- 5. Sionkovska A., Grabska S., Lewandowska K., Andjejczyk A. Polymer films based on silk fibroin and collagen – physicochemical properties // Mol. Christ t. - 2016. - 640. - 13-20.
- 6. Sangkert S., Mizan J., Kamonmattayaqul S., Chai W.L. Collagen/decellularized for bone tissue engineering in cleft palate Pulp-modified silk fibroin scaffolds: morphological struc-

tures and biofunctions // Mater. Sci. Most. C. -2016. - 58. - 1138 - 1149.

7. Hashimoto T., Taniguchi Y., Kameda T., Tamada Y., Kurosu H. Properties and protein content of silk fibroin molecules in autoclaved fabrics changes // Polym. Degrade. Stab. - 2015. -112. - 20 - 26.

# **MODIFICATION OF ZEOLITE CATALYST** WITH NICKEL AND ZINC SALTS FOR PROCESSING OF NATURAL GAS LIQUIDS

#### A. V. Saprygina, A. A. Altynov

Scientific supervisor - engineer of Research School of Chemistry & Applied Biomedical Sciences A. A. Altynov Linguist - engineer of Research School of Chemistry & Applied Biomedical Sciences A. A. Altynov

> National research Tomsk Polytechnic University 634050, Russia, Tomsk, Lenina avenue, 30 avs303@tpu.ru

In the modern world, against the backdrop of new ecological standards, oil refining with minimal energy consumption and emissions into the atmosphere comes to the fore. Zeolites have high activity, so they are used as catalysts, and by modifying zeolites, their properties can be changed to obtain the desired products.

This work, describes the process of modifying zeolite catalysts with nickel and zinc salts used for processing natural gas liquids to motor gasoline.

For modification zeolite catalyst was used that was previously dispersed to practical size of 0.5-1.0mm.

## 1. Modification zeolite catalyst with nickel salt Ni(NO<sub>3</sub>)<sub>2</sub>

The ratio of zeolite catalyst and solution used in the work was: per 100 g of catalyst 170 ml of salt solution according to [1], the concentration of the salt solution is 1 wt. %. To process the solution, the zeolite was placed on a mixing device for 5 hours, after which it was filtered, washed with hot distilled water and left overnight. The next day, the zeolite was dried for 2 hours at a temperature of 80 °C, and calcined at a temperature of 350 °C for 4 hours.

The catalyst treated with nickel salt is most active in the hydrogenation reactions of unsaturated, aromatic and carbonyl compounds. Nickel included in the impregnation increases the activity of the catalyst in dewaxing reactions.

### 2. Modification of the zeolite catalyst with zinc salt ZnF,

The ratio of zeolite catalyst and solution used in the work was: 100 g of catalyst per 500 ml of solution, according to [2].

At the first stage, the zeolite was treated for 1 hour with an aqueous solution of  $Zn(NO_3)_2$  salt with a concentration of 0.1 M at a temperature of 80 °C. At this stage, ion exchange takes place, during which the Zn<sup>2+</sup> cation is incorporated into the zeolite crystal lattice. After ion exchange, the zeolite was washed and decanted.

At the second stage, the zinc form of the zeolite was impregnated with a solution of NH4F salt, at a concentration of 1.0 M, the impregnation was carried out at a temperature of 80 °C for 1 hour. Fluorine ions contribute to the retention of zinc ions, forming an insoluble compound ZnF2 on the surface of the zeolite.

In the third step, the zeolite catalyst was decanted and washed. Dried at a temperature of 120 °C for 6 hours, then calcined at 600 °C for 6 hours.

The zeolite catalyst treated with ZnF, salt does not require hydrogen treatment for the dewaxing process, which significantly reduces the hazard and production costs. The stability of the catalyst depends primarily on the state of the zeolite crystals outer surface; the presence of an insoluble compound on the surface reduces the rate of petroleum coke formation.

Summary, in the work, a zeolite catalyst was modified with Ni(NO<sub>3</sub>)<sub>2</sub> and ZnF<sub>2</sub> salts for processing natural gas liquids in order to obtain components of motor gasoline.

## References

- Doroshenko A.A., Utemov A.V., Semikin K.V. Zeolite-containing catalysts modified with Ni for the alkylation of isobutane with olefins // St. Petersburg State Technological Institute. – 28 p.
- 2. Pat. 2017107255 RF IPC B01J 29/40 C10G 11/05. Zeolite catalyst and method of hydrogen-free dewaxing of hydrocarbon raw mate-

rials using it / Ponomarev A.B.; Patent owner: Federal State Budgetary Institution of Science Institute of Organoelement Compounds named after. A.N. Nesmeyanov of the Russian Academy of Sciences (INEOS RAS); appl. 2017.03.06; publ. 2018.03.22.

# CYTOTOXIC COPPER (II) COMPLEXES WITH DIPHENYLPHOSPHINIC ACID AND 1,10-PHENANTHROLINE / 2,2'-BIPYRIDINE DERIVATIVES

P. E. Savinykh<sup>1,2</sup>

Scientific supervisor – PhD, researcher Yu. A. Golubeva<sup>1,2,3</sup> Linguistic advisor – PhD, researcher Yu. A. Golubeva<sup>1,2,3</sup>

<sup>1</sup>Nikolaev Institute of Inorganic Chemistry SB RAS 630090, Russia, Novosibirsk, 3 Academic Lavrentiev Avenue

<sup>2</sup>Novosibirsk State University 630090, Russia, Novosibirsk, 1 Pirogov Street

<sup>3</sup>Institute of Molecular Biology and Biophysics, Federal Research Center of Fundamental and Translational Medicine (IMBB FRC FTM) 630060, Russia, Novosibirsk, 2/12 Timakova Street p.savinykh@g.nsu.ru

The search of new drugs for oncotherapy remains one of the main problems of modern medicine. Since metal-based clinically approved drugs (cisplatin and its derivatives) possess severe side effects and chemotherapy resistance, the development of less toxic anticancer medications based on biologically relevant metals is of great interest. Copper, one of the first-row transition metals, is involved in a variety of fundamental biological processes [1] and has been acknowledged as a limiting factor for multiple aspects of cancer progression (growth, angiogenesis, metastasis) [2]. Currently, many cytotoxic copper complexes with various N-, O-, S-donor ligands have been synthesized, and one of the compounds (Casiopeína III ia - [Cu(4,4'-dimethylbipyridine)(acac)]NO<sub>2</sub>) registered as Mark Title Casiopeínas® has even reached the clinical phase I [3]. In view of this, the research into preparation and investigation of 1,10-phenanthroline / 2,2'-bipyridine based copper (II) complexes has been quite active recently.

In the present study, six mixed-ligand copper (II) complexes with diphenylphosphinic acid (*HL*) and 1,10-phenanthroline or 2,2'-bipyridine derivatives ( $L^{N-N}$ ), namely, 1,10-phenanthroline (*phen*), 4,7-dimethyl-1,10-phenanthroline (*dmphen*), 5-chloro-1,10-phenanthroline (*Cl-phen*), 2,2'-bipyridine (*bipy*) and 4,4'-dimethyl-2,2'-bipyridine (*dmbipy*) were synthesized. The use of diphenylphosphinic acid, bioisostere of carboxylic acids, as a secondary ligand was supposed to alter physical properties of the complexes and improve their cytotoxic activity and selectivity. The basis of the synthesis method was to dissolve the sample of the corresponding phenanthroline or bipyridine derivative in ethyl or isopropyl alcohol with the further addition of copper (II) acetate monohydrate and *HL* samples.

The composition and structures of the complexes were established using physicochemical methods: CHN, thermogravimetric, powder X-ray diffraction and single-crystal X-ray diffraction analysis, EPR and IR-spectroscopy. In most of the experiments the composition of mixed-ligand copper (II) complexes can be described by the general formula [Cu( $L^{N-N}$ )(H<sub>2</sub>O)L<sub>2</sub>]. Phenanthroline and bipyridine derivatives have been shown to be chelating agents in these complexes, while anion of diphenylphosphinic acid exhibits monodentate coordination.

The cytotoxicity of the complexes and ligands was investigated against cancer (Hep2, HepG2) and non-cancerous (MRC5) cell lines by Hoechst 33342/propidium iodide fluorescent dyes staining in 0,1–100  $\mu$ M concentration range. The complexes possess significant cytotoxic activity comparable to that of cisplatin.

This work was supported by the Russian Science Foundation (Project № 20-73-10207).