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SYNTHESIS AND STUDY OF THE STRUCTURE OF Pd AND Mn NANOPARTICLES IN THE PRESENCE OF POLYVINYLPIRROLIDONE

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Abstract: Poly-N-vinylpyrrolidone is widely used among synthetic polymers due to its non-toxicity and solubility in water and other organic solvents. Complex compounds with metals and non-metals find widespread application in various fields of industry and medicine. The purpose of this study is to synthesize metal-polymer complexes for obtaining a new type of catalyst. Poly-N-vinylpyrrolidone was first dissolved in water and then re-mixed with the addition of the PdCl₂ salt. A reducing agent was added to the solution, and finally the resulting substance was established by means of a binder. The same process was typical for MnCl₂ salt. Complexes obtained studied by various research methods (FTIR, XRD, SEM, UV-Vis). Proceeding from the results of the research methods, we can say that the construction process was successful and the metal nanoparticles settled on the surface and inside the polymer. The obtained complex compounds are intended to be used as catalysts.

Keywords: polymer, Poly-N-vinylpyrrolidone, immobilization, manganese-containing polymer, palladium-containing polymer.

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Introduction

At present, the problem of purposeful creation of catalysts which demonstrate high activity and at the same time provide high selectivity of catalytic processes, is of greater importance. It is known that the effectiveness of the heterogeneous catalytic system is significantly affected by the nature of the carrier. In this regard, the development of new materials that provide the localization and dispersion of active centers necessary for a particular chemical process is considered to be rather important issue. The use of these systems allows the active centers to be evenly distributed on the surface of the carrier, which in turn increases the efficiency of the applied catalysts. Acquisition of hybrid materials based on metal-polymer creates the basis for the development of new prospects in many areas of the chemical

industry. Thus, polyvinylpyrrolidone, a synthetic polymer, is of great interest. Most important features of this polymer are that it is non-toxic, soluble in many organic solvents and water, good adhesion, high tendency to complex. It is these properties that characterize the superiority of polyvinylpyrrolidone over other high-molecular compounds [1-14].

Nickel nanoparticles stabilized by polyvinylpyrrolidone (PVP) were synthesized through modifications to the polyol method. Controlling the Ni/reducing agent (NaBH₄) ratio used in the synthesis led to different nanoparticles samples with average sizes of 3.4, 2.8 and 2.2 nm. Several parameters were evaluated, including the presence of PVP on the nanoparticles, the NaOH concentration, the Ni/Nujol/graphite ratio, the number of cycles

applied and the type of support electrolyte. The application of the Ni nanoparticle-modified electrode as an amperometric sensor showed a good sensitivity of 24.4 $\mu\text{A M}^{-1}$ and a low detection limit of 95.0 $\mu\text{mol L}^{-1}$. [15]

Very narrow and pure silver nanoparticles were synthesized by modified thermal treatment method via oxygen and nitrogen flow in succession. The structural and optical properties of the calcined silver nanoparticles at 600°C with diverse Poly(vinylpyrrolidone) concentrations varying from 2% to 4% were studied by means of different techniques [16].

Poly(vinylpyrrolidone) (PVP) is a polymer capable of complexing and stabilizing Ag and Au nanoparticles formed through the reduction of Ag^+ or AuCl_4^- ions with *N,N*-dimethylformamide. The reduction can be efficiently performed both at reflux and under microwave irradiation; however, each of these methods leads to different nanoparticle morphology and colloid stability. The use of microwave irradiation provides an extra degree of control of the reduction process. The use of PVP with different polymer chain lengths results in particles with similar sizes though with a different degree of stability.

Nanoparticles of Ag, Au, Pd, and Cu were prepared by the reduction of their salts by ethyl alcohol under refluxing conditions in the presence of polyvinylpyrrolidone (PVP). When it comes to Au and Cu, it was necessary to use magnesium metal as a catalyst during the reduction. The nanoparticles are in the 5–35 nm range in the case of Ag, Au, and Pd, but there is considerable agglomeration in the case of Cu even in the presence of PVP. [17]

Manganese (II) compounds are effective catalysts in the large-scale syntheses of many chemically important materials [18].

The research results over the past 10–15 years revealed new promising applications of manganese compounds as catalysts of various organic reactions, such as oxidation of alkanes, alcohols, aldehydes, sulfides, and amines and carbometalation, telomerization, hydrosilylation, chlorination, cross coupling, hydrohydrazination, aziridination, etc.

Manganese compounds are commonly known as stoichiometric oxidizers (KMnO_4 or MnO_2); however, this notwithstanding, Mn and its derivatives have been less studied in the catalysis than other 3d transition metals, although manganese has several advantages. Manganese is actually the third most common transition metal after iron and titanium. In contrast to other metals, this metal is not considered to be a critical resource by the European Union, i.e. there is neither supply risk, nor excessive price volatility which is a persistent problem with precious metals. Another advantage is that Mn is a heavy metal with low toxicity. All of these appealing properties make manganese an ideal candidate for catalytic processes [19,20].

Metal polymer nanocatalysts are widely used in catalytic organic reactions, electrocatalysis and other fields. The main advantages of metal polymer nanocatalysts are that it is possible to conduct a number of reactions at high temperatures and pressures in more moderate conditions. The current article deals with the synthesis and structure of PVP/Pd and PVP/Mn nanocatalysts.

Materials

Polyvinylpyrrolidone, Palladium(II) chloride, Manganese(II) chloride, *N,N'*-Methylenebisacrylamide were procured from SIGMA-ALDRICH, CHEMIE GmbH, Germany.

Polyvinylpyrrolidone

Polyvinylpyrrolidone (average M_w 360,000) is soluble in water and other polar solvents. When dry it is a light flaky hygroscopic powder, readily absorbing up to 40% of its weight in

atmospheric water.

Palladium (II) chloride

Palladium(II) chloride is a palladium coordination entity consisting of palladium(II) bound to two chlorine atoms. It acts as a catalyst. Palladium chloride appears as dark brown crystals.

Manganese (II) chloride

Manganese(II) chloride is the dichloride salt of manganese MnCl_2 . This inorganic

chemical exists in the anhydrous form, as well as the dihydrate ($\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$) and tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$), with the tetrahydrate being the most common form. Like many Mn(II) species, these salts are pink, with the paleness of the color being characteristic of transition metal complexes with high spin d^5 configurations. It is a paramagnetic salt.

N,N'-Methylenebisacrylamide

N,N'-Methylenebisacrylamide (MBAA) is a cross-linking agent used during the formation

of polymers such as polyacrylamide. Its molecular formula is $\text{C}_7\text{H}_{10}\text{N}_2\text{O}_2$; *N'*-methylenebisacrylamide is a white and crystalline solid that does not dissolve very much in cold water.

In considering the above, the work presented deals with the creation of hybrid materials based on metal-polymer frames. Synthetic polymer polyvinylpyrrolidone (PVP) was used as a carrier, and palladium and manganese were used as metals.

Experimental

During the experiment, 1 g of the polymer was first dissolved in 100 ml of water and stirred on a stirrer brand " IKA RCT standard safety control" without heating it for 6 hours to achieve its complete dissolution. After that, the solution was heated at a temperature of 60°C for 4 hours with constant stirring; after the time had elapsed, the prepared solution of metal salt (PdCl_2) was added in the amount of 0.1-0.6 g of metal per 1 g of polyvinylpyrrolidone (PVP) and stirred again in for 3 hours, following which a redox agent (NaBH_4) was added to the solution to reduce palladium ions to Pd^0 and a precipitate was observed, the color of the solution changed from colorless to silvery white. At the end, the resulting precipitate was

washed with ether, distilled water to remove Cl^- ions and from the remains of the PdCl_2 salt. Then the precipitate was dried in a Petrik dish in an oven at 60°C . The catalyst for the production of the constructed complex was dissolved in 10ml of water and added 15ml of 0.2 g of sewing agent *n,N'*-methylene bis acrylamide and mixed in the mixer at 60°C temperature for 6 hours. The obtained solution evaporated at room temperature. The films obtained after evaporation were irradiated under ultraviolet light at $30\text{-}40^\circ\text{C}$ temperature for 6 hours. As a source of ultraviolet light, Mercury-Quartz CKP-4 lamps were used. The films were washed with ethanol-water, 1N hydrochloric acid-water and 0.01 N NaOH-water.

Results and discussion

The obtained material was examined by Fourier-transform infrared spectroscopy (FTIR), Ultraviolet-visible spectroscopy (UV), Scanning Electron Microscopy (SEM) and X-ray diffraction analysis (XRD) devices and regular distribution of metal ions on the surface and volume of the carrier was observed. In the FTIR spectra in Figure1, PVP becomes asymmetric when the peak metal salt characteristic of the $\text{C}=\text{O}$ compound is added, which is a clear example of the strong interaction between PVP and Pd (II) in the PVP- PdCl_2 complex. PVP in studied complex has a characteristic absorption band of 3400 cm^{-1} . The absorption band belonging to the carbonyl group in PVP is 1651 cm^{-1} , which is due to the

expansion of the $\text{C}=\text{N}$ compound in the lactam ring. In the obtained hybrid material, this strip slides as $1510\text{-}1645\text{ cm}^{-1}$.

As can be seen from Fig. 2, initially PVP is an amorphous substance, but when palladium salt is added to the polymer and then reduced, the result is a hybrid material (PVP / Pd^0) with a crystalline structure on the radiograph. The data obtained as a result of UV studies of the obtained hybrid material (Fig. 3) show the formation of covalent bonds of palladium with the polymer through the donor-acceptor mechanism. It can be concluded that during the interaction, radicals are formed in the polymer, and their recombination creates the basis for the formation of built structures.

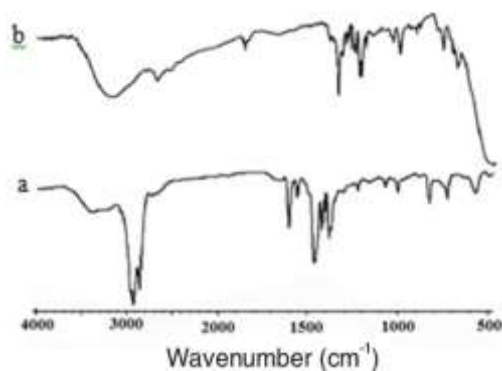


Fig. 1. a) Poly-N-vinylpyrrolidone; b) Poly-N-vinylpyrrolidone / Pd⁰

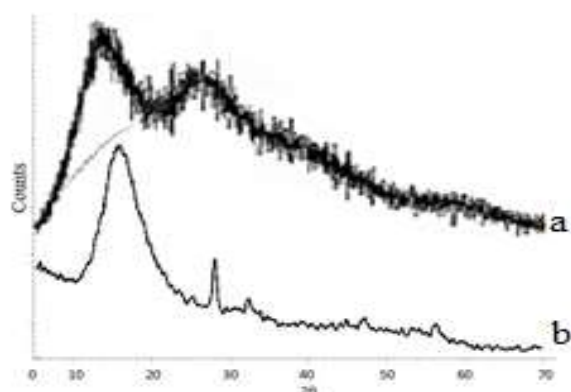


Fig. 2. Diffractograms: a) Poly-N-vinylpyrrolidone; b) Poly-N-vinylpyrrolidone/Pd⁰

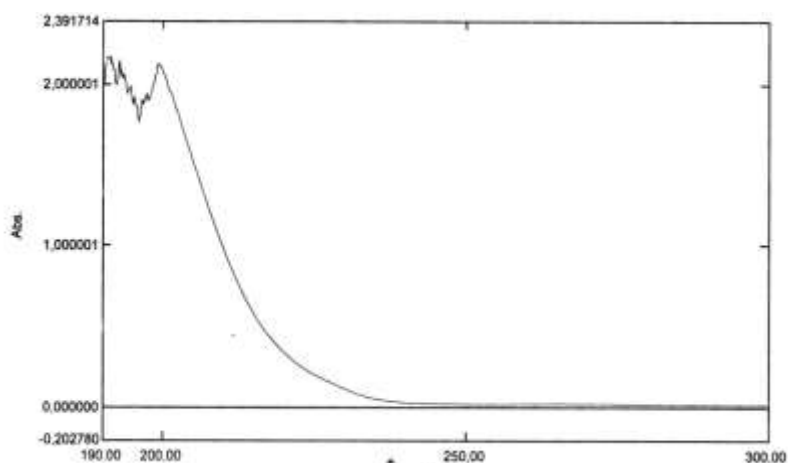


Fig. 3. UV structure of poly-N-vinylpyrrolidone (PVP)

Initially, polyvinylpyrrolidone (PVP) was imaged in an SEM apparatus and which showed that its surface structure was scattered (Fig.4)

The SEM description of the constructed polymer (PVP) was drawn and it was determined that it has a regular structure. The

regular structure of the polymer is due to the fact that it forms a reticulated structure (Fig. 5).

After the addition of metal to the polymer (PVP), its structure becomes regular, and during the measurements made by the device, the size of the spherical shape of the domains in the image varies between 3-5 microns (Fig.6). The

particle size was found to be 35-50 nm (a) in the poly-N-vinylpyrrolidone / Pd complex and 15-20 nm (b) in the poly-N-vinylpyrrolidone / Mn complex. Because these nanoparticles are ultradispersed, the metal nanoparticles are evenly distributed over the polymer.

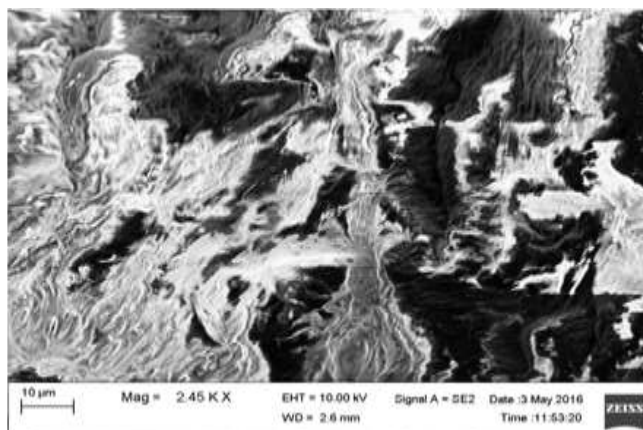


Fig . 4. SEM structure of poly-N-vinylpyrrolidone (PVP)

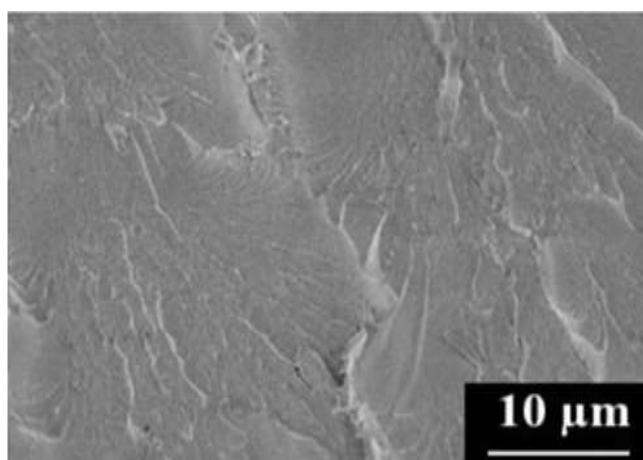


Fig. 5. SEM structure of crosslinked poly-N-vinylpyrrolidone (PVP)

We carried out the same experiment with Mn using manganese (II) as chloride salt for it. Our experiment's results are studied by FTIR spectrum (Figure 6).

In the FTIR spectrum of the polymer-metal (Mn / PVPr) complex, a wide absorption band of 3485 cm^{-1} - 2891 cm^{-1} is hydroxyl, 2891 cm^{-1} to 1647 cm^{-1} CH, 1647 cm^{-1} to 1410 cm^{-1} C = O and 1410 cm^{-1} to 1142 cm^{-1} belong to the OH groups. Contrary to the PVR FTIR

spectrum, shifts are observed in the absorption bands in the spectrum of the complex.

The diffraction peaks observed mainly in the diffraction diagram of Mn / PVPr composite material can be attributed to the monoclinic phase. It is also found in tetrachannel and orthorombic diffraction peaks along with the monocline phase. This is explained by the addition of Mn ions to the surfactant PVPr, which causes phase changes in the PVPr (Fig.7).

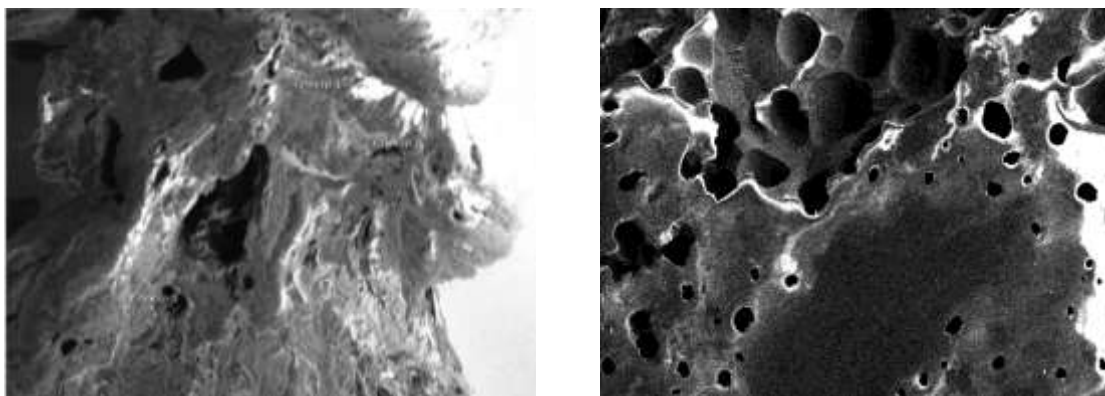


Fig. 6. a) SEM structure of poly-N-vinylpyrrolidone-Pd complex
b) SEM structure of poly-N-vinylpyrrolidone-Mn complex

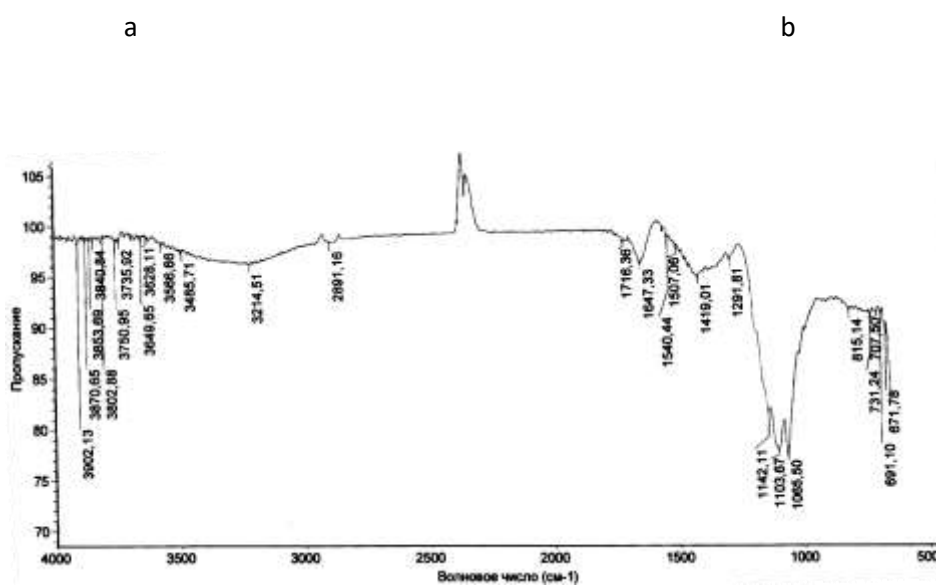


Fig.7. FTIR spectrum of the constructed poly-N-vinylpyrrolidone-Mn complex

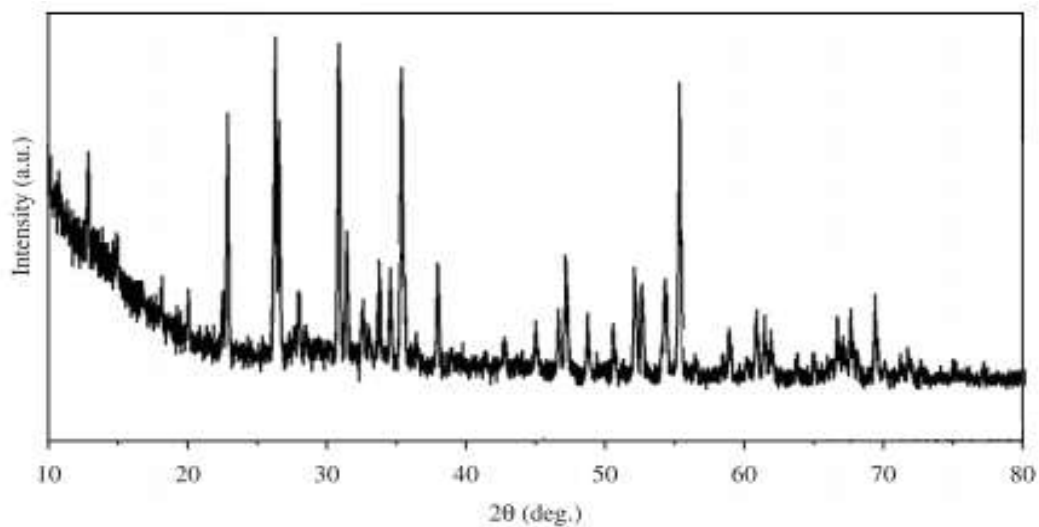
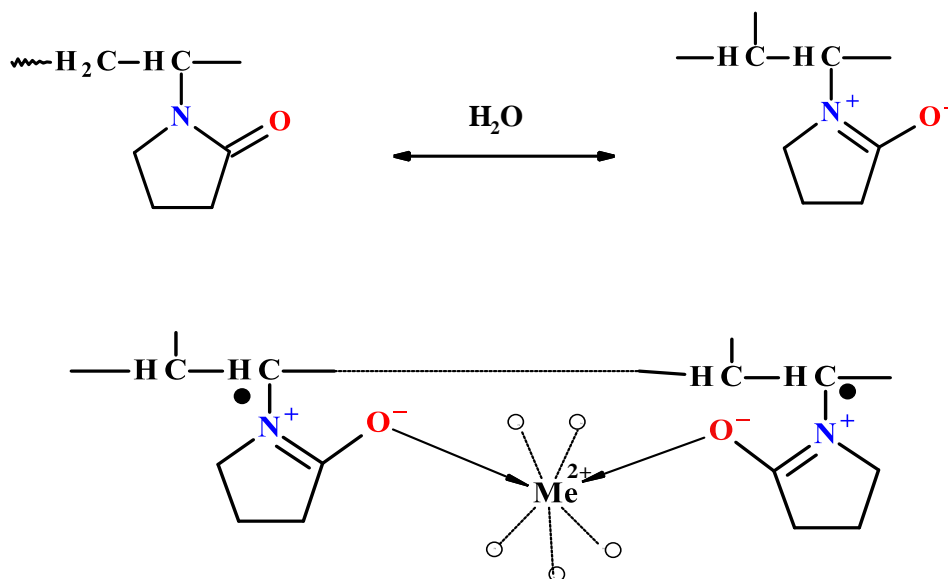


Fig. 8. Diffractogram of the constructed poly-N-vinylpyrrolidone-Mn complex

Schematic structure of final product



Me – Mn, Pd

○ - crystallization water

● - NO_3^-

Conclusion

The structure of poly-N-vinylpyrrolidone and palladium, polyN vinylpyrrolidone and manganese complexes obtained as a result of the research work was studied by Fourier-transform infrared spectroscopy, Ultraviolet-visible spectroscopy, Scanning Electron Microscopy and X-ray diffraction analysis methods. It is

intended to use synthesized catalysts as catalysts in the process of hydrogenation of aromatic hydrocarbons (benzene, toluene). The use of a number of metal-polymer catalysts in the same practice is aimed at investigating which of them is more selective and active for this process.

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POLİVİNİLPIRROLİDON MÜHİTİNDƏ Pd və Mn METAL NANOHİSSƏCİKLƏRİNİN SİNTEZİ VƏ QURULUŞUNUN ÖYRƏNİLMƏSİ

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Xülasə: Poli-N-vinilpirrolidon suda və digər üzvi həlledicilərdə həll olması və qeyri-toksiklik xüsusiyyətinə görə sintetik polimerlər arasında geniş istifadə olunur. Metallar və qeyri-metallarla

əmələ gətirdiyi mürəkkəb birləşmələr sənayenin və təbabətin müxtəlif sahələrində tətbiq olunur. Bu tədqiqatın məqsədi yeni növ katalizator əldə etmək üçün Pd və Mn metal-polimer komplekslərini sintez etməkdir. Poli-N-vinilpirrolidon əvvəlcə suda həll edilmiş, PdCl₂ duzu əlavə edildikdən sonra qarışdırılmışdır. Məhlulə reduksiyaedici maddə əlavə edilir və maddə tikici agent vasitəsi ilə tikilir. Eyni proses manqan duzu ilə də aparılmışdır. Alınan kompleks birləşmələr müxtəli tədqiqat üsulları ilə (FTIR, XRD, SEM, UV-Vis) tədqiq edilmişdir. Tədqiqat üsullarının nəticələrinə əsasən tikilmə prosesi uğurla aparılmış, metal nanohissəciklər polimerin səthində və daxilində yerləşmişdirlər. Alınan kompleks birləşmələrin katalizator kimi tətbiq olunması nəzərdə tutulur.
Açar sözlər: polimer, Poli-N-vinilpirrolidon, immobilizasiya, manqan tərkibli polimer, palladium tərkibli polimer.

СИНТЕЗ И ИССЛЕДОВАНИЕ СТРУКТУРЫ НАНОЧАСТИЦ Pd и Mn В СРЕДЕ ПОЛИВИНИЛПИРРОЛИДОНА

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Аннотация: Поли-N-винилпирролидон широко используется среди синтетических полимеров, благодаря своей нетоксичности и растворимости в воде и других органических растворителях. Комплексные соединения его с металлами и неметаллами широко используются в различных областях промышленности и медицины. Целью данного исследования является синтез Pd и Mn металлополимерных комплексов для получения катализаторов нового типа. Первоначально поли-N-винилпирролидон растворяли в воде, затем добавляли соль PdCl₂ и перемешивали. После чего к раствору добавляли восстановитель и, наконец, полученное вещество шивали с помощью шивающего агента. Тот же процесс был проведен с марганцевой солью. Полученные комплексы изучались различными методами исследования (ИК, РФА, СЕМ, УФ-Vis). По результатам исследования можно сказать, что процесс модификации прошел успешно и наночастицы металла расположились на поверхности и внутри полимера. Полученные комплексные соединения предполагается использовать в качестве катализаторов.

Ключевые слова: полимер, поли-N-винилпирролидон, иммобилизация, марганец-содержащий полимер, палладий-содержащий полимер.