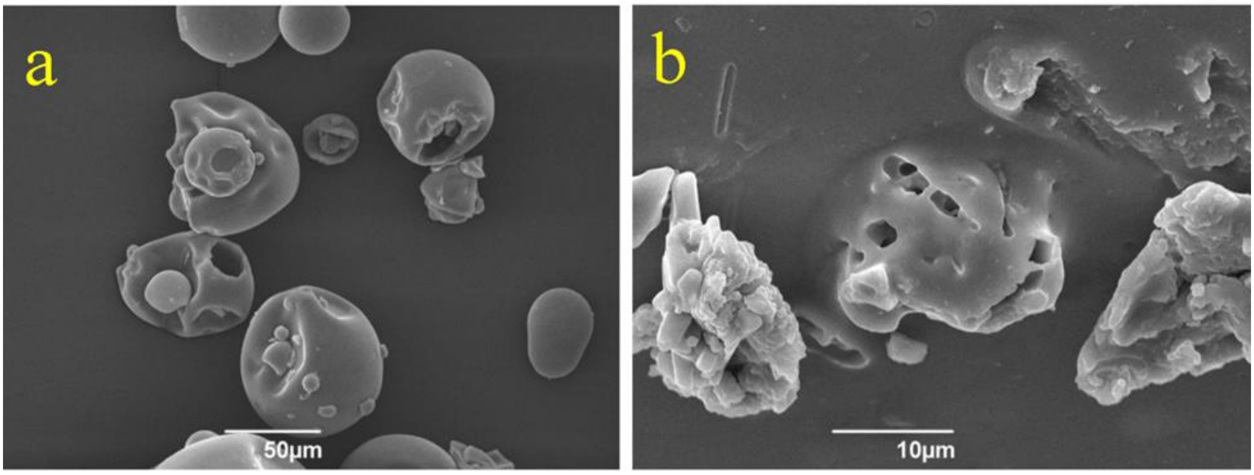


Figure 7. SEM images of a PVP ligand (a) and complex $Pd(PVP)_3Cl_2$ before experiment (b)

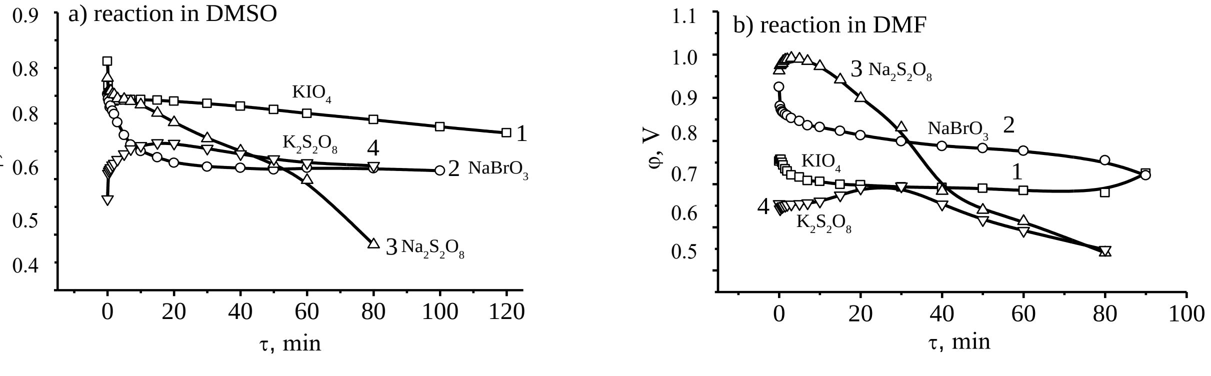


Figure 8. Potentiometric curves of octene-1 oxidation in the presence of $[Pd(PVP)_3Cl_2]$. Reaction conditions: $Pd(PVP)_3Cl_2$ (0.057 mmol), octene-1 (C_8H_{16}) (1 mmol), oxidizer (3 mmol), solvent/water (4:1, 10 mL), 80-120 min, 70 °C, P_{N2} 1 atm (solvent: (a) DMSO; (b) DMF)

oxidizers (KIO_4, $NaBrO_3$, $Na_2S_2O_8$, $K_2S_2O_8$) in DMSO and DMF under mild conditions (70 °C, P_{N2} = 1 atm). According to the obtained experimental data the potentiometric curves were constructed. Potentiometric curves of liquid-phase oxidation of octene-1, shown in the Figure 8, have the falling appearance and generally pass through a minimum with $\Delta\varphi$ = 0.083-0.184 V for DMSO and $\Delta\varphi$ = 0.073-0.536 V for DMF. Addition of octene-1 leads to the shift of initial potential in the cathode region and within 30-50 minutes remains constant, then comes back to the anodic region to initial value. The average duration of experiments in presence palladium-polymeric catalyst made 80-120 min. Reaction conditions and conversion of liquid-phase oxidation of octene-1 by oxidizers in water-organic solutions are given in Table 4. Yield of octanone-2 is established by a gas-chromatographic method of the analysis and made 80-98 %.

According to Table 4 in DMSO the conversion of octene-1 as well as the yield of octanone-2 made up 97-98 % whereas in DMF these values decrease insignificantly to 80-95 %. According to data of GC analysis and mass-spectrometry in cases when the selectivity was 80 % only the formation of the target product - octanone-2 was observed. Based on polarity index, DMSO and DMF have values of 7.2 and 6.4, respectively. Hence, they have comparable polarity with DMSO slightly higher than DMF. The components of reaction solution would be expected to dissolve more in DMSO relative to DMF [23].

The oxidation of Pd(0) and the reduction of IO_4^-, BrO_3^-, $S_2O_8^{2-}$ are thermodynamically allowed, proceed quite easily and are characterized by negative values of ΔG^o of these processes (-126, -88 and -197 kJ, respectively) (Table 4). Considering the transitions $IO_4^- + 2H^+ + 2e \rightarrow IO_3^- + H_2O$, $BrO_3^- + 6H^+ + 6e \rightarrow Br^- + 3H_2O$ и $S_2O_8^{2-} + 2e \rightarrow 2SO_4^{2-}$, it should be noted that the highest oxidation-reduction potential is observed for the oxidants $Na_2S_2O_8$ и $K_2S_2O_8$ (2.010 V).

3.7 Mass Spectrometry

Existence in mass spectra of pure octanone-2 and obtained octanone-2 from reaction solution of identical intensive peaks with m/z: 41, 43, 58, 85, 129, confirms formation of octanone-2 as is shown in Figure 9.

3.8 Recycling Catalyst

The catalyst could be recycled as is shown on Figure 10. In general, the catalytic activity of the $PdCl_2$ seriously declines, while it is demonstrated in this system that $Pd(PVP)_3Cl_2$ can be recycled for at least five times. The activity of the PVP-$PdCl_2$ catalyst falls in the initial runs in DMSO stronger than in DMF. The activity of the catalyst in DMSO correlates best with the level of Pd(II) immobilized on the PVP, and this Pd(II) complex therefore seems to be the primary catalytic species. It is possible to speculate that the loss of Pd in the earlier cycles probably occurs from sites at which the Pd is bound by a single PVP ligand. The more stable Pd centers are probably bound by two or three PVP ligands or are immobilized in a local polymer conformation which provides a surplus of PVP ligand sites. Thus, when a solu-

Table 4. Wacker process of octene-1 oxidation in the presence of $Pd(PVP)_3Cl_2$[a]

Entry	Oxidizer	$\Delta\varphi$ (V) [b]	Time (h)	Conversion (%)	Octanone-2 yield (%) [c]
			DMSO		
1	KIO_4	0.158	120	98	98
2	$NaBrO_3$	0.138	100	97	97
3	$Na_2S_2O_8$	0.184	90	98	98
4	$K_2S_2O_8$	0.083	90	98	98
			DMF		
5	KIO_4	0.073	90	90	90
6	$NaBrO_3$	0.302	90	80	80
7	$Na_2S_2O_8$	0.536	80	80	80
8	$K_2S_2O_8$	0.307	80	95	95

[a] Reaction conditions: octene-1 (1 mmol), $Pd(PVP)_3Cl_2$ (0.057 mmol), oxidizer (3 mmol), solvent/water (4:1, 10 mL), 80-120 min, 70 °C, P_{N2} = 1 atm;
[b] $\Delta\varphi$ - redox potential shift in the cathodic region after addition of octene-1 in reaction solution;
[c] Yields were determined by GC analysis of samples.

tion of the yellow complex was heated at 70 °C the solution became brown-black, indicative of cluster or colloidal palladium formation. The yield of product reached 15-47 % in DMSO and 47-88 % in DMF after the fifth recycling process. A noticeable problem in homogeneous Pd-mediated oxidation is catalyst deactivation by aggregation into inactive metallic Pd. The selectivity does not change and octanone-2 was observed as only product, as previously.

The IR spectra of fresh PVP-$PdCl_2$ complex and used one are given in Figure 11. Both IR spectra contain bands at 3402 cm^{-1} characteristic for PVP. The carbonyl group in PVP-$PdCl_2$ complex is characterized by peak at 1646 cm^{-1}. It is slightly shifted to 1652 cm^{-1} in the PVP-

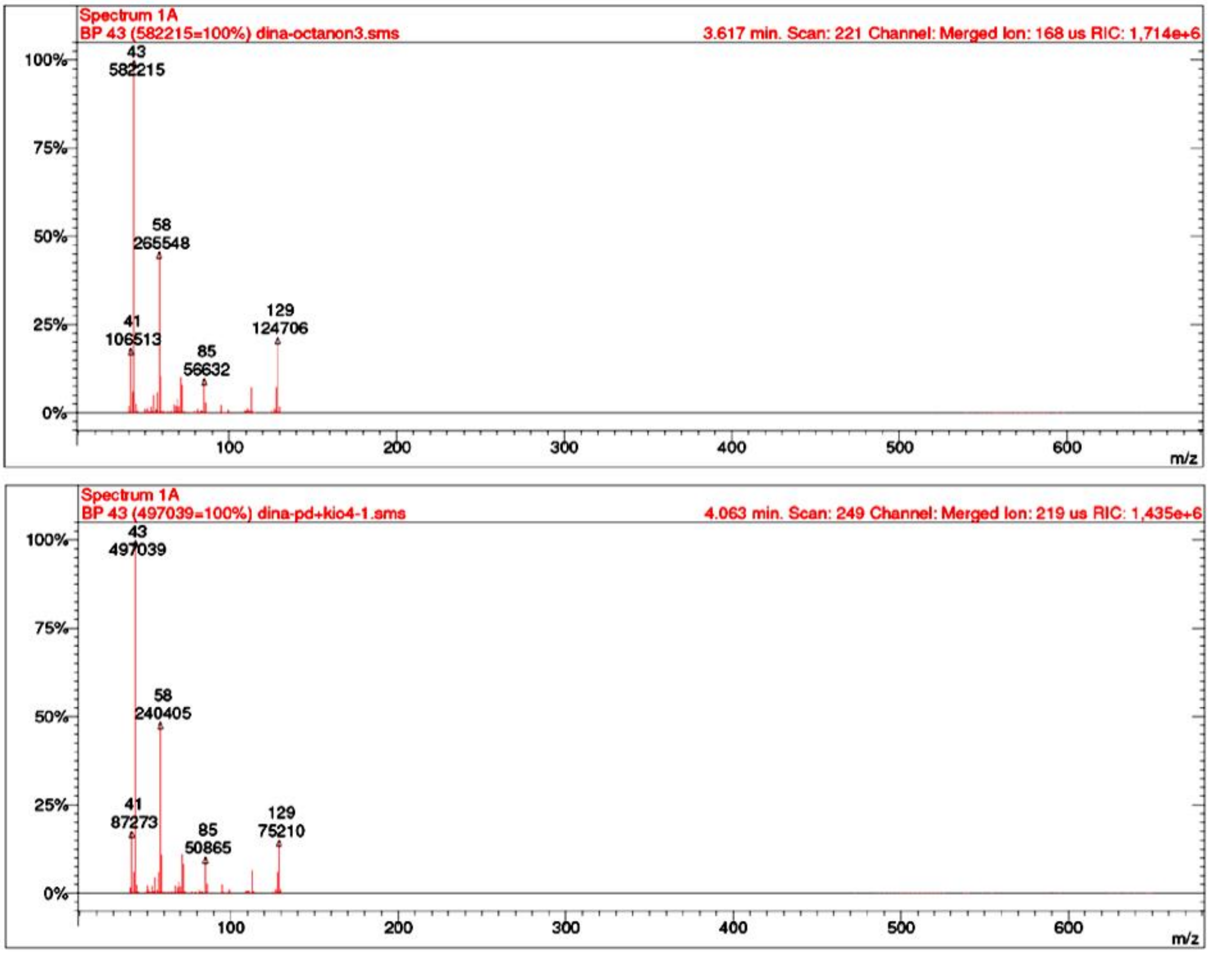


Figure 9. Mass spectra of pure octanone-2 (top of Figure 9) and comparison with mass spectra of the reaction solution (lower part). Reaction conditions: $Pd(PVP)_3Cl_2$ (0.057 mmol) - C_8H_{16} (1 mmol) - KIO_4 (3 mmol) - $DMSO/H_2O$ (4:1, 10 mL), 120 min, 70 °C, P_{N2} = 1 atm

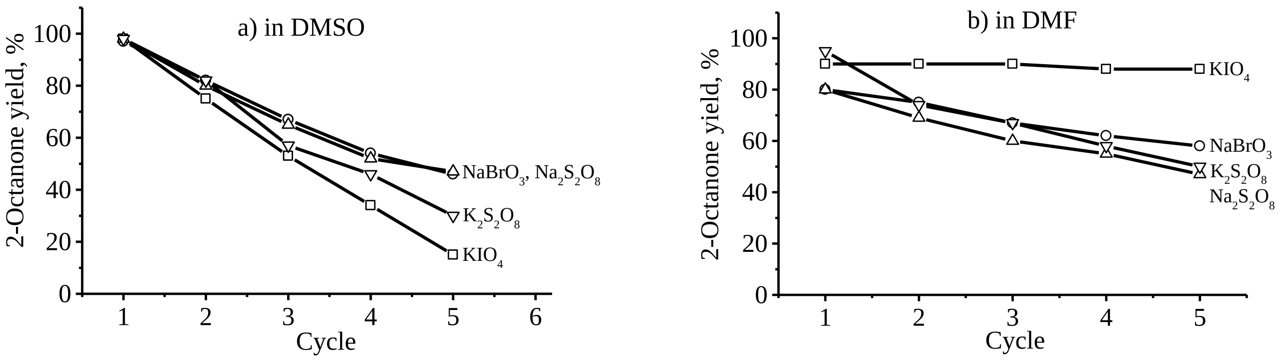


Figure 10. Recycling of catalyst

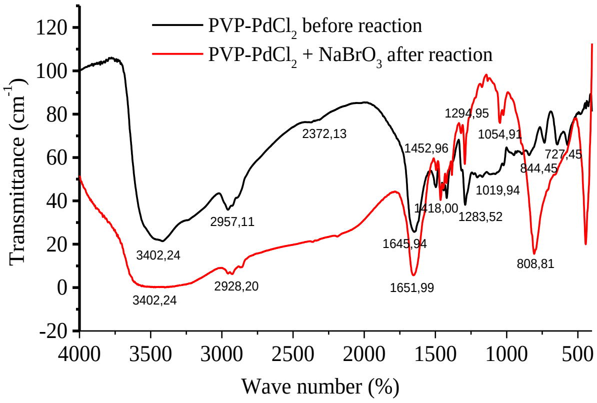


Figure 11. IR spectra of fresh and used catalyst

PdCl$_2$ complex after experiment. IR spectrum of used PVP-PdCl$_2$ catalyst contains band at 809 cm^{-1} characteristic for BrO$_3^-$ anion.

SEM and EDX techniques are employed to evaluate the structure and morphology of the catalysts after experiment and to identify the arrangement and nature of phases present on the catalyst surface. For instance, Figure 12 shows the SEM micrograph, along with the corresponding elemental mapping and images EDX, of a selected region of a Pd catalyst used for the octene-1 oxidation. As shown in Figure 12a, the SEM images of the Pd(PVP)$_3$Cl$_2$ after the fifth recycling experiment did not show any significant morphological change compared to

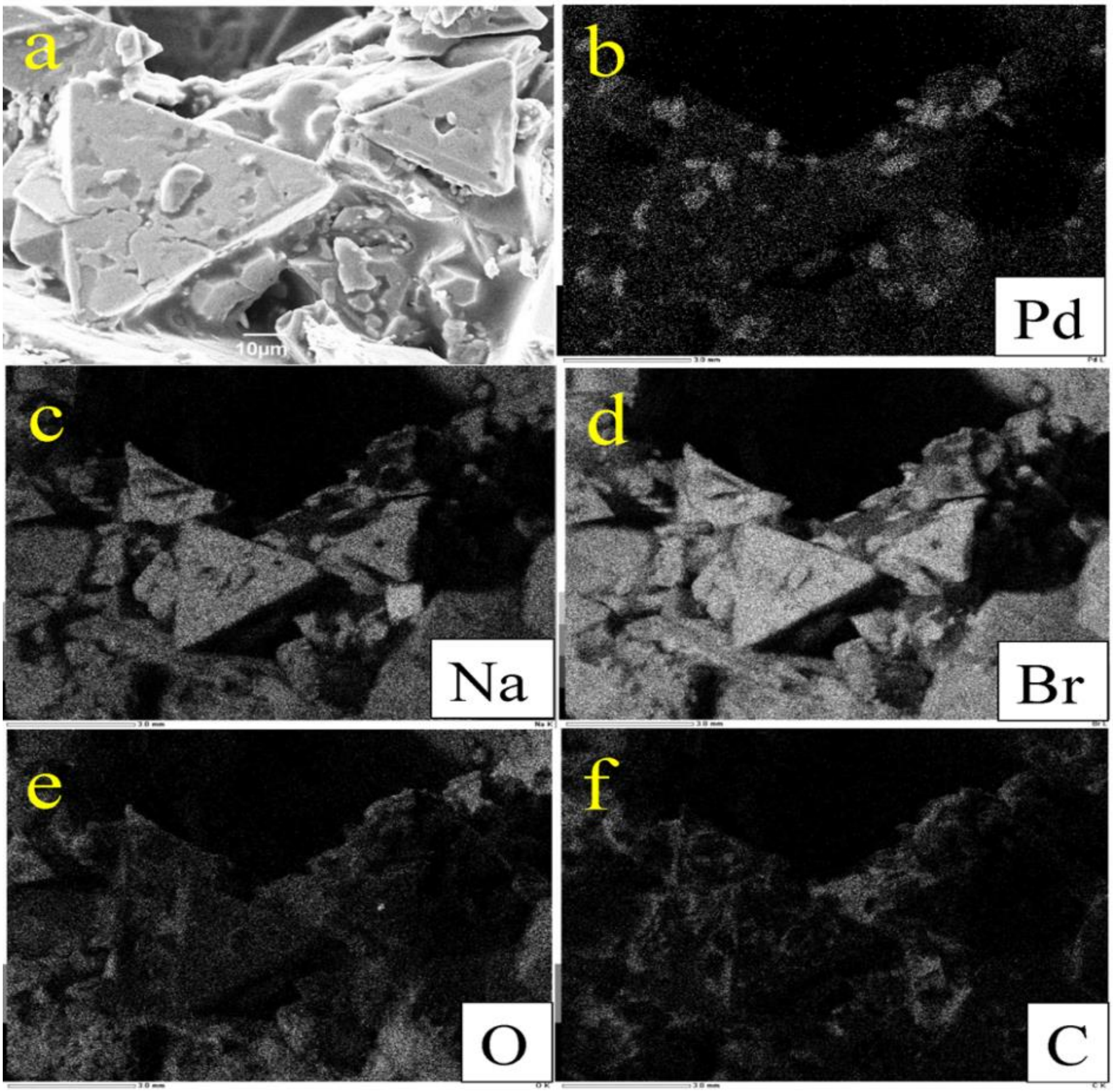


Figure 12. Top view SEM image of a selected area of a Pd(PVP)$_3$Cl$_2$ catalyst (a) after the octene-1 oxidation (70 °C, NaBrO$_3$, DMSO/H$_2$O (4:1), 70 °C, P_{N2} = 1 atm, 100 min), along with the corresponding elemental mapping (b1-b5) of Pd, Na, Br, O, and C.

those of the original sample. As a consequence, in these micrographs, a large concentration of sodium (Figure 12b) was found on the Pd catalyst surface. This demonstrated that Na^+ ions of $NaBrO_3$ were able to migrate through the catalyst film and reached the catalyst surface. As also revealed by the EDX analysis taken from different areas of the micrograph (Figure 12c,d,e), bromine-, oxygen-, and carbon-containing surface compounds seemed to be formed on the metal catalyst film during the octene-1 oxidation runs, probably in form of some sodium bromides or corresponds to polymer chains of PVP ligand. In fact, an excess of these surface species could block the Pd active sites causing a decrease in the catalytic reaction rate [24].

3.9 Mechanistic Aspects

Presumably processes proceed on the oxidation-reduction mechanism and consist of two key stages: reduction of Pd(II)(PVP) by octene-1 to Pd(0)(PVP) with formation of octanone-2 and oxidation of Pd(0)(PVP) to Pd(II)(PVP) by oxidizer. In the following hypothetical reaction Equations (5–7) and in Figure 13 the term PVP denotes one polymer-bound pyrrolidone ligand coordinated to palladium.

Activation:

$$[Pd(II)(PVP)_3Cl]^+ + C_8H_{16} + H_2O \rightarrow [Pd(0)(PVP)_3] + C_8H_{16}O + 2H^+ + Cl^- \quad (5)$$

Periodate oxidation, protonation:

$$[Pd(0)(PVP)_3] + KIO_4 + H^+ \rightarrow [HOPd(II)(PVP)_3]^+ + KIO_3 \quad (6)$$

Dissociation of one PVP ligand:

$$[HOPd(II)(PVP)_3]^+ \rightleftharpoons [HOPd(II)(PVP)_2]^+ + (PVP)_{dangling} \quad (7)$$

This cationic hydroxo-Pd(II) fragment $[HOPd(II)(PVP)_2]^+$ with three ligands is postulated to be the working catalyst. Not palladium, but the hydrogen ligand changes its oxidation state from -I when directly coordinated to the central palladium atom to +I when the oxidating agent delivers one oxide ion O^{2-} in return for two electrons received from the hydride complex, e.g. $KIO_4 + 2e^- \rightarrow KIO_3 + O^{2-}$. In the first step octene-1 is reversibly coordinated to the cationic $[(PVP)_2PdOH]^+$ site and enters a cyclic transition state, where the hydroxo ligand is transferred to the olefin in 2-position. A rotational move of the 2-hydroxyoctyl ligand leads to a cyclic transition state followed by *β*-hydride elimination with C=C double bond

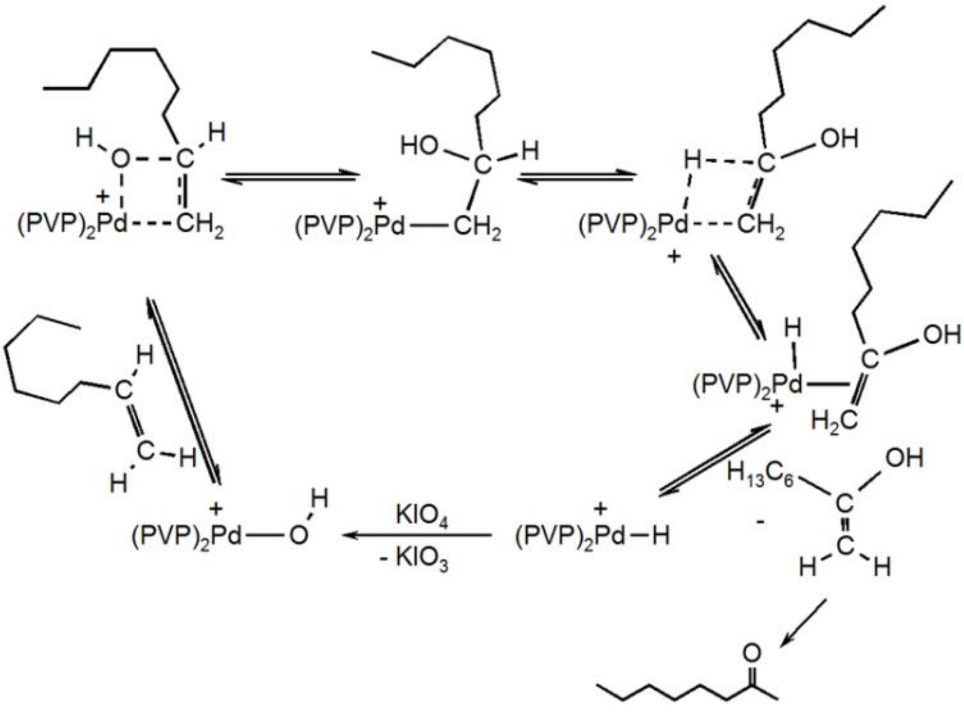


Figure 13. Hypothetical reaction mechanism for the conversion of octene-1 to octanone-2 with inorganic agents oxidation catalyzed by a palladium(II) complex fragment coordinated to the polyvinylpyrrolidone carrier material. The notation PVP in the formula scheme and in the hypothetical equations written before denotes one polymer-bound pyrrolidone moiety coordinating to the palladium central ion

formation. The vinyl alcohol octene-1-ol-2 is eliminated and rearranges via hydrogen migration from the enol to the more stable ketone octanone-2. The cationic palladium(II) hydride fragment $[(PVP)_2PdH]^+$ is then oxidized by the oxidizing agent to the initial $[(PVP)_2PdOH]^+$ cation. Oxidation of olefins by palladium salt in carbonyl compounds proceeds with high rate and the yield of carbonyl compound depends on the olefin. During the continuous olefin oxidation the palladium complex will be regenerated and plays a catalyst role: the oxidizers used in this work are known to be capable oxidize the reduced form of palladium to the divalent species. According to the known redox potential data, KIO_4, $NaBrO_3$, $Na_2S_2O_8$, and $K_2S_2O_8$ were selected as oxidants. Thermodynamic parameters of redox semi-reactions for Pd^{2+}, IO_4^-, BrO_3^-, $S_2O_8^{2-}$ are given in Table 5.

The thermodynamic probability of oxidation-reduction reactions was estimated on values of standard potentials of oxidizers and reducers and change of free energy of these processes [25]. For the redox processes proceeding in catalytic solution the free energy (ΔG^o, kJ) were calculated by a formula [26]:

$$\Delta G^o = -z_e F \times (E^\circ_{ox} - E^\circ_{red}) \qquad (8)$$

where, z_e - number of the electrons transferred from reducer to oxidizer; E°_{ox} - the standard potential of oxidizer (V); E°_{red} - the standard potential of reducer (V); F – Faraday's constant, equal to 96,485 C.

The calculated values of free energy specify that the reduction Pd(II) by octene-1 are resolved thermodynamically.

4. Conclusions

A palladium−polymer complex $[Pd(PVP)_3Cl]^+$ has been obtained from palladium(II) chloride and polyvinylpyrrolidone (PVP). Using potentiometric and conductometric titration as well as IR spectroscopy, the structure of the polymeric complex was established and stability constants were calculated. The polymer complexes were tested for catalytic activity in octene-1 oxidation by the inorganic oxidizers KIO_4, $NaBrO_3$, $Na_2S_2O_8$, $K_2S_2O_8$ in dimethylsulfoxide and dimethylformamide under mild conditions (70 °C, P_{N2} = 1 atm). Conversion of octene-1 was achieved in 80-98% yield. The final reaction product was octanone-2 (or *n*-hexylmethylketone). The catalysts can be easily recycled five consecutive runs. To evaluate the structure and morphology of the catalysts after experiment and to identify the arrangement and nature of phases present on the catalyst surface SEM and EDX techniques were employed.

Acknowledgements

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Table 5. Thermodynamic parameters of redox semi-reactions of Pd^{2+}, IO_4^-, BrO_3^-, $S_2O_8^{2-}$

Redox-semi-reaction	E^o (V)[a]	Redox-semi-reaction	ΔG°, kJ
Catalyst Pd(II)			
Oxidizer Pd(II)		Reduction of Pd(II) (H(+I))	
$Pd^{2+} + 2e \rightarrow Pd^0$	0.987	$C_8H_{16} + Pd^{2+} \rightarrow C_8H_{16}O + Pd^0$	
Oxidation of Pd(0) (H(-I)) with the oxidizing agent 1			
$Pd^0 + 4Cl^- \rightarrow PdCl_4^{2-} + 2e$	-0.620	$Pd^0 + Ox \rightarrow Pd^{2+}$ $H^- + Ox1 \rightarrow H^+ + Red1$	
Oxidizer KIO_4			
$IO_4^- + 2H^+ + 2e \rightarrow IO_3^- + H_2O$	1.640	$Pd + KIO_4 + 2HCl \rightarrow Pd^{2+} + 2Cl^- + KIO_3 + H_2O$ $H^- + KIO_4 \rightarrow OH^- + KIO_3$	-126
Oxidizer $NaBrO_3$			
$BrO_3^- + 6H^+ + 6e \rightarrow Br^- + 3H_2O$	1.440	$Pd + NaBrO_3 + 6HCl \rightarrow Pd^{2+} + 6Cl^- + NaBr + 3H_2O$ $3H^- + NaBrO_3 \rightarrow 3OH^- + NaBr$	-88
Oxidizers $Na_2S_2O_8$, $K_2S_2O_8$			
$S_2O_8^{2-} + 2e \rightarrow 2SO_4^{2-}$	2.010	$Pd + S_2O_8^{2-} + 2HCl \rightarrow Pd^{2+} + 2Cl^- + SO_4^{2-} + H_2SO_4$ $H^- + S_2O_8^{2-} + H_2O \rightarrow OH^- + 2HSO_4^-$	-197

[a] E^o (V) – reference redox potentials in aqueous solutions.

low phosphorus, alcohols and unsaturated hydrocarbons»).

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