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Article

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Gulsym K. Burkeyeva[1], Anna K. Kovaleva[2*], Madinabonu N. Ibadullaeva[1],
Magzhan Ubaydullauly[1], Jiri Plocek[3], Kamila E. Sergaziyeva[1]

[1]*Department of Organic Chemistry and Polymers, Karaganda Buketov University, Karaganda, Kazakhstan;*
[2]*Research Institute of Chemical Problems, Karaganda Buketov University, Karaganda, Kazakhstan;*
[3]*Institute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec-Rez, Czech Republic;*
*(*Corresponding author`s e-mail: cherry-girl1899@mail.ru)*

Synthesis and Investigation of Catalytic Properties of Metal-Polymer Nanocomposites Based on Unsaturated Polyester Resins

This paper focuses on the hydrogenation process in metal-polymer complexes based on copolymers of polypropylene glycol fumarate phthalate and polypropylene glycol maleate phthalate, using acrylic acid and immobilized cobalt metal particles as catalysts. A classical reaction of the electrocatalytic hydrogenation of pyridine to piperidine was applied. SEM and dynamic light scattering were utilized to investigate the average size and dispersity of cobalt metal nanoparticles. The experimental findings show that the efficiency of hydrogenation can be improved by increasing the temperature from 25 to 40 °C and the current to 2 A. More specifically, increasing the temperature to 40 °C promotes swelling of the polymer and its transition from a globular collapsed state to an open one, which leads to an increase in the number of active catalytic centers and, as a consequence, acceleration of the hydrogenation process. Increasing the current strength to 2 A also helps to increase the rate of the hydrogenation process. Further increasing the current to 3 A is undesirable due to an increase in the yield of by-products and a decrease in the yield of the target product, piperidine. Based on a comparative analysis, it was established that the use of a copolymer of polypropylene glycol maleate phthalate with acrylic acid as the polymer matrix base is the most preferable for obtaining polymer-metal complexes with nanosized cobalt.

Keywords: nanocatalytic systems, nanocatalysts, catalytic activity, electrocatalytic hydrogenation, metal-polymer complex, nanoparticles, unsaturated polyesters, polypropylene glycol maleate phthalate, polypropylene glycol fumarate phthalate.

Introduction

Most organic molecules are produced on an industrial scale using catalytic processes. Due to successful application and commercialization, the search and development of novel heterogeneous nanocatalytic systems is currently one of the most sought-after areas in nanoscience [1]. Metal nanoparticles have been utilized as active catalytic centers in numerous chemical processes for more than a century [2]. This is explained by the high catalytic activity of nanoparticles, which is determined by their enormous specific surface area to volume. Advances in materials science over the past few decades have had a direct impact on the development of nanocatalysis [3–5].

Technological aspects of constructing nanosystems have undergone significant development under the influence of advances in nanotechnology. Catalysts can be tailored to specific industrial processes by precisely controlling of nanoparticle dispersity, shape, content, and spatial distribution of the constituents of nanostructured catalytic systems. Improving the catalytic activity of novel nanocatalysts while simultaneously exploring their stability and selectivity against catalytic poisons is a crucial path in this area. The fact that nanocatalysts can be regenerated and reused is another factor contributing to their widespread use.

New routes to synthesize nanoscale catalysts have become possible thanks to technological developments, especially in the field of nanotechnology-based advanced catalysis [6–8]. Nowadays, nanocatalysis is widely used in the chemical industry due to its ease of use, environmental friendliness and efficiency in carrying out processes of hydrogenation and oxidation of organic compounds. In this context, special attention is paid to metal-polymer complexes (MPC) with immobilized nanosized metals. These next generation nanocatalysts exhibit enzyme-like activity at room temperature and atmospheric pressure. Therefore, the creation of MPCs based on available polymer compounds with immobilized metal nanoparticles is a relevant direction in nanoscience.

Unsaturated polyesters are promising coreactants for the synthesis of the polymer base of nanocatalysts due to their functionality and reactivity. High resistance to external factors, ease of production, convenience in use in combination with availability, low cost and environmental friendliness significantly increase interest in unsaturated polyesters as co-reactants for obtaining new functional polymer materials [9–11]. The ability of unsaturated polyesters to cure in the presence of vinyl monomers results in the formation of a polymer compound with a cross-linked structure [12, 13]. This property makes the finished product useful as a polymer base, a matrix that effectively immobilizes nanosized metal particles to create effective nanocatalytic systems.

Previously, copolymers of unsaturated polyesters polyethylene (propylene) glycol maleates with acrylic acid and nanometric cobalt, nickel, and silver metals were used to create mono- and bimetallic metal-polymer nanocomposite composites. It has been shown that these copolymers can be used as a polymer matrix to create efficient hydrogenation catalysts. The examined metal-polymer complexes were found to contain discrete cobalt and nickel nanoparticles with a diameter of 30–120 nm, which are uniformly dispersed throughout the polymer matrix and have a predominantly spherical shape [14, 15].

The purpose of this work is to study the electrocatalytic activity and physicochemical characteristics of nanocomposites based on acrylic acid and metallic cobalt (Co) in a polymer matrix of polypropylene glycol fumarate phthalate (p-PGFPh) and polypropylene glycol maleate phthalate (p-PGMPh).

Experimental

Propylene glycol, maleic and phthalic anhydrides, acrylic acid, benzoyl peroxide, pyridine (Sigma-Aldrich), fumaric acid, diethyl ether (Vekon), zinc and cobalt chlorides, and sodium hypophosphite (Reakhim) are among the reagents employed in the study. None of the reagents required additional purification.

The initial unsaturated polyesters — polypropylene glycol maleate phthalate and polypropylene glycol fumarate phthalate — were obtained using polycondensation reactions of propylene glycol with maleic anhydride (or fumaric acid, respectively) and phthalic anhydride. The ratio of acidic reagents (maleic anhydride or fumaric acid to phthalic anhydride) was 0.7:0.3 moles. The reaction was carried out at temperatures from 423 to 433 K with zinc chloride as a catalyst [16, 17]. The molecular weights of the obtained compounds were calculated using gel permeation chromatography and were approximately ~2350 Da (p-PGMPh) and ~2500 Da (p-PGFPh).

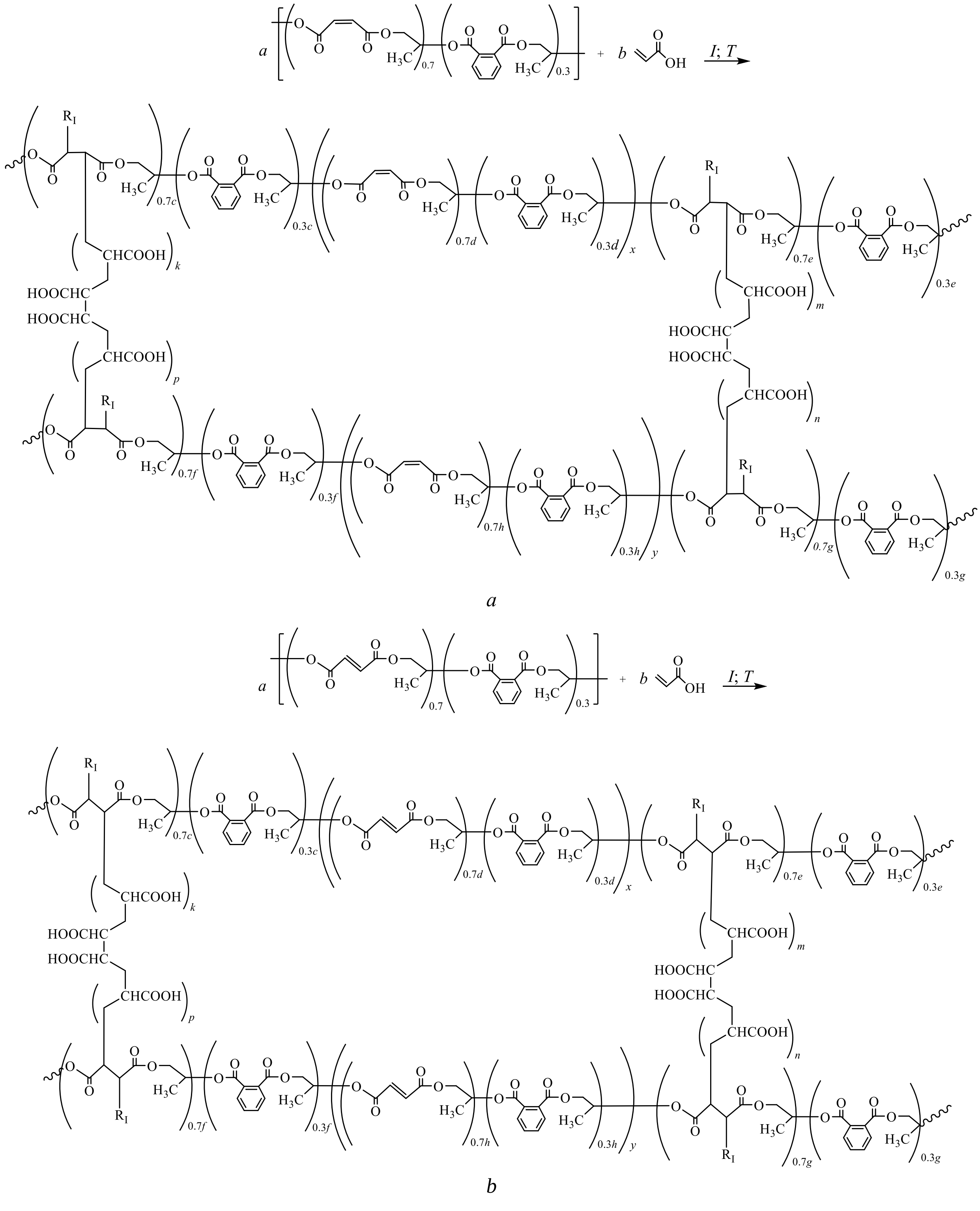
The curing of the synthesized p-PGMPh and p-PGFPh was carried out with acrylic acid (AA) at a temperature of 333 K in the presence of benzoyl peroxide as a radical initiator (1 mass.% of the mass of the initial reaction mixture).

The scheme of synthesis of copolymers of p-PGMF and p-PGFF with AA is presented in Figure 1 (*a*, *b*).

Using the residual principle, the mother solutions in dioxane were analyzed by HPLC method on a Shimadzu HPLC 20 chromatograph (Japan) to determine the copolymer composition. After removing the unreacted amount, the p-PGMPh–AA and p-PGFPh–AA copolymers were dried until their mass remained constant.

The use of copolymers of p-PGMPh and p-PGFPh with AA as a polymer base for the production of nanocomposites is due to their stimulus sensitivity depending on varying environmental factors. In particular, the behavior of these copolymers under the influence of increasing temperature and alkalinity was previously studied [18]. It was established that an increase in temperature promotes the transition of the polymer network to a swollen state. This is explained by the occurrence of a mixed-type volume-phase transition (“swelling–collapse–swelling”), which polymer matrices based on p-PGMPh–AA and p-PGFPh–AA undergo. Thus, samples at room temperature (20 °C) initially increase to a certain size. Next, with an increase in temperature (up to 30 °C), a predominance of hydrophobic interactions is observed, as a result of which the polymer network decreases in size and is collapsed. Further heating of the external solution (over 30 °C) leads to an increase in the role of hydrogen bonds, which significantly weaken with rising temperature. This promotes an increase in the size of the polymer network, i.e. the polymer swells. Accordingly, the specific contact area of immobilized cobalt with pyridine increases, which enhances the efficiency of the process of electrocatalytic hydrogenation of organic compounds.

The rise of the medium alkalinity is a favorable factor for the unfolding of the polymer network. The explanation for this is the presence of ionized carboxyl groups in the microchains, which are attached to the main chain by covalent bonds. As a result, the electrostatic repulsion of like-charged carboxyl groups plays a decisive role in the behavior of gels. The resulting increase in the degree of dissociation of the above carboxyl groups, accompanied by a shift to the region of high pH values, leads to an increase in their electrostatic repulsion. A shift towards increasing the alkalinity of the medium promotes the unfolding of the globular structure of the polymer network (in the case of an acidic medium), which leads to swelling of the gel. This is explained both by more complete dissociation as a result of the formation of salt molecules in the solution, and by the weakening of the dominance of hydrogen bonds that cause the collapse of the gel. The hydrophobic interactions that take place are not capable to have a significant effect on the processes of attraction between the links of the polymer network.



a

b

Figure 1. Scheme of radical copolymerization of p-PGMPh and p-PGFPh with AA

It is worth noting that such a course of the swelling curve depending on the change in the acidity/alkalinity of the medium indicates the typical polyelectrolyte behavior of the gels we synthesized based on p-PGMPh and p-PGFPh with AA.

Thus, the use of the presented copolymers as a polymer matrix for the immobilization of metal cobalt nanoparticles into it in order to get nanocatalysts for electrocatalytic hydrogenation in an alkaline medium at elevated temperatures is promising.

In order to immobilize cobalt particles in polymer matrices, p-PGMPh–AA and p-PGFPh–AA copolymers with compositions of 13.1:86.9 mass.% and 14.2:85.8 mass.%, respectively, were kept in a 0.1 N solution of cobalt chloride for 6 hours, after which the Co^{2+} ions were reduced to Co^0 using a 0.2 N solution of sodium hypophosphite NaH_2PO_2 in the presence of an ammonia solution of silver chloride (0.2 N) as a catalyst. Schematically the reaction is as follows:

$$7Co^{2+} + 2H_2PO^{2-} + 6H_2O \rightarrow 7Co^0 \downarrow + 2PO_4^{3-} + 16H^+.$$

It's important to note that the obtained MPC's properties with reduced Co^0 are practically independent of the AgCl concentration in the silver chloride ammonia solution.

There are multiple steps involved in the reduction of Co^{+2} to Co^0 in the volume of the p-PGMPh-AA and p-PGFPh-AA polymers. First, Co^{2+} ions are added to the matrix of polymers. Subsequently, reagent diffusion occurs inside the polymer volume. At the final phase, cobalt chloride ($CoCl_2$) and sodium hypophosphite (NaH_2PO_2) are mixed, causing direct reduction from Co^{2+} to Co^0 [19].

At T = 293K the reduction process lasted for two hours. After washing with distilled water, the resulting metal-polymer composites were dried in a vacuum oven until their mass remained constant. The immobilization of cobalt particles into the polymer matrix was confirmed by visual inspection, which showed a color change from white (empty p-PGMPh–AA and p-PGFPh–AA polymer matrices) to gray in the studied samples.

Identification of MPCs was carried out using infrared spectroscopy on an FSM 1201 IR spectrometer. The surface morphology of the polymer matrix with immobilized cobalt metal nanoparticles was studied using scanning electron microscopy on a MIRA 3 TESCAN instrument at an accelerating voltage of 5 kV. The nanoparticle size distribution was determined by photon correlation spectroscopy using a Zetasizer Nano S90 instrument from Malvern Instruments. The metallic cobalt content in the composites was determined by energy-dispersive analysis using a 4210 MP-AES instrument from Agilent Technologies Bayan Lepas Free.

To evaluate the effectiveness of the obtained MPCs in comparison with the skeletal cobalt catalyst, a model reaction of pyridine hydrogenation to piperidine was carried out in an electrochemical system, yielding the dipiridyl as a by-product. Additionally, the effect of temperature and current on the yield of the target product (piperidine) and by-product (dipiridyl) in the pyridine hydrogenation reaction was investigated.

The pyridine hydrogenation process was carried out using a diaphragm electrocatalytic thermostat cell composed of Pyrex glass. A 3 MK-40 membrane diaphragm served as the barrier between the anodic (platinum mesh) and cathodic (copper plate with $S_{surface} = 0{,}048$ dm^2) compartments in this cell. This two-chamber diaphragm cell, as well as the parameters and conditions of hydrogenation were developed by Doctor of Chemical Sciences, Professor Kirilyus I.V. [20]. The cell's airtightness was ensured by fittings attached to “masts” located in the anode and cathode spaces of the electrolyzer. The evolved gases (hydrogen and oxygen) were vented through a nozzle, and their volume was monitored using burette scales [21, 22].

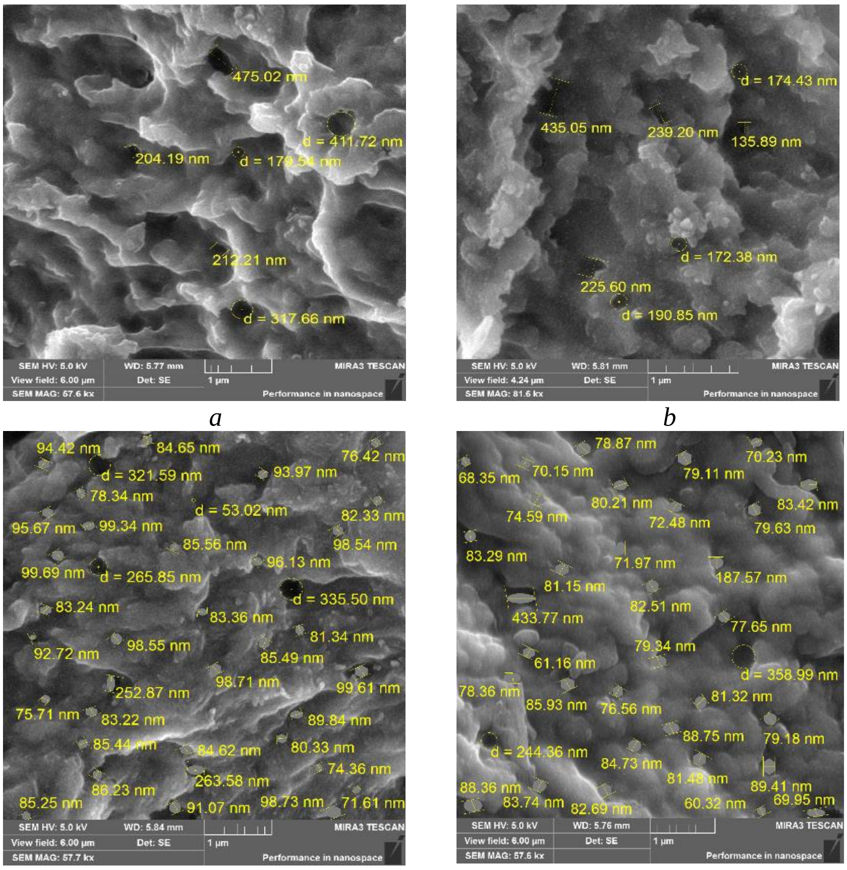
The pyridine electrocatalytic hydrogenation process was carried out while varying the current (from 1 A to 3 A) and temperature (from 20 °C to 40 °C) to evaluate the yield of piperidine and dipiridyl. Initially, solutions of the anolyte and catholyte (20 % and 5 % sodium hydroxide solutions, respectively) were introduced into the electrocatalytic thermostat cell, and the reaction conditions were adjusted. After establishing the desired reaction conditions, saturation of the MPCs with electrocatalytic hydrogen was carried out in the cathode part of the electrocatalytic thermostat cell. The mass of metal-polymer composites introduced into the cathode part of the electrocatalytic cell was 1 g ± 0.1 %. The cobalt content in MPC based on p-PGMPh–AA was 0.87 g, and 0.9 g in MPC based on p-PGFPh–AA. To get comparable experimental results, skeletal cobalt of similar mass was taken (0.87 g ± 0.1 % — for comparison with the effectiveness of MPC based on p-PGMPh–AA and 0.9 g ± 0.1 % — for comparison with MPC based on p-PGFPh–AA). This process lasted for about 30 minutes and ended when the ratio of the volumes of hydrogen and oxygen released in the burettes reached 2:1. Subsequently, the pyridine hydrogenation process was directly conducted by introducing a pyridine ($V_{pyr.} = 1$ ml) into the cathodic part of the electrocatalytic cell, and the volume of evolved gases H_2 and O_2 in the burettes was recorded every 2 minutes. The reaction concluded once the volume of hydrogen ceased to change, indicating the cessation of its absorption by the substrate (pyridine). Following this, the reaction rate of electrocatalytic hydrogenation W (mol·L^{-1}·s^{-1}) was determined.

The target and by-products of pyridine hydrogenation received on the cathode were analyzed by gas chromatography on an Agilent 7890A/5975C chromatograph equipped with a mass spectrometric detector. The analysis was carried out after their extraction with diethyl ether (mass ratio 1:1).

Results and Discussion

Electrocatalytic hydrogenation is one of the most common industrial methods for the synthesis of new chemical products. Transition metals, their alloys, or oxides are typically used as catalysts in such reactions [23]. However, as follows from the experience gained in the electrocatalytic hydrogenation of unsaturated organic compounds, transition metal oxides do not exhibit catalytic properties in such processes [21, 22]. Due to their greater functionality, efficiency and lower cost, increasing attention is being paid to the use of MPCs obtained by immobilizing nanoscale catalytically active metals within a polymer matrix. Previously, polymer matrices based on unsaturated polyesters were synthesized from polyglycol maleinates with some vinyl-type ionogenic monomers, followed by immobilization of nickel, cobalt, and silver nanoparticles in them. The obtained metal-polymer composite catalysts showed excellent catalytic properties [24].

In continuation of studies on the possibility of using unsaturated polyester resins as a polymer matrix for the production of metal-polymer composite catalysts, we immobilized cobalt nanoparticles into copolymers of p-PGMPh–AA and p-PGFPh–AA with a composition of 13.1:86.9 mass.% and 14.2:85.8 mass.%, respectively. The surface morphology of the copolymer samples was examined using scanning electron microscopy (Fig. 2) with subsequent processing of the obtained results. As a result of the analysis, the average pore size of the three-dimensional polymer network was found to be no more than 0.5 µm, which meets the requirements for polymers used as the polymer matrix base for nanocatalysts [25].



a *b*

c *d*

a — p-PGMPh–AA (13.1:86.9 mass.%); *b* — p-PGFPh–AA (14.2:85.8 mass.%);
c — p-PGMPh–AA–Co^0; *d* — p-PGFPh–AA–Co^0

Figure 2. Surface morphology of the polymers and MPCs

As a continuation of our work, we also studied the effect of the concentration of $CoCl_2$ solution on the size and polydispersity of immobilized nanoscale cobalt in the polymer matrix. Specifically, photon correlation spectroscopy with the help of a Zetasizer Nano S90 device from Malvern Instruments was used to evaluate the cobalt dispersion in the metal-polymer composite. Table 1 presents the findings.

Table 1

Effect of $CoCl_2$ concentration on the size and polydispersity of metallic nanoparticles

Copolymer	Concentration of $CoCl_2$, N	Concentration of ammoniacal solution of AgCl, N	Nanoparticle yield, %	Average particle size, nm	Polydispersity
p-PGMPh	0.01	0.2	92.5±1.9	42	0.136
	0.05		91.4±1.8	51	0.144
	0.1		88.9±1.8	88	0.198
	0.2		62.8±1.3	167	0.743
p-PGFPh	0.01		87.8±1.8	35	0.129
	0.05		86.2±1.7	48	0.134
	0.1		82.6±1.7	76	0.187
	0.2		55.2±1.1	159	0.734

As can be seen in Table 1, the average size and polydispersity of Co^0 nanoparticles rise with increasing concentration of the cobalt salt solution, but their yield decreases. Based on this, it was determined that 0.1 N was the optimum concentration of cobalt chloride to achieve a suitable balance of metal particle yield, size and polydispersity.

Figure 3 presents the diagram illustrating the distribution of cobalt particles within the volume of the p-PGMPh–AA polymeric matrix when using a 0.1 N $CoCl_2$ solution.

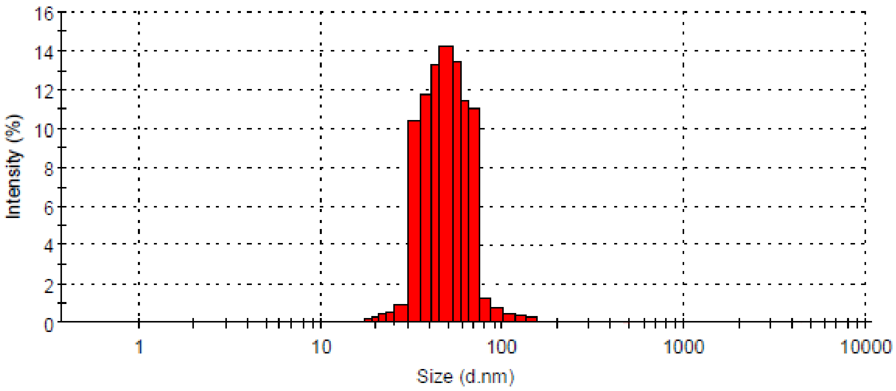


Figure 3. Distribution diagram of cobalt particles within the volume of the p-PGMPh–AA polymer matrix when using a 0.1 N solution of $CoCl_2$

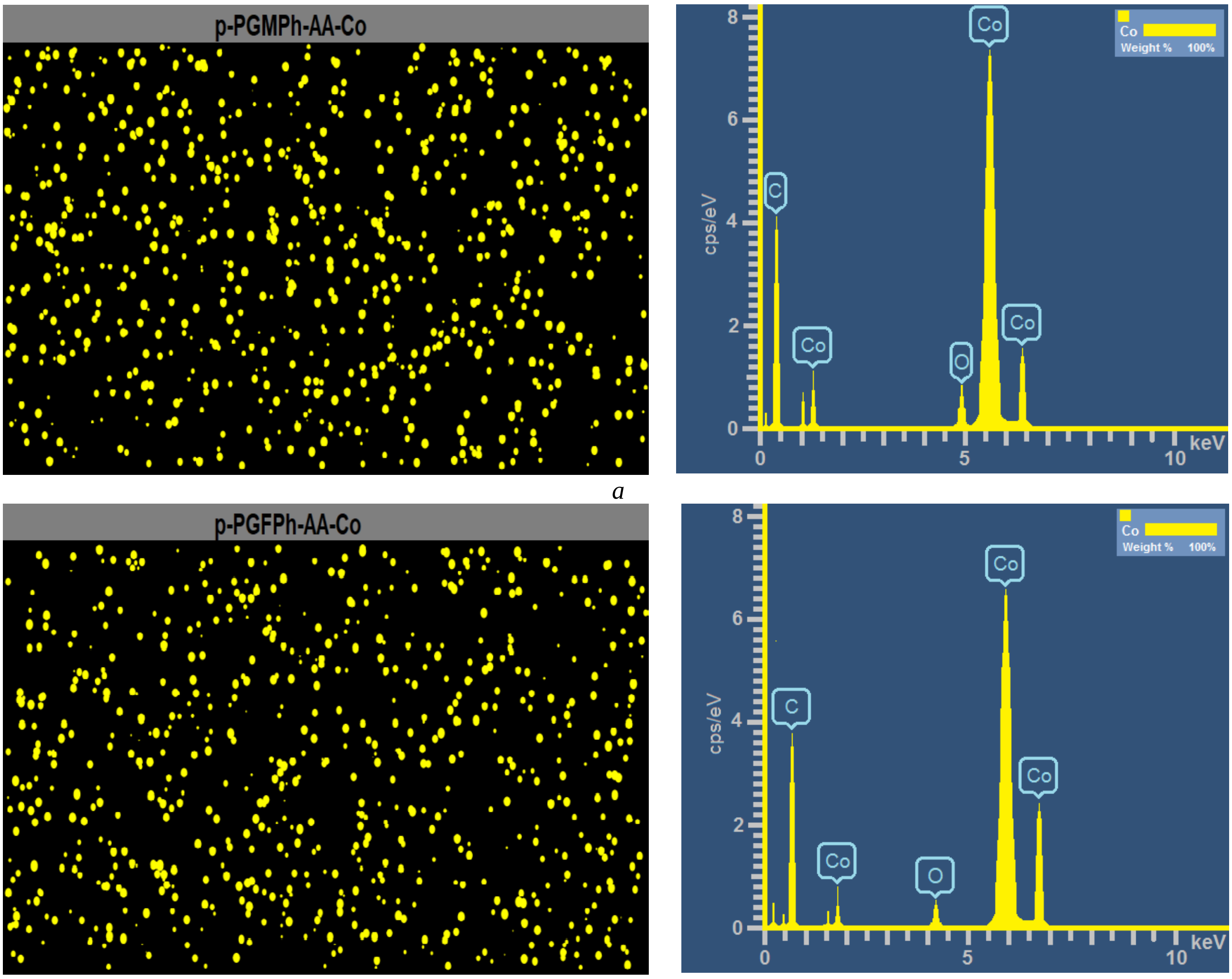
Analyzing the data presented in Figure 3, it can be noted that most nanoparticles have sizes from 53 to 100 nm. The agglomerates (clusters of small particles) observed on the surface of the polymer network do not exceed 260 nm in size.

Similar results were obtained for the composite with the p-PGFPh–AA polymeric matrix (Table 1). As mentioned earlier, changing the AgCl ammonia solution concentration did not have a noticeable effect on the dispersion of nanoparticles within the polymer matrix volume.

The concentration of metallic cobalt in the metal-polymer composite was quantitatively determined using energy dispersive spectroscopy. Figure 4 (*a*, *b*) presents energy-dispersive spectroscopy results for the metal-polymer composites based on p-PGMPh and p-PGFPh with AA and 0.1 N cobalt chloride.

Distinct peaks in the 1570–1590 cm^{-1} range were observed when the polymer matrices including immobilized cobalt particles were subjected to infrared spectroscopy. These peaks correspond to the unsaturated double bonds observed in p-PGMP and p-PGFP. Furthermore, bands of absorption were detected in the range of 2860–2885 cm^{-1}, which is associated with the unsaturated polyesters $–CH_3$ methyl group.

–CH_2–CO– groups are characterized by the emergence of strong thin bands in the 1400–1440 см$^{-1}$ region. The presence of the complex –COOC=C– ether group is confirmed by peaks at 1778 cm^{-1} and 1792 cm^{-1}. The peaks at 1722 cm^{-1} in the IR spectrum of the p-PGMPh–AA copolymer, as well as peaks at 1706 cm^{-1} and 1729 cm^{-1} in the spectrum of the p-PGFPh–AA copolymer, confirm the presence of –COOH carboxyl groups, while the peaks at 2854 cm^{-1} and 2921 cm^{-1} characterize the –CH_2– methylene groups of acrylic acid.



a

b

a — p-PGMPh–AA–Co^0; *b* — p-PGFPh–AA–Co^0

Figure 4. Micrographs of the distribution of Co^0 particles in the metal-polymer composites

Peaks in the 600–800 cm^{-1} range indicate that metallic cobalt particles have been mechanically included (immobilized) into the polymer matrix. The dispersion of the nanoparticles affects the intensity of these bands [26].

The study examined the possibility of using cobalt nanoparticles as electrocatalysts. These metal nanoparticles were immobilized into p-PGMPh–AA and p-PGFPh–AA polymer matrices.

The efficiency of electrocatalytic hydrogenation depends greatly on the process conditions, in particular on the current and temperature. It has been established that increasing the current contributes to the acceleration of the hydrogenation rate of unsaturated and cyclic compounds. Electrolysis carried out in a galvanostatic mode demonstrates an inverse relationship between the process time and the current. As a result, the electrolysis duration decreases as current increases. On the other hand, increasing the current may have adverse effects such as triggering side reactions and reducing the yield of the target product [27]. As a result, determining the ideal ratio of current to process time is critical to achieving maximum efficiency.

The reaction was carried out in the presence of p-PGMPh–AA–Co^0 and p-PGFPh–AA–Co^0 metal-polymer composites at a temperature of 20 °C while adjusting the current in the range of 1 to 3 A in order to identify the ideal conditions for catalytic hydrogenation of pyridine. Table 2 presents the achieved results.

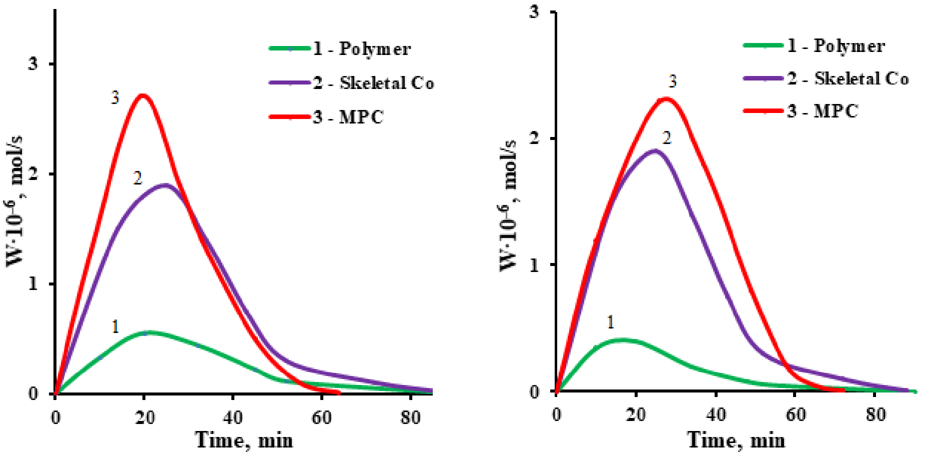
Table 2

Effect of current on the yield of the target product (piperidine)

Current, A	Current density, A/dm²	Time, min		Yield of piperidine, %	
		p-PGMPh–AA–Co^0	p-PGFPh–AA–Co^0	p-PGMPh–AA–Co^0	p-PGFPh–AA–Co^0
1	21	88	92	78	72
2	42	67	75	71	66
3	63	41	49	61	53

According to Table 2, an increase in current from 1 to 3 A (cathode — copper plate with $S_{surf.} = 0.048$ dm^2) results in a significant decrease in the yield of the target product due to the occurrence of side reactions and, consequently, an increase in the yield of by-products. Therefore, increasing the current to 3 A in order to reduce the hydrogenation time is undesirable. Analyzing the yield of piperidine at current of 1 A and 2 A, it is important to note their close values, while the process duration is significantly reduced, indicating greater efficiency of hydrogenation at a current of 2 A.

Figures 5 (*a*, *b*) presents the pyridine hydrogenation curves in the absence of a catalyst (1), with a skeletal Co-catalyst (2), and for metal-polymer composites based on p-PGMPh–AA–Co^0 and p-PGFPh–AA–Co^0 at a temperature T = 298 K and current I = 2 A.



a *b*

Figure 5. Change in the rate of pyridine electrohydrogenation in the absence of a catalyst (1), in the presence of skeletal Co catalyst (2), and in the presence of metal-polymer composite (MPC) based on p-PGMPh–AA–Co^0 (3, *a*) and p-PGFPh–AA–Co^0 (3, b) (I = 2 A, T = 298 K)

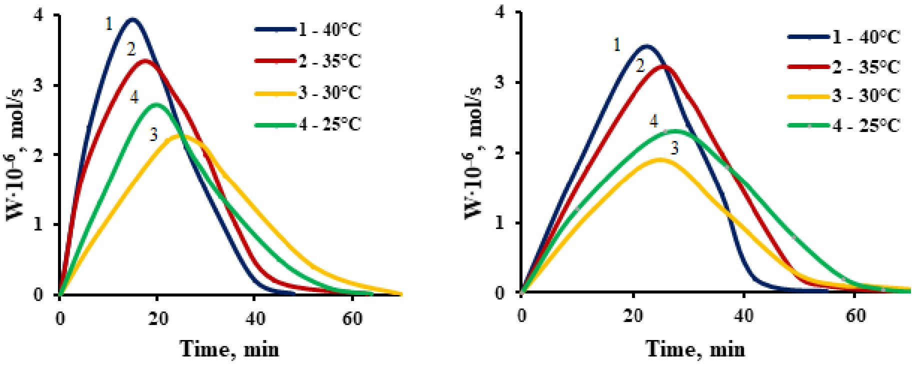
Analyzing curve (1) in Figure 5, which corresponds to hydrogenation without a catalyst, it is notable its subdued nature, although a small absorption of H_2 is observed. This circumstance can be explained by the partial saturation of the double bonds present in the structure of the copolymers. This assumption is confirmed by the bromide-bromate method, as a result of which it was found that before the start of the hydrogenation process, the content of unsaturated double bonds for the p-PGMPh–AA copolymer (13.1:86.9 mass.%) was 14 %, after hydrogenation this figure decreased to 9 %. Similarly, for the p-PGFPh–AA copolymer (14.2:85.8 mass.%), the degree of unsaturation was 17 % and 11 %, respectively. Curve (2) in Figure 5, on the other hand, demonstrates a pronounced character, indicating catalytic hydrogenation of pyridine with the formation of both target and by-products. Compared to the hydrogenation process with a skeletal cobalt catalyst (2), curve (3) in the presence of metal-polymer composites based on polymer matrices with immobilized nanoscale Co^0 particles shows a more extreme character. This suggests a more intense hydrogenation process of pyridine, with a high rate of H_2 absorption. The maximum rate of the electrocatalytic hydrogenation process is reached at approximately 19–26 minutes (Fig. 5 *a*, *b*). After reaching the maximum, there is a sharp decrease in the reaction rate, attributed to the consumption of some of the substrate (pyridine) undergoing hydrogenation to piperidine and by-products such as tetrahydropyridine (less than 1 %) and dipiperidyl (from 4 % to 9 %). No further significant changes in the hydrogen absorption curve are observed, indicating the completion of the hydrogenation process.

Previous studies have demonstrated that the first binary systems, p-PGMPh–AA and p-PGFPh–AA, are “smart” polymers due to their sensitivity to various variables such as temperature changes. In particular, polymers undergo a volume-phase transition of the “swelling-collapse-swelling” type with increasing temperature, the minimum of which is observed at 30 °C. The behavior of the metal-polymer composites (MPCs) containing immobilized Co particles is comparable. As a result, additional studies of pyridine hydrogenation in the presence of these MPCs were carried out with temperature variations of up to 5 °C between 25 °C and 40 °C. The obtained data are presented in Table 3 and Figure 6 (*a*, *b*).

Table 3

Effect of temperature on the yield of the target product (piperidine) and by-product (dipyridyl) of pyridine hydrogenation

Catalyst	Temperature, °C	Time, min	Yield of products, %		Pyridine, %
			Piperidine	Dipyridyl	
Skeletal Co	25	88	60.51	4.1	35.39
	30	80	66.24	5.4	28.36
	35	72	73.91	6.8	19.29
	40	58	79.03	8.8	12.17
p-PGMPh–AA–Co^0	25	64	71.28	3.9	24.82
	30	70	72.12	4.9	22.98
	35	61	86.71	6.5	6.79
	40	48	89.64	7.6	2.76
p-PGFPh–AA–Co^0	25	72	67.15	5.2	27.65
	30	80	69.07	6.0	24.93
	35	69	83.29	6.8	9.91
	40	55	85.83	8.9	5.27



a *b*

Figure 6. Hydrogenation of pyridine in the presence of MPC based on (*a*) p-PGMPh–AA–Co^0 and (*b*) p-PGFPh–AA–Co^0 at various temperatures and current I = 2 A

As can be seen from Table 3, increasing the temperature to 40 °C stimulates the expansion of the polymer matrix, which significantly increases the specific surface area of the MPC. As a result, the hydrogenation reaction rate accelerates (Fig. 6*a*, *b*). A decrease in the selectivity of the target products yield, associated with the activation of side reactions and, as a consequence, an increase in the yield of side products, makes it undesirable to increase the temperature to 40 °C. In terms of p-PGMPh–AA–Co^0 and p-PGFPh–AA–Co^0, the ideal temperature for the hydrogenation process in the presence of MPC is 35 °C.

It is important to note the higher efficiency of MPC based on p-PGMPh–AA–Co^0 when comparing the catalytic activity of MPCs based on p-PGMPh and p-PGFPh with AA and immobilized Co^0 nanoparticles, taking into account the duration of the hydrogenation process and the target product yield. The physicochemical characteristics of the original p-PGMPh–AA polymer matrix are responsible for this. These characteristics include a higher sorption capacity, sensitivity to external factors (such as fluctuations in temperature and current), and a more porous structure within the polymer network. MPCs based on p-PGMPh–AA–Co^0 and p-PGFPh–AA–Co^0 demonstrated a preference for the skeletal cobalt catalyst due to their greater dispersity.

Conclusions

Heterogeneous catalysis involves the reaction occurring at the interface of different phases, where one of the determining factors is the larger specific surface area of the catalyst. Therefore, an increase in the system dispersity leads to an increase in the contact area (interaction) between the reactant and the catalyst. Particle size is also of great importance. Specifically, with a decrease in particle size, the number of catalytically active surface centers per unit area of the polymer matrix increases. This results in an increase in the rate of hydrogenation.

Consequently, the results of the studies indicate high catalytic activity of MPCs based on p-PGMPh–AA–Co^0 and p-PGFPh–AA–Co^0. The production of nanoscale cobalt metal particles and their immobilization within the volume of the polymer matrix contributes to an increase in the specific contact surface area of the MPCs with the reaction medium, which leads to enhanced hydrogenation efficiency. Immobilization of cobalt particles in a polymer matrix prevents their coagulation and oxidation. The obtained SEM images demonstrate a uniform distribution of predominantly isolated spherical Co^0 nanoparticles in the volume of the studied MPC polymer matrices. The presence of aggregates formed by nanoparticle agglomeration, with sizes exceeding 280 nm, is observed on the surface of the polymer mesh. In the presence of created MFCs, the hydrogenation proceeds faster than when using a skeletal cobalt catalyst for all the reasons described earlier. Furthermore, the use of MFCs obtained from p-PGMPh–AA–Co^0 and p-PGFPh–AA–Co^0 improves the selectivity of the target product yield.

The obtained research results indicate the prospects for developing new nanocatalysts based on p-PGMPh and p-PGFPh with AA polymer systems with subsequent immobilization of catalytically active nanoscale transition metals within the polymer matrix.

*Author Information**

**The authors' names are presented in the following order: First Name, Middle Name and Last Name*

Gulsym Kabayevna Burkeyeva — PhD, Associate Professor of Chemical Sciences, Karaganda Buketov University, Universitetskaya street, 28, 100024, Karaganda, Kazakhstan; e-mail: guls_b@mail.ru; https://orcid.org/0000-0003-1993-7648

Anna Konstantinovna Kovaleva (*corresponding author*) — PhD, Senior Researcher, Karaganda Buketov University, Universitetskaya street, 28, 100024, Karaganda, Kazakhstan; e-mail: cherry-girl1899@mail.ru; https://orcid.org/0000-0001-9758-648X

Madinabonu Nabizhon kizi Ibadullaeva — Master Student, Karaganda Buketov University, Universitetskaya street, 28, 100024, Karaganda, Kazakhstan; e-mail: madinabanu02ibadullaeva@mail.ru; https://orcid.org/0009-0005-0709-9191

Magzhan Ubaydullauly — Master Student, Karaganda Buketov University, Universitetskaya street, 28, 100024, Karaganda, Kazakhstan; e-mail: ubaidullamagzhan@gmail.com

Jiri Plocek — PhD, CSc., Institute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec-Rez 1001 25068 Rez, Czech Republic; e-mail: plocek@iic.cas.cz; https://orcid.org/0000-0001-6082-5766

Kamila Erdaurenkyzy Sergaziyeva — Student, Karaganda Buketov University, Universitetskaya street, 28, 100024, Karaganda, Kazakhstan; e-mail: sergazievakamila72@gmail.com

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Gulsym Kabayevna Burkeyeva** conceptualization, validation, visualization, supervision & editing; **Anna Konstantinovna Kovaleva** conceptualization, data curation, methodology, validation, visualization, writing-original draft, writing-review & editing; **Madinabonu Nabizhon kizi Ibadullaeva** data curation & methodology; **Magzhan Ubaydullauly** data curation & investigation; **Jiri Plocek** supervision & editing; **Kamila Erdaurenkyzy Sergaziyeva** data curation & investigation.

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Conflicts of Interest

The authors declare no conflict of interest.

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