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## Structure of catalysts with gold nanoparticles

Catalyst by an immobilization of gold nanoparticles in a matrix of amphoteric cryogel on the basis of methacrylic acid and a dimethylaminoethylmethacrylate (MAK/DMAEM) were synthesized. The structure of cryogel and catalyst was investigated by the method of scanning electronic microscopy.

*Key words:* amphoteric cryogel, gold nanoparticles, catalyst, structure, scanning electronic microscopy.

Nowadays, the catalysis chemistry nanoparticles or colloidal solutions of nanodimensional particles of metals rapidly develops. It is connected with their high specific surface that approaches a catalysis to homogeneous type as well as with the existence on a surface of nanoparticles of considerably bigger share of atoms of metal, than in the ordinary heterogeneous catalyst. The term «nanocatalysis» which is considered as peculiar «bridge» between a heterogeneous and homogeneous catalysis [1] has been introduced.

Activity of the catalysts with gold nanoparticles is unique as allows to work at ambient temperature and even below. Already, scientists have achieved a certain progress in the development of competitive methods of production of a significant amount of the catalyst based on gold nanoparticles and have created reliable methods of their storage for ensuring appropriate durability of catalysts under the demanded service conditions [1–5].

Characteristic morphological feature of the cryogels which are formed in superficially frozen environment is their macroporosity and as growth of each crystal of the freezing solvent happens up to close contact with a side of other crystal, after thawing of system of a macrotime at the created gel material become interconnected. The formed cryogels usually have macroporous or supermacroporous structure that gives to such materials a unique set of physical and chemical properties, and also allows to use them for the solution of a number of biomedical and technological tasks. Cryogels are perspective material for creation of catalytic reactors of flowing type. When using cryogels as carriers of the immobilized catalysts the macroporous structure of cryogels provides diffusive and unhindered transport of substrate by the immobilized operating beginning and branch of products from it.

Besides, polyamphoteric cryogels are capable to restore ions of precious metals when heating with formation of nanoparticles [6, 7].

Among the modern methods of research of microstructures of catalysts there is the X-ray spectral analysis. The X-ray spectral analysis is carried out by means of the modern equipment — a raster electronic microscope. The low-vacuum electronic microscope of JSM-6390 LV («JEOL», Japan) with system of the X-ray spectral microanalysis of INCA ENERGY 250 is intended for visualization micro- and nanostructures of a surface of various samples; studying of morphology of a surface of a sample; measurements of the sizes, forms, orientations of objects; studying of element structure of samples; map developments of distribution of chemical elements on the area of a sample; supervision of features of structure of material.

The goal of this work is preparation catalysts with gold nanoparticles and research of a microstructure of catalysts by the method of scanning electronic microscopy.

Synthesis of catalysts with gold nanoparticles was carried out on the basis of «Institute of polymeric materials and technologies» of Almaty, the microstructure was investigated on the basis of «Test regional laboratory of the engineering profile “Scientific Center of Radio Ecological Researches”» of Shakarim State University of Semey.

### *Experimental part*

Firstly, the amphoteric cryogel on the basis of methacrylic acid and a dimethylaminoethylmethacrylate (MAA/DMAEM) in the ratio 1:1 was synthesized. For this purpose the reactionary mix consisting of MAA, DMAEM and methylenebisacrylamide (MBAA) was dissolved in water then cooled the initial monomeric mix (IMM) to 0 °C, further the tetramethylenediamin (TMED) was added and reactionary mix was blown nitrogen within 10 min. Then added 0,1 ml of 10 % of solution of persulphate of ammonium to reactionary mix and spilled in vessels of a cylindrical form. Cryopolymerization was carried out in the cryostat at –12 °C

within 48 hours. After defrosting cryogels were washed out by the distilled and bidistilled water within 2 days with replacement of water in each 4 hours.

The gold nanoparticles stabilized by cryogel were prepared by the following technique. 2 ml of working solution of gold ( $\text{HAuCl}_4$  with concentration of Au 100 mg/l) was dissolved in 18 ml of bidistilled ultraclear water. Then lowered the dry weighed cryogel in solution and heated solution on a water bath within 30 minutes. Change of a color of cryogel was resulted.

Investigated a microstructure of the synthesized cryogel, and also the cryogel containing gold NPs, a X-ray spectral method on a low-vacuum raster electronic microscope of JEOL firm (Japan). For this purpose cryogels were dried up in vacuum drying before full drying. Increasing the received pictures of cryogels, photographed a microstructure, and also measured the size of the prepared gold nanoparticles.

### Results and discussion

Determination of the synthesized cryogel composition was carried out by a spectrophotometric method on the Specord 210 Plus spectrophotometer (Germany).

For this purpose the samples of cryogel which are previously weighed and bulked up in water were placed in solution of dyes with concentration  $1 \cdot 10^{-5}$  mol/l. As dyes methylene blue (MB) and methyl orange (MO) were chosen. As a part of the methyl orange there is a sulfonate group which is capable to interact with a tertiary amino group of DMAEM, and as a part of the methylene blue there is a tertiary amino group capable to interact with the MAA carboxyl group.

For quantitative electrostatic interaction of acid and main groups of cryogel with molecules of dyes value pH solution of dye was maintained so that the functional group of cryogel was completely loaded opposite to a dye charge. For this purpose pH solution of the methyl orange was supported at pH=4.8, and methylene blue at pH=9.18.

The composition of amphoteric cryogel determined by a spectrophotometric method — by amount of the adsorbed anion and cationic dyes cryogel — corresponds to composition of initial monomeric mix and is equal to equimolar composition (Table).

Table

Results of spectrophotometric research of interaction of cryogels with dyes

Specific adsorption, $G \cdot 10^{-6}$ , mol/g		Share of carboxyl groups, %	Share of amino groups, %
Methylene blue	Methyl orange		
1.73	1.74	49.84	50.16

The microstructure of the cryogel synthesized by us studied by us by method of the X-ray spectral analysis with increase in 150 and 600 times is presented in Figure 1.

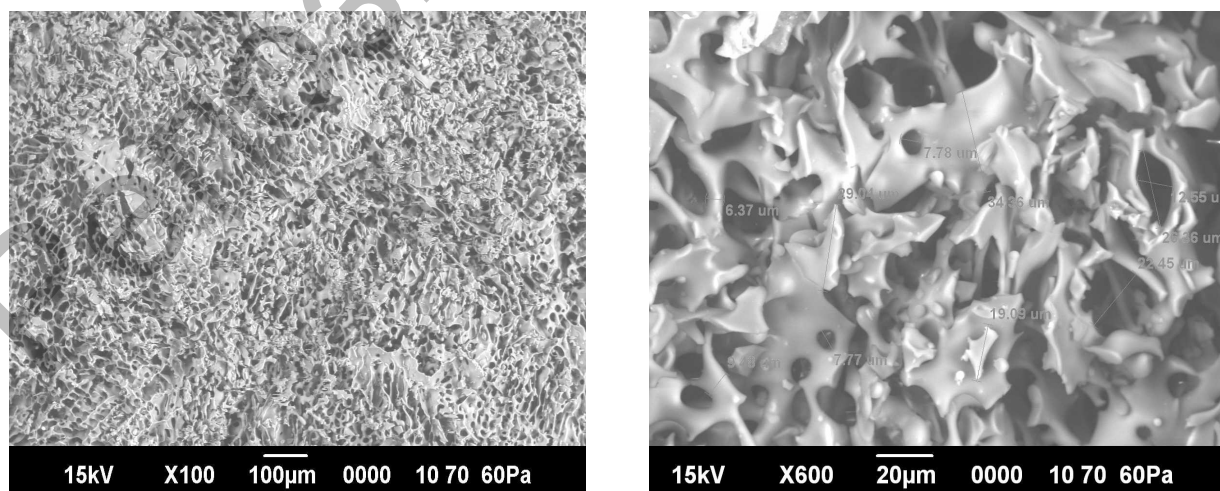


Figure 1. Microstructure of MAA/DMAEM (1:1) cryogel

From figures it is visible that cryogel has porous structure, the size of pores of cryogel makes from 7,7 nm to 26,36 nm.

As a result of a gold immobilization colourless cryogel was colored in crimson color (Fig. 2), characteristic for colloidal gold nanoparticles.

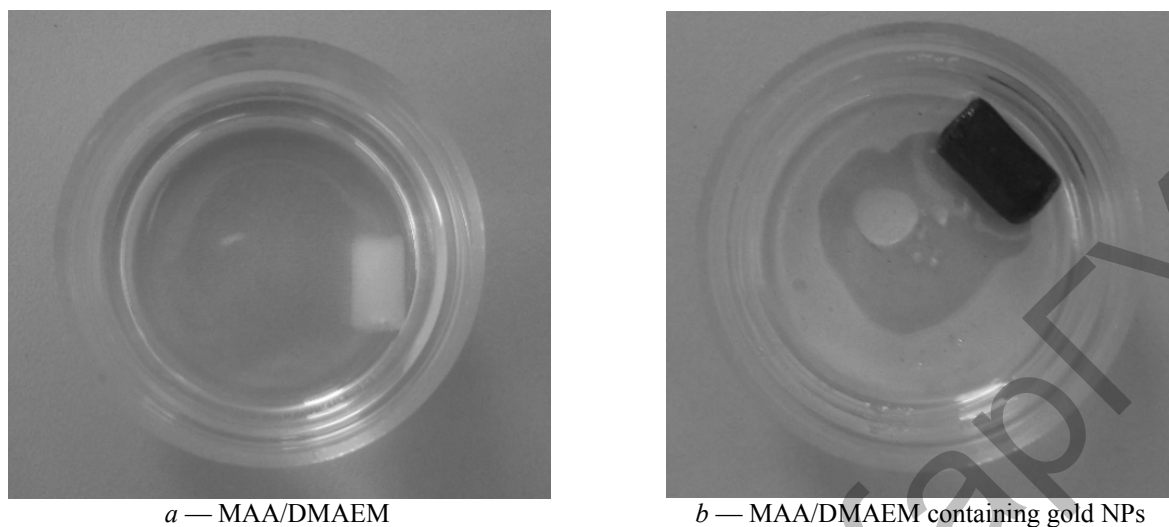


Figure 2. Change of coloring of cryogel after heating in  $\text{HAuCl}_4$  solution within 30 minutes

The microstructure of cryogel was investigated by a X-ray spectral method on a low-vacuum raster electronic microscope of JEOL firm (Japan). For this purpose cryogel in vacuum drying dried up before the full drying. Then cryogel was placed on a microscope. Increasing the received cryogel pictures, photographed a microstructure and measured the size of the received gold nanoparticles. The photo of a microstructure of the catalyst is given in Figure 3.

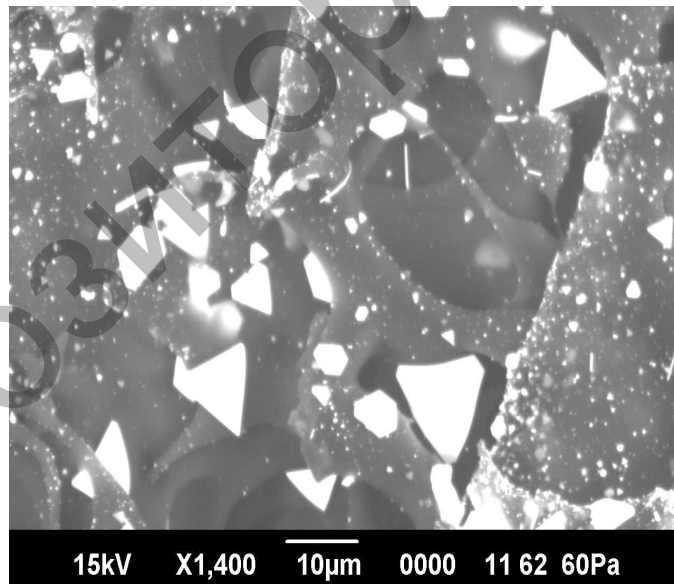


Figure 3. Microstructure of catalyst with gold nanoparticles

To be convinced how gold nanoparticles in cryogel were distributed, a longitudinal section from the middle was made and investigated. As a result the following picture was received (Fig. 4).

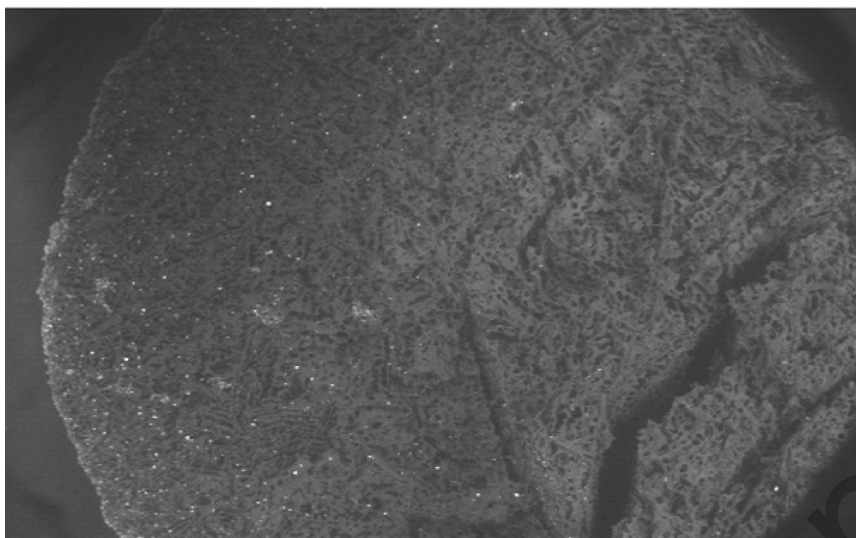


Figure 4. The microphoto of a longitudinal section of cryogel with gold nanoparticles

When mapping elements it is possible to see uniform distribution of gold nanoparticles (Fig. 5).

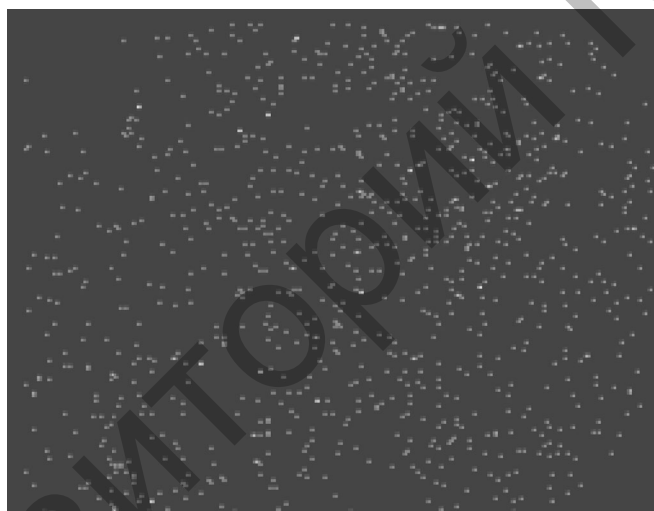


Figure 5. Distribution of gold NPs in volume of cryogel

### Conclusion

Thus, the MAA/DMAEM amphoteric cryogel of composition 1:1 was synthesized. Cryogel has porous structure, the size of cryogel pores makes from 7.7–26.36 nm.

The gold nanoparticles stabilized by cryogel were synthesized. The prepared gold nanoparticles have a triangular form and are evenly distributed in volume of cryogel.

The received samples were approved as flowing catalysts for *p*-nitrophenol reduction reaction. For what cryogel with gold nanoparticles was placed in a glass tube and through it passed a substrate, sodium borohydride and bidistilled water. Concentration of *p*-nitrophenol and *p*-aminophenol was determined by spectrophotometric method after each transmission of a substratum via the catalyst to a complete reduction of *p*-nitrophenol. According to the preliminary data for the catalyst with gold NPs high values of conversion, activity and stability are characteristic.

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### **Алтын нанобөлшектері бар катализаторлардың құрылысы**

Алтын нанобөлшектерін метакрил қышқылы мен диметиламиноэтилметакрилат (МАК/ДМАЭМ) негізінде алынған амфотерлі криогель матрицасына иммобильдеу арқылы катализатор алынды. Катализатор құрылысы сканирлеуші электрондық микроскопия әдісімен зерттелді.

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### **Структура катализаторов с наночастицами золота**

Синтезирован катализатор путем иммобилизации наночастиц золота в матрицу амфотерного криогеля на основе метакриловой кислоты и диметиламиноэтилметакрилата (МАК/ДМАЭМ). Структура катализатора исследована методом сканирующей электронной микроскопии.