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Synthesis and characteristics of metal-polymer complexes of p-EGM/AA-Ni^0-Co^0 and p-PGM/AA-Ni^0-Co^0

Possibility of using the copolymers of poly-(ethylene)-propylene glycol maleate (p-EGM, p-PGM) with acrylic acid (AA) as a matrix for obtaining effective metal-polymer complexes of different application was shown. The compositions, structures and dimensions of particles of nickel and cobalt stabilized in polymeric matrix were determined using the methods of transmission electron microscopy and scanning microscopy, infrared spectroscopy, laser-emission spectroscopy, dispersive microscopy and thermogravimetric analysis. The average size of nanoparticles, which have spherical shape and equal distribution along cross-section of polymer, was 100–170 nm. Percentage content of nickel and cobalt in the complex was equal to 0.52 and 0.48, respectively, in the p-EGM/AA copolymer, 0.49 and 0.51 in the p-PGM/AA copolymer. The analysis of electromagnetic force-pictures of p-EGM/AA (14.8:85.2 mass.%) and p-PGM/AA (15.1:84.9 mass.%) copolymers' films showed a relatively equal distribution of the filler (Ni^0, Co^0) along the cross-section of polymer. The average number of metal particles on 10 microns was 600–700 units for particles of Ni and 550–650 units for particles of Co. Thermal decomposition of metal-polymer complexes occurred in the temperature range of 200–500 ºC. The average weight loss on TG — curves was 80 %. Therefore, p-EGM/AA-Ni^0-Co^0 and p-PGM/AA-Ni^0-Co^0 metal-polymeric complexes obtained can be used as a template for the creation of catalytically effective composite materials.

Keywords: copolymer, polyethylene glycol maleate, polypropylene glycol maleate, polymeric matrix, nanoparticles, catalyst, metal-polymer complex, matrix.

Introduction

Catalytic hydrogenation is one of the most important processes used in chemical industry. The main fields of applying such process are the fields of production of synthetic fuel by destructive hydrogenation of coal, purification and refining of liquid transportation fuel, hydrogenation industry and so on [1]. As it is known, catalytic reactions are divided into two basic classes, namely, homogeneous and heterogeneous. Heterogeneous catalysts are chemical compounds insoluble in the reaction medium. According to literature data nanostructured polymer systems are used as nanoreactors for nanoparticles formation [2] and these metal-polymeric complexes demonstrate a high level of catalytic activity, stability and selectiveness of effect. Reducing catalyst particles up to nanometric dimensions lets us broaden polymer surface contacting with reaction medium and increase the effectiveness of catalysis in several times, and gel matrix preserves particles against coagulation and oxidation. New type of nanocatalysts based on metal-polymeric matrix and catalytically effective transition metals based on polymer carriers can be used in many spheres. At the present time the search for new catalytic systems, particularly nanocatalysts characterized by high degree of activity and selectivity is the relevant task.

Polymers based on unsaturated polyester resins are economically profitable and these polymers can be used as obtainable carrier of metals nanoparticles. Comparing hydrophobic polymers with other thermally active polymers we can see that attractiveness of these hydrophobic polymers is due to their ability to solidify at room temperature or other relatively low temperature and almost without separation of co-products [3]. The aim of this work is the synthesis of new metal-polymeric complexes with transition metals based on the «smart» copolymers of p-EGM/AA, p-PGM/AA obtained by us earlier [4].

Experimental

On the basis of copolymers p-EGM/AA, p-PGM/AA contained (14.8:85.2 mass.%) and (15.1:84.9 mass.%) metal-polymeric nanocomposites were obtained using the reduction method of salt solution of transition metals such as nickel and cobalt, namely, p-EGM/AA-Ni^0-Co^0, p-PGM/AA-Ni^0-Co^0. Ions reduction of metals (from Ni^{+2}, Co^{+2} up to Ni^0, Co^0) was carried out by sodium hypophosphate in the presence of ammonia solution of silver chloride used as a catalyst according to the following equations (1–2):

$$Ni^{2+} + H_2PO^-_2 + H_2O \rightarrow Ni^0\downarrow + H_3PO_3 + H^+ \quad (1)$$
$$NiCl_2 + NaH_2PO_2 + H_2O \rightarrow Ni^0\downarrow + H_3PO_3 + HCl + NaCl$$

$$Co^{2+} + H_2PO^-_2 + H_2O \rightarrow Co^0\downarrow + H_3PO_3 + H^+ \quad (2)$$
$$CoCl_2 + NaH_2PO_2 + H_2O \rightarrow Co^0\downarrow + H_3PO_3 + HCl + NaCl$$

Reduction of Ni^{+2}, Co^{+2} in the volume of p-EGM/AA, p-PGM/AA polymeric matrix is carried out in the several stages (Fig. 1):

– insertion of ions (Ni^{+2}, Co^{+2}) in polymeric matrix;
– diffusion of reagents in polymeric matrix;
– reaction between chlorides of nickel, cobalt and sodium hypophosphate leading to the formation of metals nanoparticles.

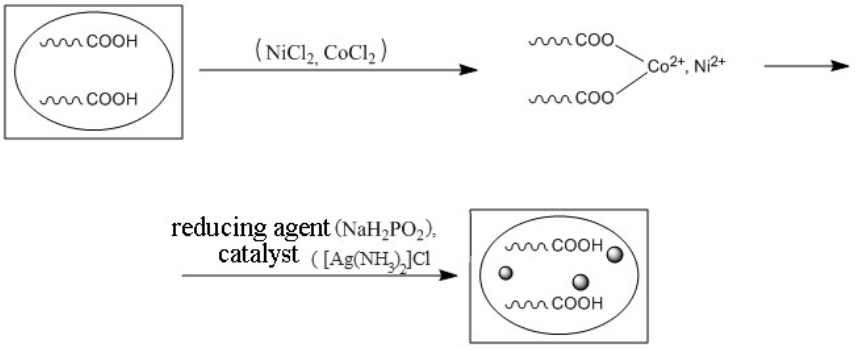
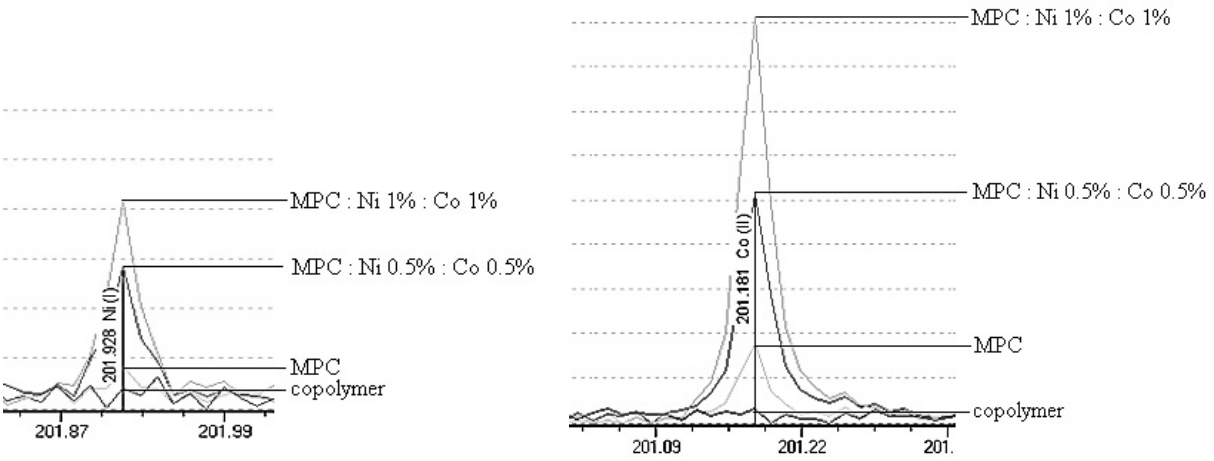


Figure 1. Principle diagram of obtaining the metal-polymeric complex
(formation of metals' nanoparticles in polymer)

Reaction between chlorides of nickel, cobalt and sodium hypophosphate leading to the formation of metals nanoparticles was performed during two hours at room temperature. Quantitative content of nickel and cobalt in a complex was determined by the use of laser-emission spectrometer (Laes matrix spectrometer produced by «Spectroscopic systems» firm, Russia, 2014). Elementary and phase analysis of nanocomposites were determined by the method of energy dispersive spectroscopy with the use of highly effective X-Max80T silicium-drift detector (with superfine window) and X-Max80TLE (without window). Active area of detectors is 80 mm^2. Infrared spectra of copolymer were registered on FSM 1201 infrared Fourier spectrometer. Thermal properties of copolymer were studied on DTA/DSC differential scanning calorimeter produced by the «Setaram» firm under dynamic conditions in 0–1500 ºC temperature range with the heating rate 10 degree/minute in a nitrogen atmosphere in an Al_2O_3 crucible. Characteristics of surface relief pattern were analyzed using scanning electron microscopy (REM) on the instrument MIRA 3, TESCAN «Oxford Instruments», England.

Results and discussion

In this work, hydrophilic copolymers based on ethylene-(propylene) glycol maleate with acrylic acid of the following compositions: p-EGM/AA (14.8:85.2 mass.%), p-PGM/AA (15.1:84.9 mass.%) were used as the matrix for metals immobilization. These compositions demonstrate «smart» qualities in the course of free radical copolymerization with varaiation of the initial monomers compound, particularly, reaction ability to slight changes of environmental conditions, the sharp and reversible change of their volumes, consequently they can be used as polyfunctional materials in quite diverse fields [4]. The initial task was approvement of quantitative content of nickel and cobalt in new metal-polymer complexes based on «smart» copolymers of p-EGM/AA, p-PGM/AA (Fig. 2).



a — peak intensity of Ni (I) 201.928 *b* — peak intensity of Co (II) 201.181

Figure 2. Dependence of peaks intensity from the content of metal salts at the variation of metal mass

The spectra given point out (Fig. 2) that percent composition of metals is equal to ~0.4 mass.%, and the correlation of Ni-Co is 52:48 % for p-EGM/AA copolymer, and 49:51 % for p-PGM/AA copolymer. Results of MPC (metal-polymeric complex) morphology investigation carried out are given below in the Table.

T a b l e

Morphology of p-EGM/AA-Ni^0-Co^0, p-PGM/AANi^0-Co^0 metal-polymer complexes

Sample	Content of metal, % (mass.)	Ratio Ni-Co, %	Dimension of NP (nano-particles), nm	Morphology of NP (nanoparticles)	Distribution of NP (nanoparticles) in a matrix	Average number of metal particles on 10 microns
p-EGM/AA-Ni^0-Co^0	0.40	52:48	500–700	Spherical, rhombic	Proportional	600–700 units for Ni and 550–650 units for particles of Co
p-PGM/AA-Ni^0-Co^0	0.35	49:51	600–800	Spherical, rhombic	Proportional	600–700 units for Ni and 550–650 units for particles of Co

Consequently, it was interesting to evaluate and compare qualitative and quantity characteristics of copolymers synthesized. The method of energy dispersive spectroscopy was chosen as the most appropriate determination method of the content of metal-polymer complexes p-EGM/AA-Ni^0-Co^0, p-PGM/AANi^0-Co^0 (Fig. 3*a* and *b*).

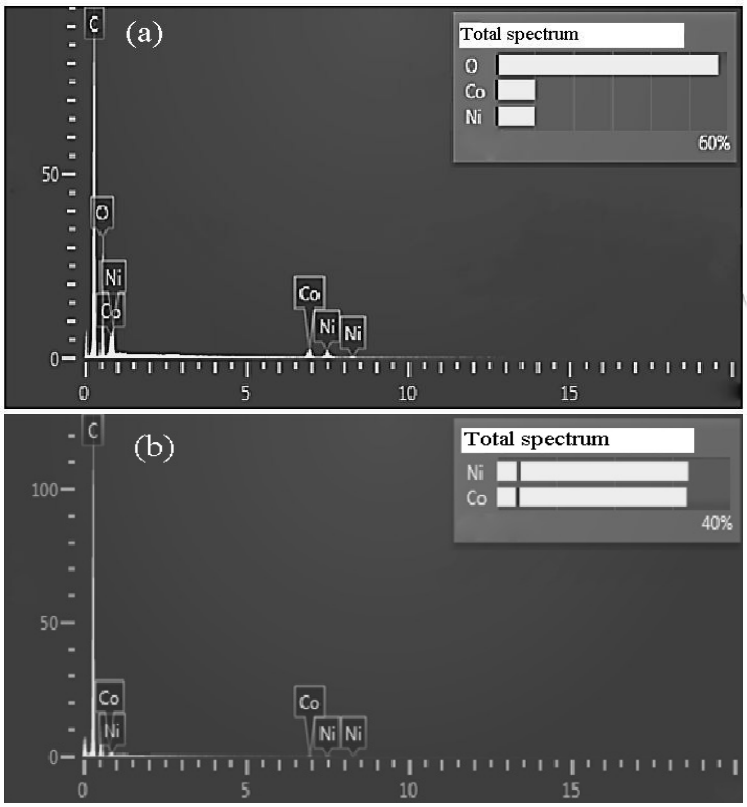


Figure 3. Energy-dispersive analysis: elementary composition of p-EGM/AA-Ni^0-Co^0 (*a*) and p-PGM/AA-Ni^0-Co^0 (*b*)

Also, it has been carried out comparison of infrared-spectra, which are presented in the Figure 4*a* and 4*b* to explain the results of the study. We can observe troughs due to stretching vibrations of methyl groups at 2923 cm^{-1}; troughs of carbonyl groups are found in the region of 1633–1639 cm^{-1}; hydroxyl groups are detected at 3448 cm^{-1}, and troughs detecting nickel and cobalt are found in the region of 513–650 cm^{-1} of the IR spectra of p-EGM/AA-Ni^0-Co^0, p-PGM/AA-Ni^0-Co^0 composites, respectively (Fig. 4*a* and 4*b*). Infrared spectroscopy data were proved by the results of thermal analysis.

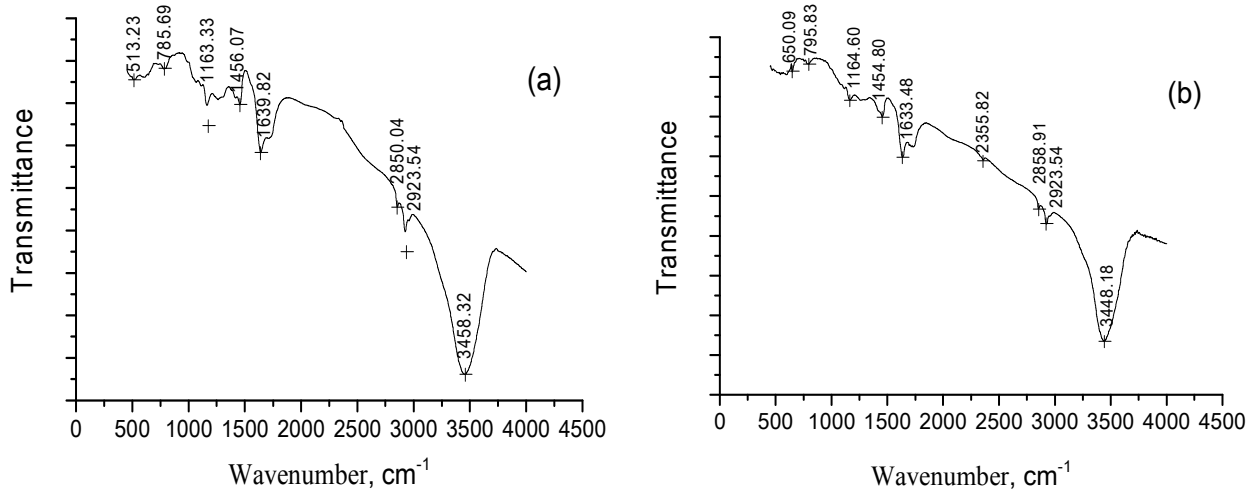


Figure 4. Infrared spectra of bimetal complexes of p-EGM/AA-Ni^0-Co^0 (*a*) and p-PGM/AA-Ni^0-Co^0 (*b*)

During the work, samples of metal-polymer complexes were studied by the method of thermogravimetric analysis. Data of thermogravimetric analysis (TGA) of metal-polymer complexes samples are presented in the Figure 5*a* and *b*: p-EGM/AA-Ni^0-Co^0 and p-PGM/AA-Ni^0-Co^0 with composition 14.8:85.2 mass.% and 15.1:84.9 mass.%.

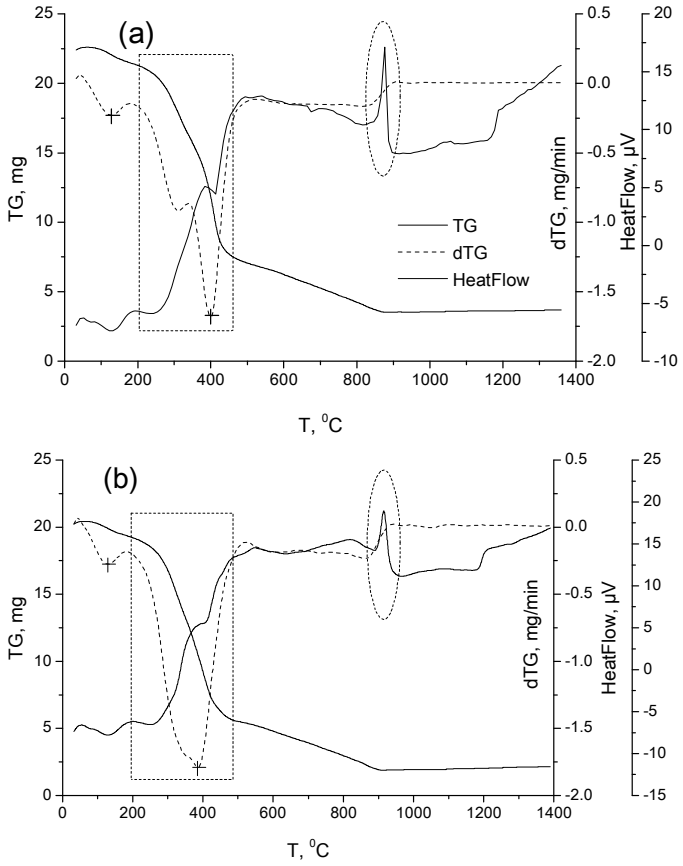
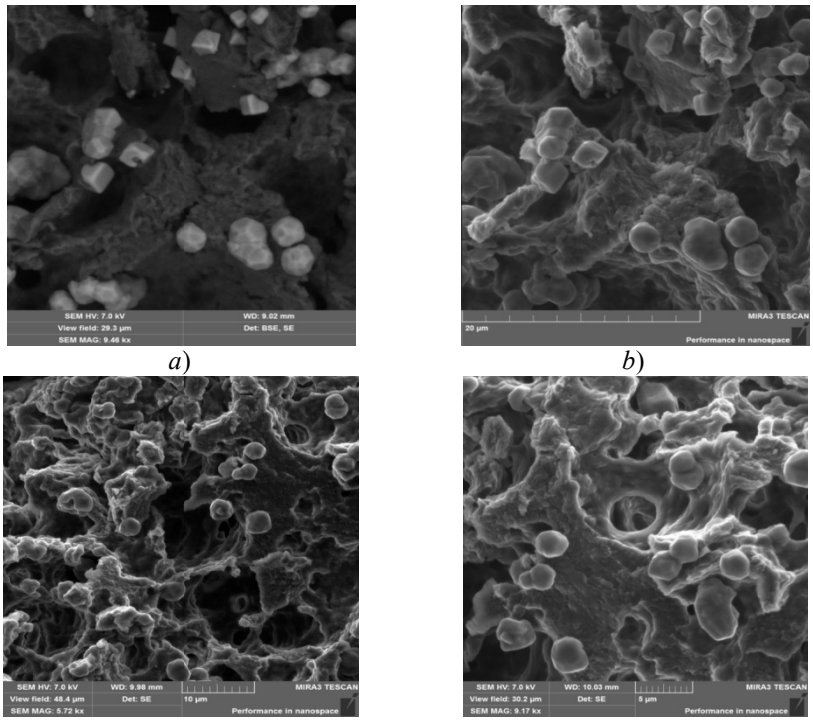


Figure 5. TG, DTG/HF curves of metal-polymer complexes p-EGM/AA-Ni^0-Co^0 (*a*) and p-PGM/AA-Ni^0-Co^0 (*b*)

Comparing thermogravimetric curves (Fig. 5*a*, *b*) obtained by the TG and HF methods, we can make a conclusion about the rate of thermal decomposition processes in main stages. Preceding slight weight loss on TG-curves at 95–100 ºC temperature can be explained by evaporation of free water from the sample. As it is seen from Figure 5 (*a* and *b*) thermal decomposition of metal-polymer complexes was carried out within the temperature range of 200–500 ºC. Moreover, weight loss on TG-curves is on an average 80 %, and we can see exothermic peak at 880 ºC and 915 ºC on the HF curves for the metal-polymer complexes of p-EGM/AA-Ni^0-Co^0 and p-PGM/AA-Ni^0-Co^0, respectively. Therefore, heat aging leads to the development of competitive structural processes in the material and these processes change the structure of the material and its resistance to aging. Morphology of the sample obtained as a result of micro-structural experiments has peculiriaty, which is shown in Figure 6*a–d*.

We can see that the metal filler was dispersed on certain grains from the pictures presented in Figure 6, where shape of Ni^0 is similar to spherical, and the shape of Co^0 is similar to rhombic. Also Figure 6 shows that the particle dimensions of metallic nickel and cobalt dispersed in the volume of gels are range within 500–800 nm. Therefore, stability of these metal-polymer complexes (p-EGM/AA-Ni^0-Co^0; p-PGM/AA-Ni^0-Co^0) to aggregating and oxidation was proved. Taking into account the fact that surface morphology is one of the most important characteristics of nanocatalysts we can approve that the study of the surface morphology using the method of scanning electron microscopy and its analysis is required to characterize the properties of metal-polymer complexes, and to plan the fields of their further study, as well as their further practical application. Results of EMF (electromotive force) analysis of metal particles distributed on matrix of p-EGM/AA and p-PGM/AA copolymers are presented in Figure 7*a, b*.

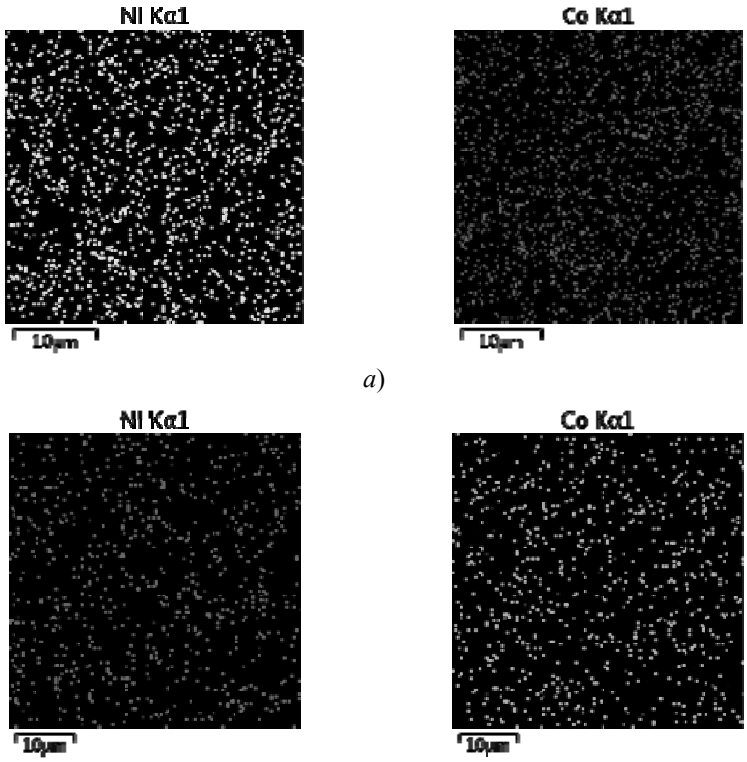
Analysis of EMF-pictures of p-EGM/AA (14.8:85.2 mass.%) and p-PGM/AA (15.1:84.9 mass.%) copolymers films revealed a relatively equal distribution of filler (Ni^0, Co^0) along the cross-section of the polymer. Average number of metal particles on 10 microns is 600–700 units for Ni and 550–650 units for particles of Co (Fig. 7*a, b*).



a) *b*) *c*) *d*)

a, b — cobalt particles; *c, d* — nickel particles

Figure 6. Electron micrographs of metal particles in nanocatalysts of p-EGM/AA-Ni^0-Co^0; p-PGM/AA-Ni^0-Co^0



a)

b)

a — p-EGM:AA; *b* — p-PGM:AA

Figure 7. Distribution of metal particles on the copolymer matrices

Conclusions

Ions of such metals as nickel and cobalt in polymeric matrix on the basis of polyethylene glycol maleate and polypropylene glycol maleate with acrylic acid were reduced by the method of wet synthesis. Compositions, structures and dimensions of particles of nickel and cobalt stabilized in polymeric matrix were determined using the methods of transmission electron microscopy and scanning microscopy, infrared spectroscopy, laser-emission spectroscopy, dispersive microscopy and thermogravimetric analysis. It was determined that nanoparticles of metals well-distributed on a whole volume and dimensions and correspond to 500–700 nanometer for p-EGM/AA-Ni^0-Co^0 bimetal catalyst and 600–900 nanometer for p-PGM/AA-Ni^0-Co^0. The shape of nickel nanoparticles is spherical and the shape of cobalt nanoparticles is rhombic. Therefore, characteristics of obtained p-EGM/AA-Ni^0-Co^0 and p-PGM/AA-Ni^0-Co^0 metal-polymeric complexes can be used as a template for the creation of catalytically effective composite materials.

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п-ЭГМ/АҚ-Ni^0-Co^0 және п-ПГМ/АҚ-Ni^0-Co^0 негізіндегі металл-полимерлі комплекстердің синтезі мен сипаттары

Металл-полимерлі комплекстердің синтезінде поли-(этилен)-пропиленгликольмалеинаттар (п-ЭГМ, п-ПГМ) мен акрил қышқылы (АҚ) негізіндегі сополимерлерді қолданудың ықтималдығы көрсетілді. Жүргізілген сараптамалар арқылы полимерлі матрицаларға тұрақтандырылған никель және кобальт бөлшектерінің құрамы, көлемдік сипаттары, құрылымы трансмиссионды-электронды және сканерлеуші микроскопия, инфрақызыл және лазерлі-эмиссиондық спектроскопия, дисперсионды микроскопия және термогравиметриялық талдау әдістерімен анықталды. Нанобөлшектердің орташа көлемі 100–170 нм, сонымен қатар полимерлі матрица бойында біркелкі таралған, сфера формасына ие екендігі көрсетілген. Никель мен кобальттың проценттік мәні сәйкесінше 0,52/0,48 п-ЭГМ/АҚ және 0,49/0,51 п-ПГМ/АҚ құрады. 10 мкм-де металл бөлшектерінің таралуы Со үшін 550–650 бірлік, ал Ni үшін 600–700 бірлікке тең. Металл полимерлі комплекстердің термиялық ыдырауы 200–500 ºС температурада жүрді. TG-қисығының масса жоғалту мәні орта есеппен 80 %-ды құрады. Синтезделген п-ЭГМ/АҚ-Ni^0-Co^0 және п-ПГМ/АҚ-Ni^0-Co^0 метал-полимерлі комплекстер каталитикалық белсенді жүйе ретінде пайдалану мүмкіндігіне ие.

Кілт сөздер: сополимер, полиэтиленгликольмалеинат, полипропиленгликольмалеинат, полимерлі матрица, нанобөлшек, катализатор, металл-полимерлі комплекс, матрица.

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Синтез и характеристики металл-полимерных комплексов п-ЭГМ/АК-Ni^0-Co^0 и п-ПГМ/АК-Ni^0-Co^0

Показана возможность использования сополимеров поли-(этилен)-пропиленгликольмалеинатов (п-ЭГМ, п-ПГМ) с акриловой кислотой (АК) в качестве матрицы для получения эффективных металл-полимерных комплексов различного назначения. Методами просвечивающей и сканирующей

микроскопии, ИК-спектроскопии, лазерно-эмиссионной спектроскопии, дисперсионной микроскопии и термогравиметрического анализа установлены состав, структура, размеры стабилизованных в полимерной матрице частиц никеля и кобальта. Средний размер наночастиц, имеющих сферическую форму и равномерное распределение вдоль поперечного сечения полимера, составил 100–170 нм. Процентное содержание никеля и кобальта в комплексе составляет соответственно 0,52, 0,48, в сополимере п-ЭГМ/АК и 0,49, 0,51 в сополимере п-ПГМ/АК. Анализ электродвижущей силы — изображения пленок сополимеров п-ЭГМ:АК (14,8:85,2 масс.%) и п-ПГМ:АК (15,1:84,9 масс.%) показал относительное равномерное распределение наполнителя (Ni^0, Co^0) вдоль поперечного сечения полимера. Среднее количество частиц металлов на 10 мкм составляет 600–700 ед. для Ni и 550–650 ед. для Co. Термическая деструкция металл-полимерных комплексов происходила в интервале температур 200–500 ºС. Потеря массы на TG-кривых составляет в среднем 80 %. Таким образом, полученные металл-полимерные комплексы п-ЭГМ/АК-Ni^0-Co^0 и п-ПГМ/АК-Ni^0-Co^0 могут быть использованы в качестве основы для создания каталитически активных композитных материалов.

Ключевые слова: сополимер, полиэтиленгликольмалеинат, полипропиленгликольмалеинат, металл-полимерный комплекс, полимерная матрица, катализатор, наночастица, матрица.

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