Chemical Journal of Kazakhstan
Volume 2, Number 82(2023), 5-15 https://doi.org/10.51580/2023-2.2710-1185.09

UDC 541.057.17

SYNTHESIS AND STUDY OF METAL-POLYMER NANOCOMPOSITES, BASED ON A COPOLYMER OF POLYETHYLENE GLYCOL MALEATE WITH ACRYLIC ACID, AND ITS CATALYTIC PROPERTIES

T.O. Khamitova[1], M.Zh. Burkeyev[2], A.K. Kovaleva[2*], D. Havlicek[3]

[1]Saken Seifullin Kazakh Agro Technical University, Astana, Kazakhstan
[2]E.A. Buketov Karagandy University N-PLC, Karaganda, Kazakhstan
[3]Charles University, Czech Republic
[*]E-mail:cherry-girl1899@mail.ru

Abstract: *Introduction*. With the development of the chemical industry, the search for and synthesis of new, and modification of the existing nanocatalytic systems are of great importance. In view of this, the preparation of new catalysts by immobilization of transition metal metals in a polymer matrix becomes an important direction in chemical synthesis. *Purpose* of this work is to submit experimental data on the synthesis and study of the catalytic properties of silver and nickel nanostructures, immobilized in polymer matrices, based on a binary system of unsaturated polyester – polyethylene glycol maleate – with acrylic acid. Nanocomposites have been obtained by reducing a solution of nickel and silver metal salts with sodium hypophosphite in the presence of an ammonia solution of silver chloride. *Methodology*. By the methods of spectroscopy, microscopy the sizes, structure and morphology of polymer-stabilized nanoparticles are determined. *Results*. The obtained nanocomposites contain isolated Ag^0 nanoparticles with a diameter of 60±10 nm, predominantly spherical in shape and metallic Ni^0 with a cubic shape of 70±10 nm, uniformly distributed in the polymer matrix, as well as agglomerates on the surface of the polymer matrix, the dimensions of which vary within 150–200 nm. The catalytic activity of the synthesized nanocomposites, which show high efficiency in comparison with the standard metal catalysts, has been also studied.

Keywords: polyethylene glycol maleate, metal-polymer nanocomposite, catalytic activity, nanocomposite, nanoparticles, polymer matrix

Khamitova Tolkyn Ondirissovna	*PhD, Senior Lecturer, Department of Soil Science and Agrochemistry, Saken Seifullin Kazakh Agrotechnical University, 010000 Astana. E-mail: khamitova.t@inbox.ru*
Burkeyev Meiram Zhunussovich	*Doctor of Chemical Sciences, Professor, Corresponding Member of the National Academy of Sciences of the Republic of Kazakhstan*
Kovaleva Anna Konstantinovna	*PhD, Senior Researcher, E.A. Buketov Karagandy University. E-mail: cherry-girl1899@mail.ru*
David Havlicek	*Associate Professor, RNDr, CSc. Charles University, Prague, Czech Republic, Prague, 400 96, Pasterova 1. E-mail: David.havlicek@natur.cuni.cz*

Citation: Khamitova T.O., Burkeyev M.Zh., Kovaleva A.K., Havlicek D. Synthesis and study of metal-polymer nanocomposites, based on a copolymer of polyethylene glycol maleate with acrylic acid, and its catalytic properties. *Chem. J. Kaz.*, **2023**, 2*(82)*, 5-15. DOI: https://doi.org/10.51580/2023-2.2710-1185.09

1. Introduction

In recent years, many works have been carried out, aimed at creating various types of nanoscale structures that include metal nanoparticles in combination with the functional polymers. Such particles, having a significant reactivity and an increased tendency to ion exchange, upon immobilization in the polymer matrices, impart new properties to the resulting nanocomposites. The stability of nanoparticles in polymer matrices is maintained for a long time. The scope of application of nanocomposite materials is very extensive: from catalytic processes in the chemical industry to the manufacture of medical and cosmetic preparations. As a result, large-scale fundamental and applied research to develop innovative materials and technologies, especially nanocomposites, is an urgent task, and is of great scientific and practical interest [1, 2].

From a practical point of view, polymer-immobilized metal nanoparticles (MPNs) are of great interest for obtaining a new generation of efficient and stable hydrogenation and oxidation nanocatalysts operating on the principle of enzymes under mild conditions (at the room temperature and atmospheric pressure).

Based on the foregoing, it can be concluded that the synthesis of new nanocatalysts of the “metal-polymer matri” type, in combination with the immobilization of catalytically active transition metals in polymeric supports, opens up a wide range of their applications. Therefore, today the search for new catalytic systems, in particular, nanocatalysts with high activity and selectivity, is an urgent task.

In previous works, we presented the results of the research on the development of new methods for the synthesis of “smart” polymers, based on unsaturated polyesters, cured with the unsaturated carboxylic acids. The properties of polymeric materials obtained on their basis are unique, providing a wide range of their practical applications in agriculture, medicine, petrochemistry, and chemical synthesis. In this regard, it should be noted that the synthesis of “smart” copolymers with a high moisture absorption capacity, based on available and inexpensive raw materials – unsaturated polyesters cured with ionic vinyl monomers – and its further study is an important direction [3-6].

Previously, new mono- and bimetallic metal-polymer nanocomposites based on the copolymers of polyethylene-(propylene)glycolmaleines (p-EGM, p-PGM) with AA and metallic cobalt were synthesized. The possibility of using copolymers of the above unsaturated polyesters with AA as a matrix for the preparation of effective hydrogenation catalysts has been shown. Thus, it has been found that the resulting MPCs contain isolated NPMs with a diameter of 30–120 nm, predominantly spherical in shape, uniformly distributed in the polymer matrix [5].

The main purpose of this work is to study the physicochemical properties and catalytic activity of nanocomposites, based on the smart polymer matrix p-EGM–AA with metals, nickel and silver.

2. Experimental part

The immobilization of metal particles into polymeric substrates of the p-EGM–AA binary system with a composition of 14.8:85.2 wt.% was carried out by reducing Ni^{+2}, Ag^{+1} to Ni^0, Ag^0 with sodium hypophosphite (0.5 N) in a 0.5 N solution of their nitrates, in the presence of a catalyst – an ammonia solution of silver chloride. The reduction of Ni^{+2}, Ag^{+1} in the volume of the p-EGM–AA polymer matrix was carried out in several stages:

– incorporation of Ni^{+2}, Ag^{+1} ions into the polymer matrix;

– diffusion of reagents inside the polymer matrix;

–the reaction between nickel and silver nitrates and sodium hypophosphite, proceeding with the formation of nanosized metal particles (NPs).

The salt reduction method used in this way had an important advantage over the other methods of NPM synthesis: reproducibility of the results and the possibility of obtaining large amounts of nanoparticles with a narrow size distribution. The type of reducing agent in this case had a significant effect on the formation of metal NPs. Thus, the MPCs of p-EGM–AA/Ag^0 and p-EGM–AA/Ni^0 were obtained. Figure 1 shows the main structural fragments of p-EGM–AA/Ag:

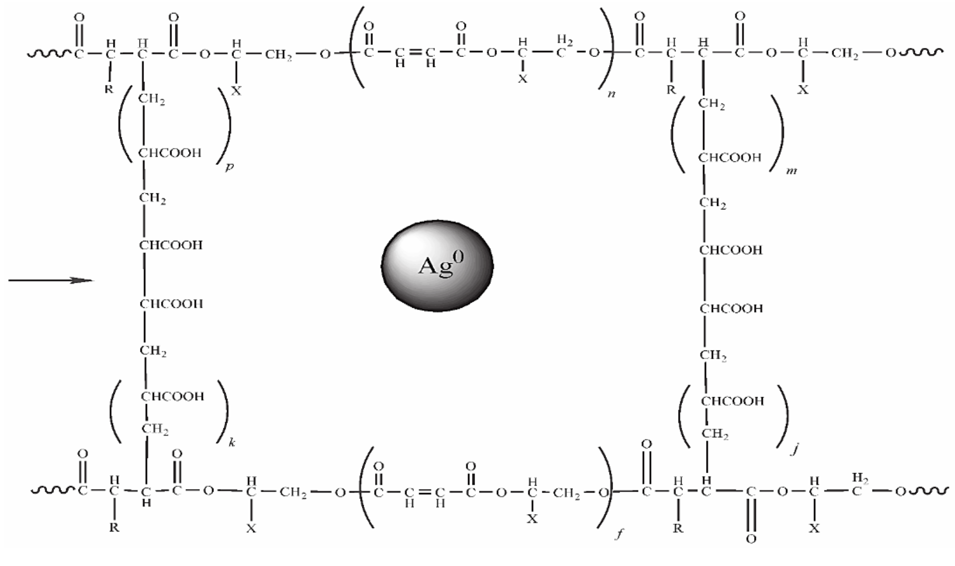


Figure 1 – Structural fragments of the p-EGM–AA/Ag monometallic polymer complex

The structure of the polymer and nanocomposites was studied by microscopy. For example, an ultrathin sample was imaged, using a universal thermal field transmission electron microscope (TEM) JEOL JEM-2100 200 kV (Japan); The resolution at the optimal working distance was 0.8 nm at 2 kV, at the convergence point was 1.2 nm at 1 kV Figure 2.

The polymers molecular weight characteristics were analyzed by gel permeation chromatography in dioxane on a PolymerLabs GPC-120 chromatograph with two PLgel columns. Molecular weight (MW) was calculated according to calibration standards.

The study of the structure, morphology, elemental composition of the synthesized complexes was established by microscopy on a MIRA 3 TESCAN SEM “Oxford Instruments” (2012) with a high-performance silicon-drift detector X-Act for elemental analysis at an accelerating voltage of 20 kV Figures 3, 4.

The amount of adsorbed metal in the complex was determined on a 4210 MP-AES atomic emission spectrometer (Agilent Technologies Bayan Lepas Free, Malaysia), based on determining the elemental composition of the substance from the optical emission spectra of atoms and ions of the analyzed sample excited by nitrogen plasma.

The study of catalytic activity was carried out by pyridine hydrogenation in a diaphragm electrocatalytic thermostatic cell, divided into anode and cathode parts by an MK-40 membrane diaphragm, according to the procedure. The anode was a platinum grid, and the cathode was a copper plate (type I conductor) with a surface area of 0.048 dm^2, which tightly adjoined the bottom of the electrolyzer and serveed as a substrate for the catalyst. Hydrogenation of pyridine was carried out at different values of the current strength and different temperatures. The hydrogenation process included the following steps:

– start of the process – an introduction of the solutions and regulation of the process conditions, 20% NaOH solution was used as anolyte, 5% NaOH solution was used as catholyte;

– the resulting metal-polymer complexes were saturated with electrocatalytic hydrogen for 30 min in the cathode part of the cell until the ratio of the volumes of released H_2 and O_2 in the burettes was equal to 2:1;

– the hydrogenation process itself – a sample of the substrate (pyridine) was introduced into the cathode space of the cell, and the volumes of the released hydrogen and oxygen were noted every 2 min. The process was carried out until the absorption of hydrogen ceased. The amount of absorbed hydrogen was used to determine the rate of reduction of pyridine $W_{(H2)}$ ($mol \cdot s^{-1}$) and the hydrogen utilization factor.

The hydrogenation reaction products were analyzed on an Agilent 7890A chromatograph with a 5975C mass selective detector. The obtained samples were extracted on catholyte with diethyl ether in a ratio of 1:1. Preliminary preparation of samples was carried out on a CryoMill vibratory mill (Retsch, Germany, 2015).

3. The discussion of the results

For the synthesis of the polymer matrix, polyethylene (propylene) glycol maleinate with a molecular weight of ~2820 Da has been used as the initial monomer. The molecular weight of the polymer affects the copolymer swelling degree and, accordingly, determines the pore size of the polymer matrix. The degree of swelling of the studied p-EGM with AA binary systems has been

~1900–2400%. The polymer matrix structure can have a significant effect on the crystal structure and morphology of the resulting metal NPs; therefore, special attention should be paid to the analysis of the surface morphology of copolymers. For example, Figure 2 shows electron micrographs of the p-EGM–AA binary systems studied by us.

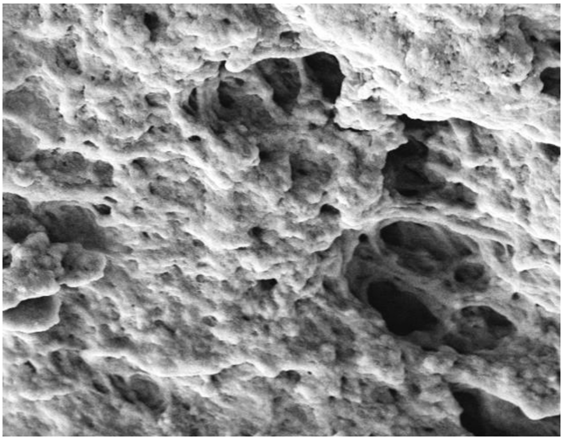
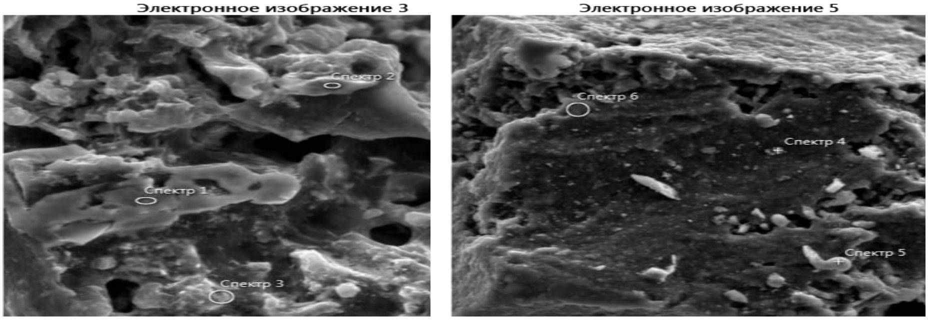


Figure 2 – Micrograph of the polymer matrix – p-EGM–AA (14.8:85.2 wt.%)

According to the TEM results for the p-EGM–AA copolymer with a composition of 14.8:85.2 wt.%, the pore size of network copolymers varies from 0.5 μm to 1.1 μm. It should be noted that the uniform pores of the polymer matrix promote the formation and growth of individual particles in the bulk of the polymer, preventing their aggregation.

Further, the nanocomposites, obtained by the reduction of a solution of salts of nickel and silver metals with sodium hypophosphite in the presence of an ammonia solution of silver chloride contain the isolated Ag^0 NPs with a diameter of 50±10 nm, predominantly spherical in shape and metallic Ni^0 NPs with a size of 60±10 nm, cubic in shape (Figure 3a), evenly distributed in the polymer matrix. In some cases, they form agglomerates on the surface of the polymer matrix with sizes in the range of 150–180 nm (Figure 3b). Previously, it was found that metal-polymer complexes based on copolymers of p-EGM with AA, immobilized in them and reduced to Co^0, are resistant to aggregation and oxidation, which gives us the right to assume a similar behavior of our samples, containing Ag^0 and Ni^0.



a b

Figure 3– Electron micrographs of metal particles in nanocatalysts:
a-nickel in p-EGM–AA/Ni; b – silver in p-EGM–AA/Ag

The main part of NPs (about 80%) of the total mass is made up of the particles with the sizes from 25 to 80 nm. A smaller part falls on larger formations, 85–110 nm in size. Aggregates larger than 210 nm (about 15%) are formed as a result of the adhesion of small particles that are marked on the polymer surface.

The use of the p-EGM–AA binary system makes it possible to achieve a high uniformity of the distribution of metal particles (Ni^0) in the volume of the polymer matrix, as evidenced by the results of energy dispersive spectrometry, shown in Figure 4.

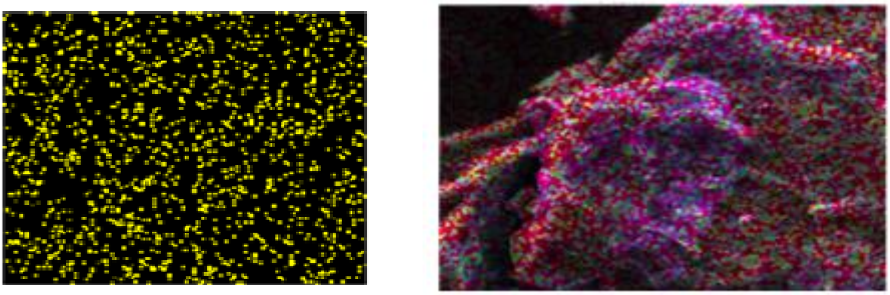


Figure 4 – Micrographs of the distribution of individual elements in the volume of the polymer matrix

According to the results of energy dispersive spectrometry, the average number of metal particles per 10 μm is ~1300±100 units. The particles for Ag^0 and ~1000±100 units – for Ni^0. The content of Ag^0 and Ni^0 metals in nanocomposites is ~20 wt.% of the total mass.

Figure 5 below shows the hydrogenation curve of pyridine, which characterizes the course of the process without a catalyst. An analysis of this curve shows that the character is not pronounced: it lies almost parallel to the abscissa axis, while at the initial stage, absorption of a certain amount of hydrogen is observed. In comparison with the process of hydrogenation without a catalyst, the hydrogenation curve of pyridine in the presence of p-EGM–AA/Ni^0 and p-EGM–AA/Ag^0 shows intense absorption of hydrogen. The maximum reaction rate is reached already by 20–25 minutes (Figure 5), and then drops sharply. During this time, in the system with the participation of p-EGM–AA/Ni^0, pyridine is hydrogenated up to 40% to the reaction products, and in the presence of p-EGM–AA/Ag^0, up to 45%. Among the reaction products, in addition to the final product – piperidine – secondary products are found: in particular, tetrahydropyridine (from 4 to 7%) and dipiperidyl (from 5 to 7%).

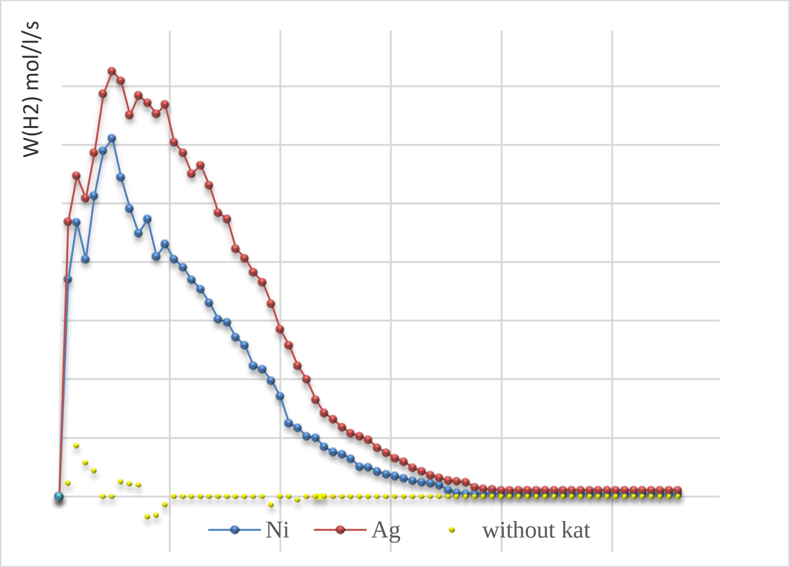


Figure 5– Change in the rate of pyridine hydrogenation during the reaction on catalysts: p-EGM–AA/Ni^0 and p-EGM–AA/Ag^0

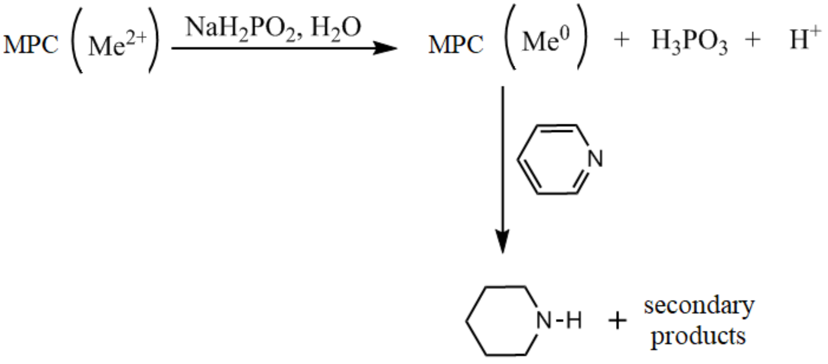
As can be seen from the curve of the dependence of the rate (W) of the reaction of hydrogenation of pyridine to piperidine on time (t), it has 3 sections, similar for the both systems under study. At the first stage, hydrogen is intensively absorbed, therefore, the main part of pyridine is hydrogenated at the initial stage of the process. In the second section of the curve, a decrease in the hydrogenation rate is observed, due to the consumption of a part of the pyridine subjected to hydrogenation in the first stage. In the final section, the reaction rate remains almost unchanged, which is proof of the completion of the process we are studying.

Chromatographic analysis (Table 1) shows that, in addition to piperidine, the catholyte after hydrogenation contains a secondary product, tetrahydropyridine, in small amounts. Table 1 also shows the main results of the electrocatalytic hydrogenation of pyridine at different current strengths in comparison. It has been found that in the presence of p-EGM/AA-Ni^0 and p-EGM/AA-Ag^0 nanocomposites at 1A, it has contributed to the uptake of ≈70 ml and 60 ml of hydrogen, respectively, which is almost 3 times higher than in the presence of Ni skeletal catalyst and in 7 times higher in the absence of a catalyst. The substance yield of piperidine has been 88% under the conditions of 1.5 A, 25°C, using p-EGM/AA-Ni^0. The yield of piperidine on the substance as a whole varies within 70–88%.

Table 1– The results of the electrocatalytic hydrogenation of pyridine at different current strengths in comparison

Catalyst	Current strength, A	Pressure, mm Hg Art.	Volume of absorbed hydrogen (Vabsorbed H_2), ml	Process duration, min	Product yield – piperidine, %	Secondary products, %
withoutcat alyst	0.5	752	5.6	40	5.12	–
	1.0	754	8.7	20	6.30	–
	1.5	754	9.1	30	8.54	–
	2.0	762	8.1	28	7.93	–
Ni	0.5	761	22.1	60	9.66	–
	1.0	765	22.9	44	13.85	0.4
	1.5	760	24.3	40	16.85	0.8
	2.0	760	23.4	40	15.48	1.1
п-ЭГМ–АК/Ni^0	0.5	772	58.7	120	72.43	5.0
	1.0	780	68.9	82	82.71	4.3
	1.5	772	76.7	66	88.21	3.5
	2.0	772	67.2	54	86.47	8.0
п-ЭГМ–АК/Ag^0	0.5	775	59.3	120	71.88	5,3
	1.0	760	61.5	86	80.89	5.1
	1.5	767	68.7	78	83.28	4.2
	2.0	760	69.9	72	79.98	9.2
Experimental conditions: T= 25°C – not determined						

MPC (Me^{2+}) p-EGM–AA/Ni^0 and p-EGM–AA/Ag^0 perform a dual role in the process: at the same time they accelerate the decomposition of hypophosphite and further the nanocomposite accelerates the reduction of pyridine to piperidine:



The activity of p-EGM–AA/Ni^0 and p-EGM–AA/Ag^0 metal catalysts in pyridinane hydrogenation is an order of magnitude higher than that of skeletal nickel. So, for example, the reaction rate with the use of nanometallic systems increases by ~5–6 times, as compared with skeletal nickel, and ~10–11 times higher, as compared with the implementation of the hydrogenation process without a catalyst. It should also be noted that the selectivity of the nanocatalytic systems under study with respect to piperidine is ~3–4 times higher than that of skeletal nickel.

4. Conclusion

As the studies show p-EGM–AA/Ni^0, p-EGM–AA/Ag^0 exhibit a high catalytic activity, chemical stability, and selectivity in the hydrogenation process. Reducing the size of the catalyst particles to nanometric ones makes it possible to increase the contact surface of the polymer with the reaction medium and, thereby, to increase the efficiency of catalysis by several times, and the gel matrix protects the particles from coagulation and oxidation. The obtained nanocomposites under the new synthesis conditions contain the isolated Ag^0 NPs, the diameter of which is 60±10 nm, having a predominantly spherical shape, and metallic Ni^0 NPs, the size of which does not exceed 70±10 nm, having a cubic shape, uniformly distributed in the polymer matrix. In some cases, on the surface of the polymer matrix, they stick together into agglomerates, the dimensions of which vary within 150–200 nm. The reaction rate of catalytic hydrogenation, using the synthesized nanometallic systems increases by ~5–6 times as compared with skeletal nickel, and by ~10–11 times as compared with hydrogenation in the absence of a catalyst. On the basis of the data obtained, it has been established that the selectivity of the nanocatalysts studied by us for piperidine is ~3–4 times higher than that for skeletal nickel. The substance yield of piperidine has been 88% under the conditions of 1.5 A, 25°C, using p-EGM–AA/Ni^0.

The work has been carried out at the Research Institute of Chemical Problems in the Laboratory of Biotechnology of the N-PLC of E.A. Buketov Karaganda University (Karaganda, Kazakhstan), and on the basis of the analytical and inorganic department of the University of Karlov (the Czech Republic).

Conflict of Interest: There is no conflict of interest between the authors.

ПОЛИЭТИЛЕН ГЛИКОЛЬ МАЛЕИНАТ ПЕН АКРИЛ ҚЫШҚЫЛЫ СОПОЛИМЕРІ НЕГІЗІНДЕГІ МЕТАЛЛ-ПОЛИМЕРЛІ НАНОКОМПОЗИТТЕРДІ СИНТЕЗДЕУ ЖӘНЕ ЗЕРТТЕУ, ОЛАРДЫҢ КАТАЛИТИКАЛЫҚ ҚАСИЕТТЕРІ

***Т.О. Хамитова*[1*], *М.Ж.Буркеев*[2], *А.К.Ковалева*[2*], *D.Havlicek*[3]**

[1] *КЕАҚ Сәкен Сейфуллин атындағы Қазақ агротехникалық университеті, Астана, Қазақстан*
[2] *КЕАҚ Академик Е.А.Бөкетов атындағы Қарағанды университеті, Қарағанды, Қазақстан*
[3]*Карлов университеті, Прага, Чехия*
[*]*E-mail: cherry-girl1899@mail.ru*

Түйіндеме: *Кіріспе.* Химия өнеркәсібінің дамуымен жаңа материалдарды іздеу және синтездеу және қолданыстағы нанокаталитикалық жүйелерді модификациялау үлкен маңызға ие болып отыр. Осыған байланысты ауыспалы металдарды полимерлі матрицада иммобилизациялау арқылы жаңа катализаторларды дайындау химиялық синтезде маңызды бағытқа айналады. *Жұмыстың мақсаты* – қанықпаған полиэфир – полиэтиленгликоль малеинат–акрил қышқылы бинарлық жүйесі негізіндегі полимерлік матрицаларда иммобилизацияланған күміс және никель наноқұрылымдарының синтезі және каталитикалық қасиеттерін зерттеу бойынша тәжірибелік деректерді ұсыну. Нанокомпозиттер никель және күміс металл тұздарының ерітіндісін күміс хлоридінің аммиак ерітіндісінің қатысуымен натрий гипофосфитімен тотықсыздандыру арқылы алынды. *Әдістеме.* Спектроскопия, микроскопия әдістерімен полимермен тұрақтандырылған нанобөлшектердің өлшемдері, құрылымы және морфологиясы анықталды. Алынған нанокомпозиттердің құрамында диаметрі 60±10 нм оқшауланған Ag^0 нанобөлшектері бар, пішіні басым сфералық және текше пішіні 70±10 нм металлдық Ni^0, полимер матрицасында біркелкі таралған, сонымен қатар полимер бетіндегі өлшемдері 150–200 нм аралығындағы агломераттар бар. Стандартты катализаторлармен салыстырғанда жоғары тиімділік көрсететін синтезделген нанокомпозиттердің каталитикалық белсенділігі де зерттелді.

Түйінді сөздер: полиэтиленгликоль малеинаты, металл-полимерлі, нанокомпозит, каталитикалық белсенділік, нанокомпозит, нанобөлшектер, полимер матрицасы.

Хамитова Толкын Ондирисовна	*PhD*
Буркеев Мейрам Жунусович	*Химия ғылымдарының докторы, профессор*
Ковалева Анна Константиновна	*PhD*
Havlicek David	*қауымдастырылған профессор, RNDr*

СИНТЕЗ И ИССЛЕДОВАНИЕ МЕТАЛЛ-ПОЛИМЕРНЫХ НАНОКОМПОЗИТОВ НА ОСНОВЕ СОПОЛИМЕРОВ ПОЛИЭТИЛЕНГЛИКОЛЬ МАЛЕИНАТА С АКРИЛОВОЙ КИСЛОТОЙ, И ИХ КАТАЛИТИЧЕСКИЕ СВОЙСТВА

Т.О.Хамитова[1*], М.Ж.Буркеев[2], А.К.Ковалева[2*], D.Havlicek[3]

[1]Казахский Агротехнический университет имени Сакена Сейфуллина, Астана, Казахстан
[2]НАО Карагандинский университет имени академика Е.А. Букетова, Караганда, Казахстан
[3]Институт неорганической химии Чешской Академии Наук, Husinec-Rez, Czech Republic
[*]E-mail: cherry-girl1899@mail.ru

Резюме. *Введение.* С развитием химической промышленности большое значение приобретают поиск и синтез новых и модификация существующих нанокаталитических систем. В связи с этим получение новых катализаторов путем иммобилизации переходных металлов в полимерную матрицу становится важным направлением в химическом синтезе. *Цель настоящей работы* – представить экспериментальные данные по синтезу и изучению каталитических свойств наноструктур серебра и никеля, иммобилизованных в полимерные матрицы на основе бинарной системы ненасыщенный полиэфир –полиэтиленгликоль малеинат – с акриловой кислотой. Нанокомпозиты получали восстановлением раствора солей металлов никеля и серебра гипофосфитом натрия в присутствии аммиачного раствора хлорида серебра. *Методология.* Методами спектроскопии, микроскопии определены размеры, структура и морфология полимер-стабилизированных наночастиц. *В результате* полученные нанокомпозиты содержат изолированные наночастицы Ag^0 диаметром 60±10 нм преимущественно сферической формы и металлический Ni^0 кубической формы 70±10 нм, равномерно распределенные в полимерной матрице, а также агломераты на поверхности полимерная матрица, размеры которой колеблются в пределах 150–200 нм. Исследована также каталитическая активность синтезированных нанокомпозитов, проявляющих высокую эффективность по сравнению со стандартными металлическими катализаторами.

Ключевые слова: полиэтиленгликоль малеинат, металл-полимерный нанокомпозит, каталитическая активность, нанокомпозит, наночастицы, полимерная матрица

Хамитова Толкын Ондирисовна	*PhD*
Буркеев Мейрам Жунусович	*Доктор химических наук, профессор*
Ковалева Анна Константиновна	*PhD*
Havlicek David	*ассоциированный профессор, RNDr*

References

1. Chow P.E. (ed.) *Gold Nanoparticles: Properties, Characterization and Fabrication*. New-York, Nova Science Publisher, **2010**, 250.

2. Pomogailo A.D., Kestelman V.N. *Metallopolymernano composites*. Heidelberg, Springer, **2005**, 563.

3. Burkeev M.Zh., Khamitova T.O., et al. Synthesis and Catalytic Properties of Polymer-Immobilized Nanoparticles of Cobalt and Nickel. *CATALYSIS IN INDUSTRY*, **2018**, *10(4)*, 270–278 pp. https://doi.org/10.1134/S2070050418040037

4. Burkeyev M.Zh., Khamitova T.O., Havlichek D., et al. Synthesis, Characterization, and Catalytic Properties of Metal–Polymer Complexes Based on Copolymers of Polyethylene(propylene) Glycol Maleates with Acrylic Acid. *Russian Journal of Applied Chemistry*, **2019**, *92(1)*, 1–8 pp. https://doi.org/10.1134/S10704272190100

5. Burkeyev M.Z., Shibayeva S.R., Khamitova T.O. Plocek J., et al**.** Synthesis and Catalytic Properties of New Polymeric Monometallic Composites, Based on Copolymers of Polypropylene Glycol Maleate Phthalate with Acrylic Acid.*Polymers*, **2021**,*13*,4369. https://doi.org/10.3390/polym13244369

6. Burkeyev, M.Z., Khamitova, T.O. et al**.** Influence of RAFT Agent on the Mechanismof Copolymerization of Polypropylene Glycol Maleinate with Acrylic Acid. *Polymers*, **2022**, *14*, 1884. https://doi.org/10.3390/polym14091884