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Creation of a polymeric matrix on the basis of polyester resins for an immobilization of metals nanoparticles

For the purpose of creation of polymeric matrixes for an immobilization of the transitional metals nanoparticles copolymers of unsaturated polyester resins with the acrylic and methacrylic acids were synthesized and their swelling ability was studied. Sensitivity of polymeric hydrogels to external factors as pH, quality of solvent and ionic strength of solution has been shown.

Key words: swelling, polymeric hydrogels, catalysis, nanoparticles, nanocatalysts, polymeric matrix.

Now the catalysis chemistry on nanoparticles or colloidal solutions of nanodimensional metals particles develops violently. This is due to the facts as they have high specific surface area which brings closer the catalysis to homogeneous type and as an existence on a nanoparticles surface of considerably larger proportion of metal atoms than in the ordinary heterogeneous catalyst. Even the term «nanocatalysis» which is considered as peculiar «bridge» between heterogeneous and homogeneous catalysis [1–3] is entered. Besides, because of a small particles size the considerable proportion of atoms is outside the boundaries of a flat surface and has greater catalytic activity. Activity of the atoms located at tops and sides of a nanocrystal is especially high. Decrease of particle sizes of solid matter below the some limit leads to the considerable change of their properties, such as melting point, a thermal capacity, an electrical conductivity, also new optical, magnetic and electronic properties appear. Threshold particle size at which there is a saltatory change of properties for the majority of materials varies from 10 to 1000 nanometers. Owing to these factors the mass (volume) of the nanodimensional catalyst demanded for carrying out reaction is considerably sometimes one thousand times less in comparison with the same catalyst in a normality. It gives the chance of economy of the expensive or infrequent components applied to preparation of catalysts. Moreover, special characteristics of nanoparticles strengthen and modify the catalytic activity leading to emergence of an opportunity to catalyze reactions which do not catalyze similar macrodimensional materials.

Synthesis of new nanocatalysts «metal-polymeric matrix», in combination with synthesis of catalytically active transitional metals brought on polymeric carriers opens huge area of their application. Therefore for today searching of new catalytic systems, in particular the nanocatalysts possessing high activity and selectivity is an actual task.

Owing to the ability to react adequately to a variation of external factors (pH, temperature, quality of solvent, etc.), thereby controlling morphology of hydrogels, and as a result to regulate structure and properties of the nanoparticles immobilized in a matrix, so-called «clever» polymers are increasingly used. Along with it, the matrix of the polymeric hydrogel can execute some kind of role of the «microreactor» suitable for carrying out oxidation-reduction, catalytic and other reactions.

The available and cheap carrier of metals nanoparticles are polymers on the basis of unsaturated polyester resins which appeal in comparison with other thermoreactive polymers is caused by ability of curing by vinyl monomers at a room or rather low temperature practically without allocation of any byproducts [4, 5].

Earlier we investigated a copolymerization of unsaturated polyester resins as at molar, and as mass ratios [4]. To obtain more hygroscopic polymers in the work reactions of a radical copolymerization of unsaturated polyester resins — ethylene-(propylene)-glycol maleate with unsaturated carboxylic acids (the acrylic (AA) and methacrylic (MAA) acids) were investigated in solution at excellent ratios of an initial mixture getting polymers with spatially cross-linked structure and the possibility of use of the latter as matrixes for obtaining catalysts on the basis of nanometric size nickel was considered. Synthesis conditions, comonomers, a ratio of monomer: solvent were changed, more efficient initiator for this process was used.

Radical copolymerization of polyethylene(propylene)glycol maleate with unsaturated carboxylic acids (the acrylic and methacrylic acids) was carried out in dioxane solution at various mass ratios of the initial polymer-monomeric mix which data are given below in Table 1. As the initiator the dinitrile of azobisisobutyric acid (DAA) was used.

From comparison of data of Table 1 it is visible that at approximately equal ratio of comonomers copolymers of unsaturated polyester resins with MAA possess larger swelling ability. More dense structure of copolymer on the basis of polyethyleneglycol maleate (p-EGM)-AA can be one of the most probable causes of it, despite lower contents in the latter of a proportion of crosslinking agent links. The similar effect is found also by other researchers [5].

Table 1

The dependence of copolymers composition on an initial mix composition at a copolymerization of p-EGM (M_1) with AA (M_2) and MAA (M_2), DAA [I] of =8 mol/m^3, T = 333 K, [p-EGM-AA, MAA]:[dioxane] — 1:3

Initial mix mass, %		Copolymer composition mass, %		Yield, %	α, %	Number of maleate groups, %
M_1	M_2	m_1	m_2			
p-EGM:AA						
13.07	86.93	15.5	84.3	81.1±3	1116.4±2	46.8
18.88	81.13	21.1	78.9	74.5±1	1323.6±3	49.7
24.84	75.16	27.1	72.9	68.7±4	877.1±1	52.9
41.59	58.41	45.6	54.4	65.9±2	555.2±2	57.6
55.30	44.70	58.9	41.1	60.3±3	396.5±3	63.5
p-EGM:MAA						
10.25	89.75	11.1	88.9	88.4±1	1169.1±4	45.4
15.56	74.44	18.2	81.8	76.7±4	1386.8±3	47.8
23.58	64.80	26.3	73.7	75.5±2	918.3±3	51.7
49.48	50.96	50.6	49.4	72.7±4	581.3±1	54.4
56.30	37.61	61.8	38.2	50.4±3	415.1±2	59.3

Also the tendency of increase in quantity of unreacted maleate groups with decrease of polymers swelling degree is observed. The maximal swelling degree of the received products is characteristic for copolymer 18.22:81.78 (1386.8 %).

It is possible to notice that swelling ability of copolymers reaches the maximal value only at a particular ratio of polyester resins and unsaturated carboxylic acids links. Above and below this ratio more cross-linked copolymers turn out. Such dependence is quite explainable assuming that two factors have an effect on swelling of copolymers: degree of cross-linking and existence of the charged groups. And so, at some point monitoring of one regulator is replaced with another. Thus, we see that there is no simple dependence of swelling degree on copolymer composition.

Copolymers of UPER with MAA possess larger swelling ability in water, than AA. Such dependence can seem to the abnormal at first sight, but it is necessary to take into consideration not only electrostatic repulsive forces, but also structural changes of copolymers upon transition from AA to MAA. Data of an electron microscopy confirm this fact. Earlier the similar case was observed by us at research of copolymers swelling of other vinyl monomer — β-vinyloxyethylacrylamide of AA with AA and MAA [6]. Data were published and quoted many times by other scientists working with unsaturated carboxylic acids.

Other objects for obtaining polymeric matrixes for synthesis of nanocatalysts were copolymers of polypropylene glycol maleate (p-PGM) with AA, MAA. Polyester resins, having hydrophobic group, can change a matrix behavior in less polar mediums. Considering a possibility of «clever» behavior for polymeric catalyst carriers, to synthesize and study this object was interesting in actual reactionary mediums.

Water absorption of copolymers with p-PGM is slightly lower than p-EGM that can be caused by some hydrophobic nature of the first though it was possible to expect smaller degree of a cross-linking because of spatial factors, i.e. large distance from each other of double bonds in p-PGM.

Some characteristics of p-PGM-AA (MAA) copolymers at various initial ratios are presented in Table 2. Unlike the previous system it is possible to observe the linear relation of swelling degree with increase in copolymer of unsaturated carboxylic acids links.

Table 2

The dependence of copolymers composition on an initial mix composition at a copolymerization of p-PGM (M_1) with AA (M_2) and MAA (M_2), DAA [I] of =8 mol/m^3, T = 333 K, [p-PGM-AA, MAA]:[dioxane] — 1:3

Initial mix mass, %		Copolymer composition mass, %		Yield, %	α, %	Number of maleate groups, %
M_1	M_2	m_1	m_2			
p-PGM:AA						
8.35	91.65	9.1	90.9	86.6±3	967.4±4	46.8
21.58	78.42	23.5	76.5	76.2±1	887.5±2	49.7
41.95	58.05	45.6	54.4	70.0±2	764.1±3	52.9
70.01	29.99	73.8	26.2	72.2±3	570.5±2	57.6
85.25	14.75	87.0	13.0	68.4±1	400.6±1	63.5
p-PGM:MAA						
7.02	92.98	8.9	91.1	82.0±3	1209.3±2	45.4
22.13	77.87	26.1	73.9	86.0±2	983.6±2	47.8
41.45	58.55	47.1	52.9	72.0±1	861.7±4	51.7
68.63	31.47	74.9	25.1	68.0±3	795.6±2	54.4
80.25	19.75	87.8	12.2	52.0±4	469.3±3	59.3

The intense absorption bands at 1670 cm^{-1}, corresponding to fluctuation of unreacted double bonds, and the intense absorption bands in the field of 1157 cm^{-1}, corresponding to the ester bond oscillations and fluctuation of the methyl groups of methacrylic acid at 2926 cm^{-1}, carboxyl groups, providing swelling in the field of 1723 cm^{-1} are present in the IR spectra of copolymers p-EGM:AA, MAA and p-PGM:AA, MAA.

The composition of the copolymers was determined by gas chromatography (GC) AGILENT 7890A Technologies DE 19808–1610 USA, equipped with a mass selective detector.

All samples of p-EGM and p-PGM copolymers with unsaturated carboxylic acids showed monomodal type curves, demonstrating that these polymers are copolymers.

Carried out microstructural analysis of the copolymers using a scanning electron microscope (IVS Supra 55VP-3249 firm Zeiss), showed that the test samples of polyester resin with MAA have a cellular structure than with AA. Moreover, copolymer structure is homogeneous enough and suggests the possibility of obtaining metal nanoclusters with predetermined size and satisfactory polydispersity in internodal spaces.

Environmental condition is an important factor in swelling of the copolymers. Previously presented data relate to normal conditions, but these settings can be crucial as in synthesis of metal NP, and in the application of ready-made polymer-immobilized materials. Further, water-absorbing properties of copolymers have been investigated by measuring pH environment, proportion of solvent in the system water-organic solvent and ionic strength for detection of the sensitivity of obtained hydrogels to changes of external factors.

The ability to swell of the polymer can vary significantly with fluctuation of the environment parameters [7]. In turn, the presence of stimulus-responsive transitions in the polymer lattice allows control the size of metal particles during their formation in the matrix. In addition an opportunity to process control appears on the release step.

A large number of foreign and domestic works devoted to the study of hydrogels on the basis of polycarboxylic acids, but the behavior of the latter which contains links of p-EGM and p-PGM have not been studied.

This paper presents the research results of the external factors effect on the copolymers swelling of p-PGM and p-EGM, and a certain mechanism of behavior has been established. However, in contrast to previous studies in this paper 1.3-propylene glycol (previously 1.2-propylene glycol) was used for the synthesis of p-PGM. Changes in the structure of the unsaturated polyester resin give an additional possibility to construct peculiar nanoreactor (in polymer pores) to obtain metal nanoparticles.

By crosslinking polymer chains of unsaturated polyester resin by vinyl monomers having a linear structure, the formation of relatively hard and chemically inert three-dimensional network of the polymer gel occurs, which has good absorption properties against water.

The presence in the structure of such gels of functional links capable of ionization increases their sensitivity to the various environmental parameters changes. As the literature sources show one of such parameters is pH that can significantly affect the properties of polymeric gels [8, 9].

It is known that gels containing groups of weak bases or acids that can be ionized even at a small change in pH have a pH-sensitivity. Uncharged gel is exposed to collapse, while the ionization provokes process of swelling gel, which is due to the arising of the osmotic pressure created by the counter-ions [10–13].

During a series of experiments, the following relationship was found: for hydrogels containing acid groups, the swelling process occurs in an alkaline medium, and in the collapsed state transition is carried out in an acidic medium. On the contrary, the swelling of hydrogels with basic groups is carried out in the acidic medium, collapse is observed at high pH values, where ionization suppression is observed [6].

It was found that the tested polymer hydrogels are in collapsed state in the acidic medium until the pH of the medium is not yet changed upward. The ionization of ionic fragments of macrochains causes an electrostatic repulsion of like-charged groups and creates the straining osmotic pressure of the counter ions that forces the hydrogel to swell even greater.

If we compare the change in the swelling ability of the copolymers range, it increases with the proportion of unsaturated acids, i.e. with an increase in the number of charged links. It is observed both in the case of AA, and MAA. Variation for copolymers of p-EGM and p-PGM is also similar, but with the difference that the depth of the contraction of the hydrogels is less pronounced in the latter.

The effect of the presence of compositions of binary mixtures of solvents on the volumetric characteristics of these gels has been studied for a more complete situation of the impact of various environmental factors on the ability of hydrogels swelling on the basis of polyethylene-(propylene)-glycol maleate.

It is especially important that the catalytic reaction is often accompanied by changes in the environment and take place in the presence of organic solvents [14, 15].

Commonly used solvents of different polarity, dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and ethanol (Et) were selected as an organic component. Their content in the mixture was varied from 0 to 1 volume fractions.

The obtained results indicate the fact that coefficient of swelling copolymers of p-EGM-AA, p-PGM-AA is higher in water than in the considered organic, that may argue that with an increase in composition of the binary mixture of the organic solvent proportion the gradual contraction of the polymer network of the investigated hydrogels on the basis of polyethylene-(propylene)-glycol maleate with unsaturated carboxylic acids is observed.

In as much as the studied polymers are ionogenic, solvent quality deteriorates due to the addition of a water-soluble organic solvent and the collapse occurs.

In all cases, we are witnessing contraction and the solvent is less polar, suppression of swelling is more pronounced. There are differences in swelling behavior depending on the nature of the copolymer. Copolymers of p-PGM with AA (MAA) are less susceptible collapse, which may be due to the presence of longer hydrophobic fragment in the structure of the unsaturated polyester resin. It can also be used when the application of copolymer nanocomposites in low-polar environments as required.

In addition to such factors as pH and solution composition the presence of low molecular salt can affect the degree of swelling polymer gels in solution and the size of the intenode space for metal immobilization.

An interaction mechanism of low molecular compound with cross-linked polymers is a key issue, inasmuch as metal NP synthesis occurs from salt as a result of a redox reaction.

In this regard, one of the most promising and challenging task is to study the processes of interaction of metal ions with gels components. As part of this study the effect of a bivalent salt with hydrogels on the basis of p-EGM and p-PGM with AA (MAA) was examined.

A series of experiments to identify the behavior of the obtained copolymers in solutions with increasing concentration of $NiCl_2$ were conducted.

It is found that low concentration values of metal salts affect slightly the polymer gels of polyethylene-(propylene)-glycol maleate. With further increase of the salt concentration a decrease of the swelling capacity is observed. This fact will be taken into account during the synthesis of nanoparticles in a polymer matrix. It should be understood that the lattice will be compressed in the presence of salt in the solution, and it is directly important to control the size and dispersion of metal NP in the system.

In studies of the effect of temperature on swelling of investigated copolymers we have found that this factor has no significant effect on the phase transition of these systems. Perhaps this is due to charged macromolecules links and domination of strength electrostatic repulsion of the hydrophobic interaction of macrochains areas.

Comparison of the experimental results shows some differences in the swelling polyester resins copolymers containing polyethylene and polypropylene fragments. In general, it is possible to observe that the curves have a common regularity. However, the nature of the substituent and copolymers and their compounds lead to a more pronounced stimulus-induces transition or contraction. In some cases, a so-called latency period, i.e. there is a delay in the change of the properties on the stimulus effect. All these features of the swelling should be considered in the synthesis of nanocatalysts.

Thus, on the basis of the above, we can draw the following conclusions:

1. The obtained new polymers on the basis of polyester resins (p-EGM, p-PGM with MAA and AA) are promising for use as matrix polymers in the synthesis of metal nanoparticles and nanocomposite use in the electrocatalytic hydrogenation reactions. It is shown that the nature of comonomers and their content in the copolymer, i.e. composition of copolymer show a significant impact on the sorption properties and porosity of the polymer. The products were identified and some of their physical and chemical properties have been studied.

2. The effect on polymer hydrogels (potential carriers of nanocatalysts) of external factors such as the pH, ionic strength, the presence of an organic solvent, the temperature change was studied. Described parameters affect the swelling capacity of the copolymers and hence are important to account for the synthesis of metallic nickel, and the development of apparatuses and conditions of use of the polymer-immobilized nanoclusters in various catalytic processes. Discovered stimulus-sensitive transitions are also important. For example, an increase in the swelling of the copolymer-containing metal nanoparticles occurs with increasing pH. This has a positive effect on the kinetics of electrocatalysis process as in the reaction conditions of pyridine hydrogenation with increasing pH of the medium nanocatalysts availability will increase symbatically.

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Металл нанобөлшектерін иммобилизациялау үшін полиэфир шайырлары негізінде полимерлік матрицаларды алу

Мақалада ауыспалы металл нанобөлшектерін иммобилизациялау үшін полимерлік матрицаларды алу мақсатында қанықпаған полиэфир шайырларының акрил және метакрил қышқылдарымен сополимерлері синтезделген, олардың ісіну қабілеті зерттелген. Полимерлік гидрогельдердің сыртқы факторларға, ортаның pH, еріткіштің сапасы және ерітіндінің иондық күші, сезімталдығы көрсетілген.

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Получение полимерной матрицы на основе полиэфирных смол для иммобилизации наночастиц металлов

В статье с целью создания полимерных матриц для иммобилизации наночастиц переходных металлов синтезированы сополимеры ненасыщенных полиэфирных смол с акриловой и метакриловой кислотами и изучена их набухающая способность. Показана чувствительность полимерных гидрогелей к внешним факторам, таким как pH среды, качество растворителя и ионная сила раствора.

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