




# Complexes of polyvinylpyrrolidone and polyethylene glycol with palladium(II) ions: characterization and catalytic activity

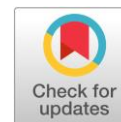
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## Abstract

In this work, we obtained complexes by mixing aqueous solution of palladium(II) chloride with polyvinylpyrrolidone and polyethylene glycol. The composition of the complex compounds was determined by potentiometric and conductometric titration. IR spectroscopy and scanning electron microscopy (SEM) confirmed the coordination of polymeric ligand to palladium and allowed evaluating the morphology and features of the complex surface. The catalytic activity of the synthesized compounds in the oxidation of octene-1 by inorganic oxidizers ( $\text{NaBrO}_3$ ,  $\text{K}_2\text{S}_2\text{O}_8$ ) in aqueous-organic media in dimethyl sulfoxide (DMSO) under mild conditions was calculated. The reaction product was octanone-2, obtained in good yield (62–98%). Quantitative analysis of octanone-2 was made by the gas-chromatographic method. Mass spectrometry confirms the formation of octanone-2. The complexes are able to participate in five consecutive catalytic cycles without significant loss of catalytic efficiency. Oxidation of octene-1 proceeds by the oxidation-reduction mechanism and consists of two key stages.

## Keywords

palladium(II) ions  
polyvinylpyrrolidone  
polyethylene glycol  
catalysis  
oxidation  
octene-1

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## Key findings

- The composition of the complex compounds was determined by potentiometric and conductometric methods.
- IR spectroscopy and SEM confirmed the coordination of polymeric ligand to palladium and allowed evaluating the morphology of the complex surface.
- The catalytic activity of the complexes in the oxidation of octene-1 by inorganic oxidizers under mild conditions was evaluated.

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## 1. Introduction

The oxidation of unsaturated hydrocarbons with different oxidants leads to the formation of different oxygen-containing compounds, which are key materials for then synthesis of fine chemicals, pharmaceuticals, and important intermediates in petroleum industrial chemistry [1]. The Pd(II)-catalyzed oxidation of alkenes to carbonyl compounds is one of the most well-known reactions mediated by palladium and has extensive synthetic applications, usually referred to as the Wacker reactions [2–4].

The use of  $\text{CuCl}_2$ , even in catalytic amount, resulted in the production of noxious copper waste, which is potentially very toxic to aquatic life. It leads to the formation of substantial amounts of ecologically hazardous chlorinated

by-products. Elimination of  $\text{CuCl}_2$  as co-catalyst would render the Wacker oxidation a completely green process [5].

The introduction of functional groups into the polymer during the development of new types of catalytic systems based on metal-polymer complexes plays an important role. Nowadays the palladium complexes with PEG and PVP ligands are widely used as catalysts for cross-coupling reactions and direct synthesis of hydrogen peroxide from hydrogen and oxygen [6–8].

Both sodium bromate ( $\text{NaBrO}_3$ ) and potassium peroxydisulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) are inexpensive, commercially available strong oxidizing agents. They have been used with different catalysts in various organic reactions as co-oxidants in stoichiometric quantities [9].

Sodium bromate has been used for selective oxidation of vicinal diols to  $\alpha$ -hydroxy ketones, oxidation of alcohols and alkyl arenes to the corresponding carbonyl compounds, and selective oxidation of sulfides to sulfoxides [10–13].

The peroxydisulfate ion is one of the strongest known oxidizing agents in aqueous solution. Potassium peroxydisulfate has been used for the oxidation of 1,4-dihydropyridines to the pyridine derivatives, selective oxidation of alcohols to aldehydes and ketones, C–Se bond formation to construct  $\alpha$ -phenylseleno carbonyl compounds and  $\alpha,\beta$ -unsaturated carbonyl compounds [14–16].

This article describes the synthesis and characterization of complexes between palladium(II) chloride and hydrophilic polymers (polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG)). The complexes were characterized by conductometric and potentiometric titration. The obtained polymer-metal complexes Pd(II)–PVP and Pd(II)–PEG were tested as catalysts in the oxidation of octene-1 by inorganic oxidants (sodium bromate ( $\text{NaBrO}_3$ ) and potassium peroxydisulfate ( $\text{K}_2\text{S}_2\text{O}_8$ )) in dimethyl sulfoxide (DMSO) under mild conditions (70 °C,  $P_{\text{N}_2} = 1$  atm).

## 2. Experimental

Palladium chloride (content of metal 59.32%), polyvinylpyrrolidone (molecular mass 40000, AppliChem, Germany), polyethylene glycol (molecular weight 10,000, Sigma Aldrich, USA), hydrochloric acid (36%), dimethyl sulfoxide, DMSO (AppliChem, Germany), distilled water, inorganic salts  $\text{NaBrO}_3$ ,  $\text{K}_2\text{S}_2\text{O}_8$  (Sigma Aldrich, USA) were used without purification.

### 2.1. Synthesis of $\text{H}_2[\text{PdCl}_4]$

The complex  $\text{H}_2[\text{PdCl}_4]$  was synthesized according to the literature [17]. Palladium(II) chloride (1.0 g, 5.6 mmol) was added to a solution of 30 mL water and 1.0 mL concentrated HCl (36%) contained in a 100-mL round-bottom flask. The resulting mixture was heated under reflux until all the palladium(II) chloride had been dissolved. The dark-brown solution of  $\text{H}_2[\text{PdCl}_4]$  was then allowed to cool to room temperature.

### 2.2. Synthesis of $\text{PdCl}_2$ – PVP

20 mL of  $\text{H}_2[\text{PdCl}_4]$  solution (0.5 mmol) was placed in a glass dish and mixed with 20 mL of an aqueous solution of PVP (0.167 g, 1.5 mmol). The mixture was stirred for 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. Synthesis of $\text{PdCl}_2$ – PEG

20 mL of  $\text{H}_2[\text{PdCl}_4]$  solution (0.5 mmol) was placed in a glass dish and mixed with 20 mL of an aqueous solution of PEG (0.124 g, 2.0 mmol). The mixture was stirred for 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: 0.17 g (95%).

The process of complexation between palladium(II) ion and polymers was investigated by potentiometric and conductometric methods with several ionic strengths and temperatures. Potentiometric studies were carried out in a commercial device (PHYWE, Germany) under thermostatically controlled conditions. Conductometric studies were performed on a ConductivityMeter 13701/93 (PHYWE, Germany) under thermostated conditions. All experiments were carried out under temperature control with an accuracy of  $\pm 0.2$  °C.

IR spectra were recorded on a FT IR-4100 type A JASCO instrument (USA) in the range of 4000–450  $\text{cm}^{-1}$ . SEM images were taken on a JSM-6490LA Jeol instrument equipped with an X-ray dispersive energy detector (EDX) for elemental analysis (Japan).

Samples for the GC and mass spectroscopy were prepared according to the literature procedure [18] by extraction with ethyl acetate. The GC analysis was carried out on Shimadzu GC-17A (Japan) and Varian 3900 (Canada) devices in the programmed mode from 70 to 280 °C with 5 °C/min heat rate using a capillary column CS-Chromatography Service of Type FS-OV-1-CB-0.25. Mass spectra were recorded on a Varian Saturn 2100T device (Canada).

IR spectra, SEM images and mass spectra were obtained in analytical laboratories at the Rheinland-Pfalz Technical University of Kaiserslautern-Landau (RPTU, Germany).

### 2.4. Typical reaction procedure

Oxidation of octene-1 by inorganic oxidizers was carried out in a temperature-controlled laboratory setup with intensive stirring in a glass temperature-controlled reactor under negligible temperature gradient ("a catalytic duck"), equipped by the potentiometric device and connected to the gas burette filled with nitrogen. Shaking the reactor with frequency of about 250–300 swingings/min minimizes both the mass transport and mass transfer resistance. The laboratory experiments were performed as follows. The reactor with an entire volume of 150 mL was charged with the catalyst (0.057 mmol) under nitrogen atmosphere. The reactor and the gas burette were preheated to 70 °C. The temperature was maintained by the water circulating between the glass reactor and the heating devices. Then, in nitrogen flow, an oxidizer (3 mmol) and aqueous solvent (8 mL, 4:1 by volume) were placed. Finally, octene-1 (1 mmol) was added, and an electric stirrer was switched on. The temperature was maintained with an accuracy of  $\pm 0.5$  °C by means of the thermostat. After the experimental runs the reaction solutions were merged and analyzed on a gas chromatograph.

### 3. Results and discussion

#### 3.1. Potentiometric titration

Figure 1 shows the potentiometric titration curves of PdCl<sub>2</sub>-PVP and PdCl<sub>2</sub>-PEG complexes. The mixing of solutions of polymer with salt is accompanied by a pH decrease, which is explained by the deprotonation of initially protonated PVP and PEG during the complexation.

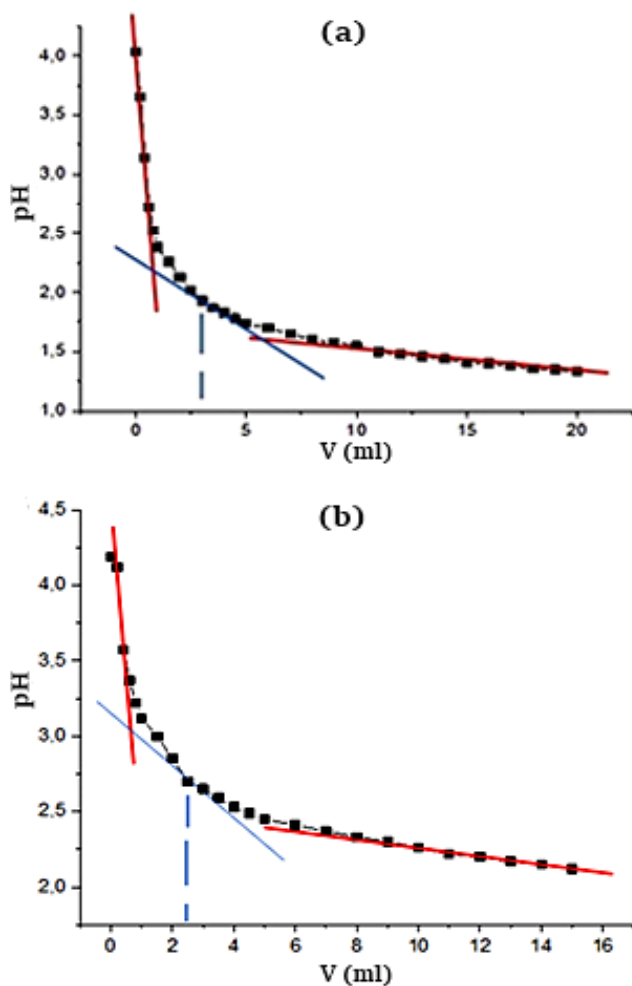
From the titration curve (Figure 1a), the optimal molar ratio of the reacting components  $k$  ( $k=[Pd^{2+}]/[PVP]=0.35$ ) was found. It means that one central metal atom bonds with three mono-links of polymer ligands.

From the titration curve (Figure 1b), the optimal molar ratio of the reacting components  $k$  ( $k=[Pd^{2+}]/[PEG]=0.25$ ) was found. It means that one central metal atom bonds with four mono-links of polymer ligands.

#### 3.2. Conductometric titration

In order to confirm the composition of the formed PVP-Pd<sup>2+</sup> and PEG-Pd<sup>2+</sup> complexes, the dependence of the conductivity corrected for the viscosity on the ratio of the initial component of the system was studied (Figure 2).

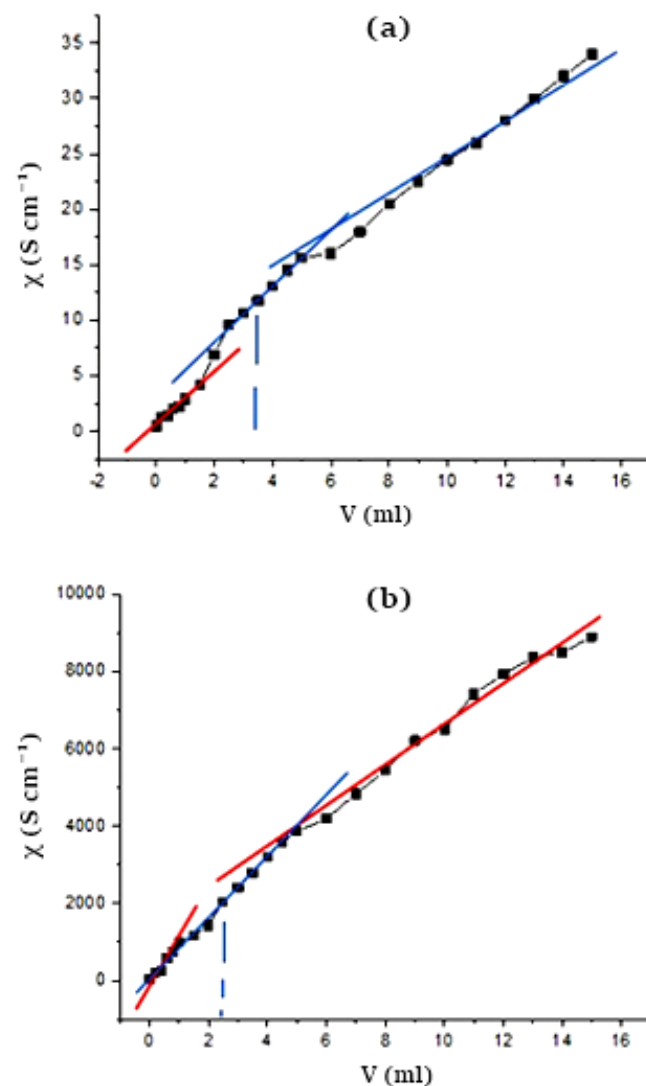
The increase in electrical conductivity is due to the released H<sup>+</sup> ions during the reaction between PVP or PEG and palladium(II) ions.



**Figure 1** Potentiometric titration curves of polymer ( $10^{-2}$  M) with palladium salt  $H_2[PdCl_4]$  ( $10^{-2}$  M) (where  $V$  - titrant volume in mL, pH - pH of solution). PVP (a); PEG (b).

As can be seen from Figure 2, the electrical conductivity of the solution passes through the inflection point with an increase in the molar content of metal ions. Based on the data obtained as a result of conducted conductometric studies, it can be argued that the complexation process is accompanied by an increase in the electrical conductivity of the system at the ratios PVP-Pd<sup>2+</sup>=3:1 and PEG-Pd<sup>2+</sup>=4:1.

The complexation process of PVP with Pd<sup>2+</sup> ions is characterized by negative values of Gibbs energy that indicates the spontaneous process of polymer-metal complex formation. For the Pd<sup>2+</sup>-PVP complex in the temperature range 298–318 K the positive value of enthalpy change ( $\Delta_r H^\circ$ ) indicates the endothermic character of complex formation. Therefore, the stability of the latter increases with increasing temperature in this range. And in the temperature range of 318–343 K the process of complexation is accompanied by the release of heat (exothermic process). As a result, the strength of the polymer-metal complex decreases with increasing temperature.



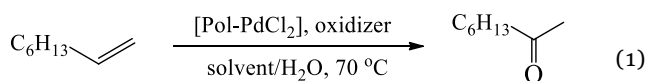
**Figure 2** Potentiometric titration curves of polymer ( $10^{-2}$  M) with palladium salt  $H_2[PdCl_4]$  ( $10^{-2}$  M) (where  $V$  - titrant volume in mL, pH - pH of solution,  $\chi$  - specific electrical conductivity of solution in  $S\ cm^{-1}$ ). PVP(a); PEG (b).

This ambiguous influence of temperature on the process of complexation is probably caused by conformational changes in the structure of PVP polymer, investigated by Liu et al. in [19]. It was found that conformational changes of PVP in aqueous medium are accompanied by exo effects that depend on temperature and molecular weight of the polymer.

### 3.3. Oxidation of octene-1 catalysed by Pd(PVP)<sub>3</sub>Cl<sub>2</sub> and Pd(PEG)<sub>4</sub>Cl<sub>2</sub> complexes

The synthesized complexes were used as catalysts in the process of oxidation of octene-1 by inorganic oxidizers (NaBrO<sub>3</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) in aqueous-organic media in dimethyl sulfoxide under mild conditions (equation 1).

Reaction conditions and conversion rates of liquid-phase oxidation of octene-1 by oxidizers in water-organic solutions are given in Table 1. The yield of octanone-1 (or n-hexyl methyl ketone) in the experiments in the presence of Pd(II)-PEG complex was determined by gas-chromatographic analysis and was 62–81%, that is lower than the product yield in the presence of Pd(II)-PVP complex. According to GC analysis and mass spectrometry of reaction solutions, when the yield was less than 100%, the formation of products other than octanone-2 was not observed. The yield of octanone-2 did not exceed 5% after experiments in the presence of inorganic oxidizers (NaBrO<sub>3</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>).



The high catalytic activity of the monometallic polymeric palladium complexes relates to their solubility in the water-organic reaction solution. As a polarity index of DMSO is equal to 7.2, the components of the reaction solution would be expected to dissolve completely in DMSO [20].

The mass spectra of octanone-2 obtained from the reaction solution contain identical intensive peaks with *m/z*: 41, 43, 58, 85, 129, which confirms formation of octanone-2 (Figure 3).

The catalysts could be recycled as shown in Figure 4. The catalytic activity of the PdCl<sub>2</sub> declines strongly, while it is demonstrated that Pd(PVP)<sub>3</sub>Cl<sub>2</sub> and Pd(PEG)<sub>4</sub>Cl<sub>2</sub> can be cycled for at least five times.

**Table 1** Wacker process of octene-1 oxidation in the presence of Pd(PVP)<sub>3</sub>Cl<sub>2</sub> and Pd(PEG)<sub>4</sub>Cl<sub>2</sub> complexes <sup>[a]</sup>.

Entry	Oxidizer	Conversion, %	Octanone-2 yield, % <sup>b</sup>
Cat Pd(PVP) <sub>3</sub> Cl <sub>2</sub>			
1	NaBrO <sub>3</sub>	97	97
2	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	98	98
Cat Pd(PEG) <sub>4</sub> Cl <sub>2</sub>			
3	NaBrO <sub>3</sub>	81	81
4	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	62	62

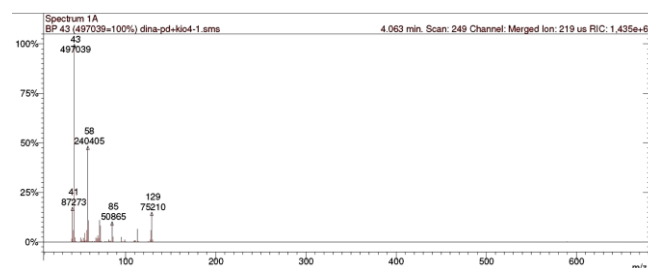
<sup>a</sup> Reaction conditions: octene-1 (1 mmol), Cat (0.057 mmol), oxidizer (3 mmol), solvent/water (4:1, 10 mL), 120 min, 70 °C, *P*<sub>N<sub>2</sub></sub> = 1 atm.

<sup>b</sup> Yields were determined by GC analysis of samples.

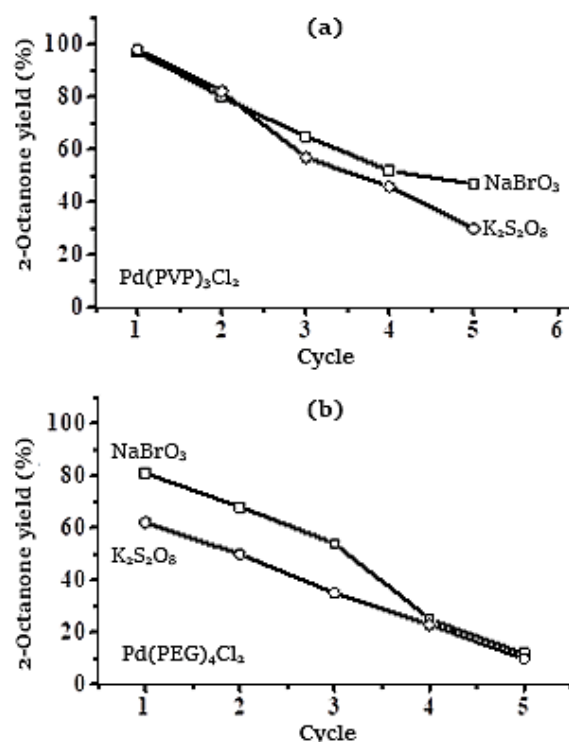
The activity of the catalyst in DMSO correlates best with the level of Pd(II) immobilized on the PVP, and this Pd(II) complex, therefore, seems to be the primary catalytic species.

Thus, when a solution of the yellow complex was heated at 70 °C it became brown-black, indicative of cluster or colloidal palladium formation. The yield of the product reached 12–30% in DMSO after the fifth cycle. 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 the only product, as in the previous experiments.

According to the known values of redox potentials, NaBrO<sub>3</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were chosen as oxidizing agents. The oxidation of Pd(0) and reduction of BrO<sub>3</sub><sup>-</sup>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup> are thermodynamically resolved, they proceed quite easily and are characterized by negative values of Δ*G*<sup>0</sup> for these processes (-88 and -197 kJ, respectively). Considering the transitions BrO<sub>3</sub><sup>-</sup> + 6H<sup>+</sup> + 6e<sup>-</sup> → Br<sup>-</sup> + 3H<sub>2</sub>O and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> + 2e<sup>-</sup> → 2SO<sub>4</sub><sup>2-</sup>, it should be noted that the oxidation-reduction potential is higher for K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2.010 V) than for NaBrO<sub>3</sub> (1.440 V) [21, 22].



**Figure 3** Mass spectra of the reaction solution. Reaction conditions: Pd(PVP)<sub>3</sub>Cl<sub>2</sub> (0.057 mmol) - C<sub>8</sub>H<sub>16</sub> (1 mmol) - KIO<sub>4</sub> (3 mmol) - DMSO/H<sub>2</sub>O (4:1, 10 mL) at 70 °C and *P*<sub>N<sub>2</sub></sub> = 1 atm.



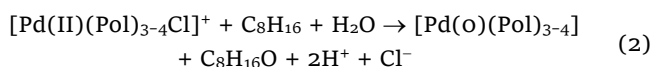
**Figure 4** Reusing the catalysts: Pd(PVP)<sub>3</sub>Cl<sub>2</sub> (a) and Pd(PEG)<sub>4</sub>Cl<sub>2</sub> (b).

The IR spectra of green PVP-PdCl<sub>2</sub> complex and the used one are given in Figure 5. Both IR spectra contain bands at 3402 cm<sup>-1</sup> characteristic of PVP. The carbonyl group in PVP-PdCl<sub>2</sub> complex is characterized by the peak at 1646 cm<sup>-1</sup>. It is slightly shifted to 1652 cm<sup>-1</sup> in the PVP-PdCl<sub>2</sub> complex after the experiment.

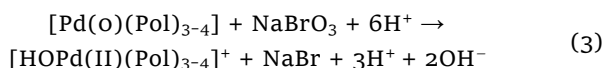
To evaluate the structure and morphology of the catalysts after the experiment and to identify the arrangement and nature of the phases present on the catalyst surface, SEM and EDX techniques were employed. Figure 6 shows the SEM micrograph of a selected region of the Pd catalyst used for the octene-1 oxidation. As shown in Figure 6b, the SEM images of the Pd(PVP)<sub>3</sub>Cl<sub>2</sub> after the fifth recycling experiment did not show any significant morphological change compared to those of the original sample. One of the reasons in decrease of the catalytic reaction rate is an excess of surface species such as the bromine-, oxygen-, and carbon-containing surface compounds, which could block the Pd active sites [23].

The oxidation-reduction mechanism consists of two key stages [24]: reduction of Pd(II)(Pol) by octene-1 to Pd(o)(Pol) with formation of octanone-2 and oxidation of Pd(o)(Pol) to Pd(II)(Pol) by oxidizer. In the hypothetical oxidation reaction equations (equations 2–4), the PVP or PEG mono link denotes one polymer ligand bound to the polymer coordinated with palladium.

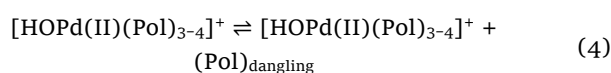
#### Activation



#### Bromate oxidation, protonation:



#### Dissociation of one polymer ligand:



## 4. Limitations

The main problem that appeared during this research is the high hygroscopicity of Pd(II)-PEG complex in comparison with Pd(II)-PVP one. A possible solution of this problem is the further immobilization of the complex on the supports.

## 5. Conclusions

Palladium-polymer complexes [Pd(PVP)<sub>3</sub>Cl]<sup>+</sup> and [Pd(PEG)<sub>4</sub>Cl]<sup>+</sup> were obtained from palladium(II) chloride, polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG). Using potentiometric and conductometric titration as well as IR spectroscopy, the structure of the polymeric complexes was established. The polymer complexes were tested for catalytic activity in octene-1 oxidation by the inorganic oxidizers NaBrO<sub>3</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in dimethyl sulfoxide

under mild conditions (70 °C, P<sub>N<sub>2</sub></sub> = 1 atm). Conversion of octene-1 was achieved in 62–98% yield. The final reaction product was octanone-2 (or *n*-hexyl methyl ketone). The catalysts can be reused at least up to five times. The SEM and EDX techniques were employed for evaluating the structure and morphology of the catalysts after experiment, and for the identification of the arrangement and nature of the phases present on the catalyst surface. The oxidation-reduction mechanism consisting of two key stages was proposed.

## • Supplementary materials

No supplementary materials are available.

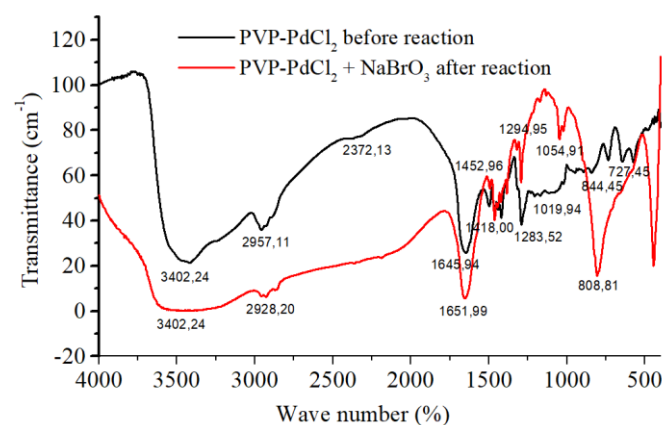


Figure 5 IR spectra of green PVP-PdCl<sub>2</sub> and the used catalyst.

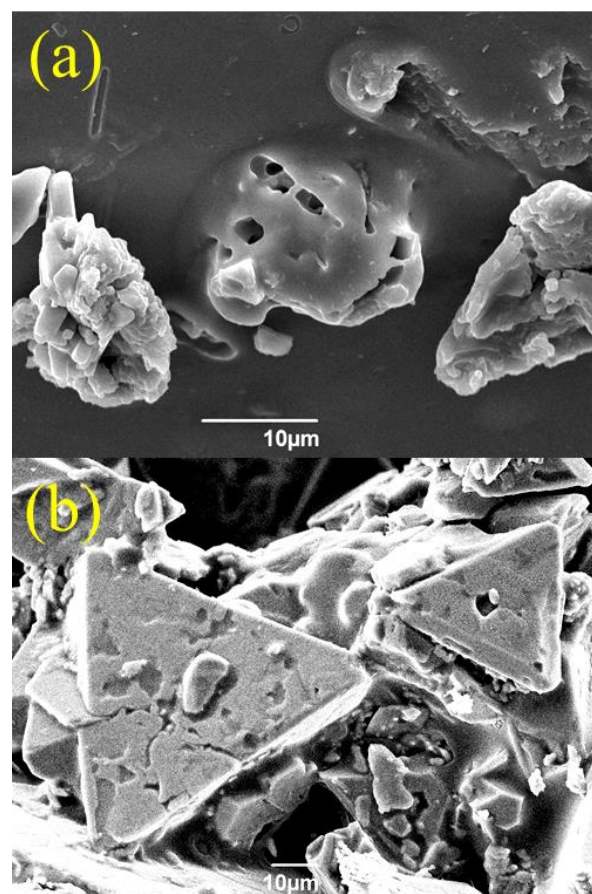


Figure 6 Electronic microphotographs of the Pd(PVP)<sub>3</sub>Cl<sub>2</sub> complex before (a) and after (b) experiment.

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## ● Author contributions

Conceptualization: D.N.A.

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Investigation: I.A.S., A.T.

Methodology: D.N.A., B.S.B.

Supervision: D.N.A.

Writing – original draft: D.N.A., B.S.B.

Writing – review & editing: D.N.A.

## ● Conflict of interest

The authors declare no conflict of interest.

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