

# Isomerization of linear hexane over acid-modified nanosized nickel-containing natural Ukrainian zeolites



Patrylak L.K.<sup>1\*</sup>, Pertko O.P.<sup>1</sup>, Yakovenko A.V.<sup>1</sup>, Voloshyna Yu.G.<sup>1</sup>, Povazhnyi V.A.<sup>1</sup>, Kurmach M.M.<sup>2</sup>

<sup>1</sup> Department of Catalytic Synthesis, V.P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry of NAS of Ukraine.

<sup>2</sup> Department of Porous Compounds and Materials, L.V. Pysarzhevski Institute of Physical Chemistry of NAS of Ukraine.

\* Corresponding author: lkpa@ukr.net

## Introduction

More and more scientists around the world are paying attention to the creation of new nanostructured materials, among them are micro/mesoporous zeolite-containing materials, which are of great importance. An advanced porous system is the key to creating highly efficient adsorbents and catalysts that will ensure the proper accessibility of reagents to the active sites. Problems with high diffusion rates of reagents or reaction products often occur for microporous zeolite materials. Highly active compositions may lose their efficiency because of partial blocking of the active sites by overlapping narrow zeolite channels and pores with reagents or coke. This moment is very relevant for mordenite zeolite with channel structure. Its bigger channels of 0.7 nm diameter are generally available for hydrocarbons, but smaller ones (0.3 nm) can adsorb predominantly water molecules. Therefore, the question of improving the porous system of mordenite zeolite, on the basis of which an industrial catalyst for the isomerization of linear alkanes is obtained, is very relevant. Modern isomerization catalysts are bifunctional systems, which, in addition to the acid component, contain hydrogenating-dehydrogenating metals. The latter is usually represented by elements of the platinum group. A number of studies have shown high activity of both bimetallic systems containing nickel and platinum [1-3] as well as monometallic nickel containing MFI zeolites [4]. Earlier it was shown that the natural mordenite-clinoptilolite rock of Transcarpathia is quite good as a carrier for palladium-coated isomerization catalyst.

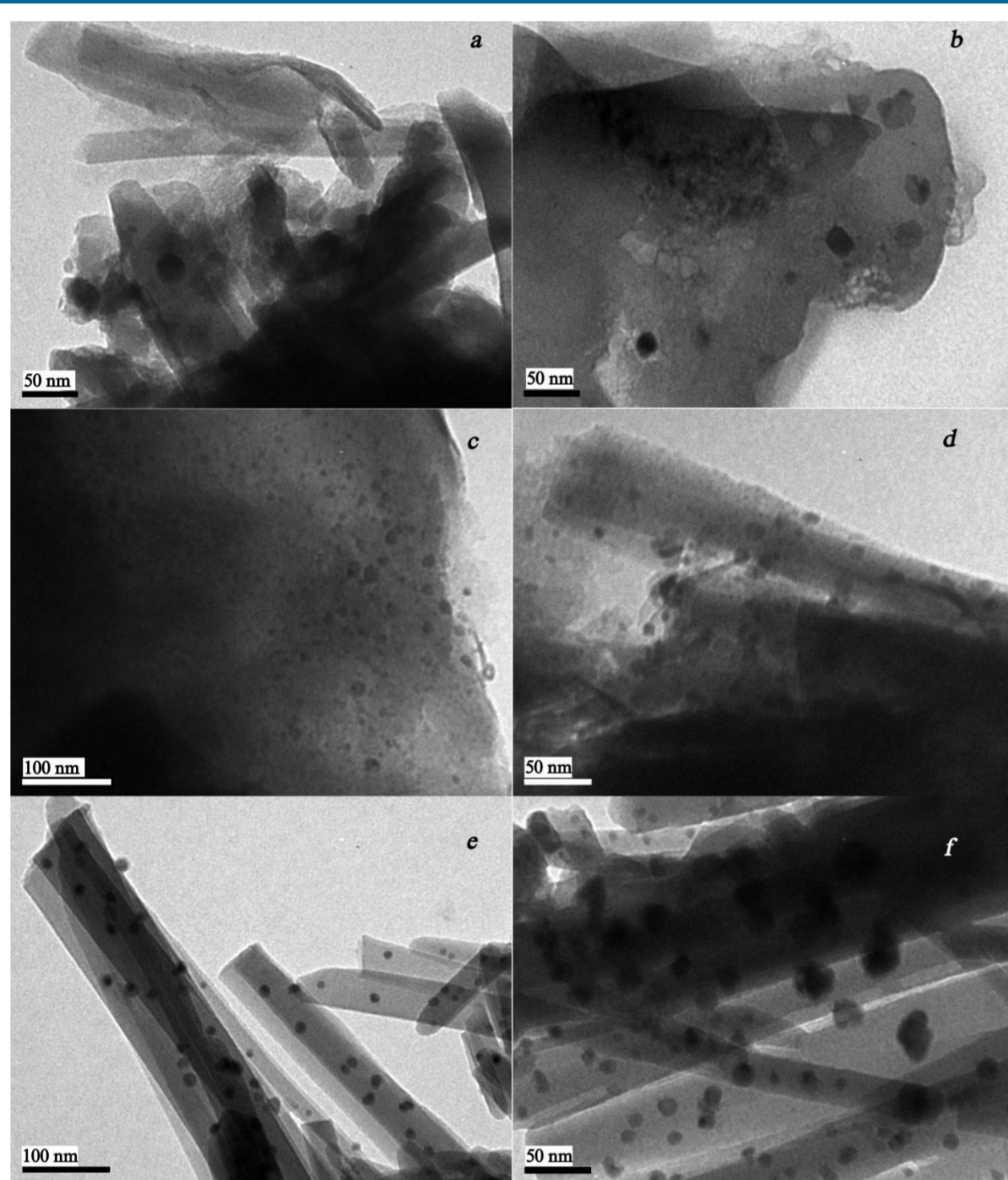
Therefore, the aim of this work was to evaluate the effect of improving the porous structure of the natural Transcarpathian zeolites on the efficiency of Ni-containing isomerization catalysts on their basis.

## Experimental

Mordenite-clinoptilolite rock (Lipcha village, Transcarpathian region) was an origin for successive modification. To start with, natural rock was grounded to a fraction of 0.5-1.0 mm. The sample was treated by ammonium chloride by being boiled at 95-100 °C for 2-3 h in a water bath with stirring. Thus, the obtained ammonium form of natural zeolite was separated by filtration, washed by distilled water from chlorine anions and dried at 100 °C. Ammonium form was converted to the hydrogen one by means of calcination for 2 h at 600 °C in a muffle furnace in the presence of air. In order to expand the size of pores of the natural material, the rock was dealuminated by removing structural aluminum from the zeolite lattice with hydrochloric acid. For this purpose, the samples of zeolite hydrogen form were treated by concentrated HCl solutions (1, 3 and 5 mol dm<sup>-3</sup>) at the boiling point of the water bath for 3 h. The obtained samples were filtered off, washed with distilled water until neutral reaction and dried at 100 °C. Thus, samples HMLP-1, HMLP-3 and HMLP-5 were obtained. The samples were impregnated by nickel. The metal nominal loading for the samples obtained were 1.0, 1.5, 2.0, 2.5, 3.0 wt %. Nickel-containing samples were prepared by wetness impregnation using solution of nickel (II) nitrate hexahydrate. The solution was evaporated for 12 h at ambient conditions. Then the samples were dried for 2 h at 100 °C. As a result, catalysts with different nickel content were synthesized. Nickel recovery was carried out in a hydrogen flow at 380 °C for 6 hours. The amount of nickel in the samples is indicated before the symbol Ni.

Samples have been characterized by means of XRD, XRF, FTIR-spectroscopy, low temperature nitrogen adsorption/desorption, DTA/TG, TEM. Catalysts have been tested in micro pulse linear hexane isomerization using micro pulse set-up based on gas chromatograph equipped with a flame ionization detector.

## Results



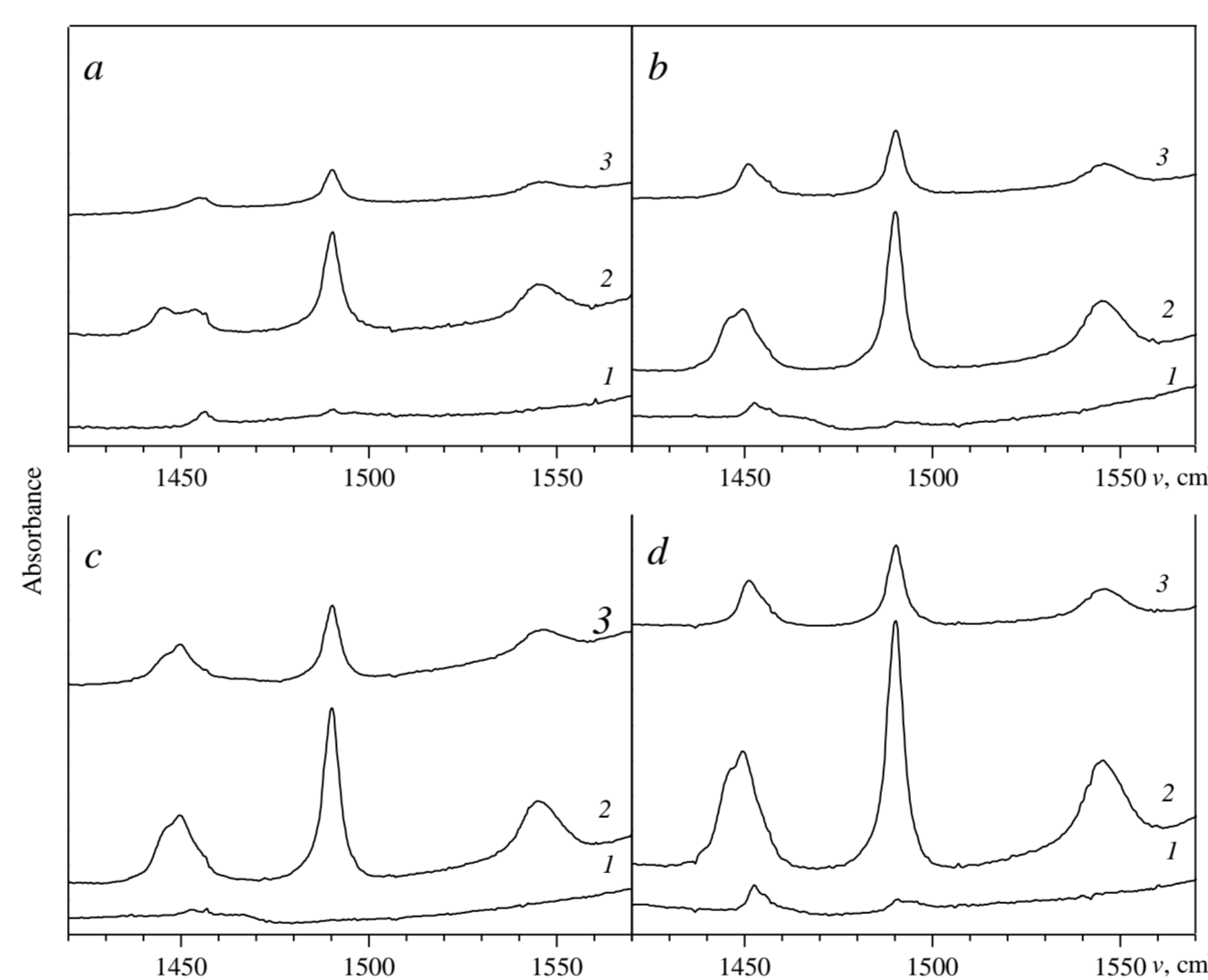
**Figure 1** TEM images of nickel nanoparticles over zeolite samples with different metal content: a, b - HMLP-1-1Ni; c, d - HMLP-1-2Ni; e, f - HMLP-1-2.5Ni

**Table 1** - Characteristics of nickel specimens over the catalysts

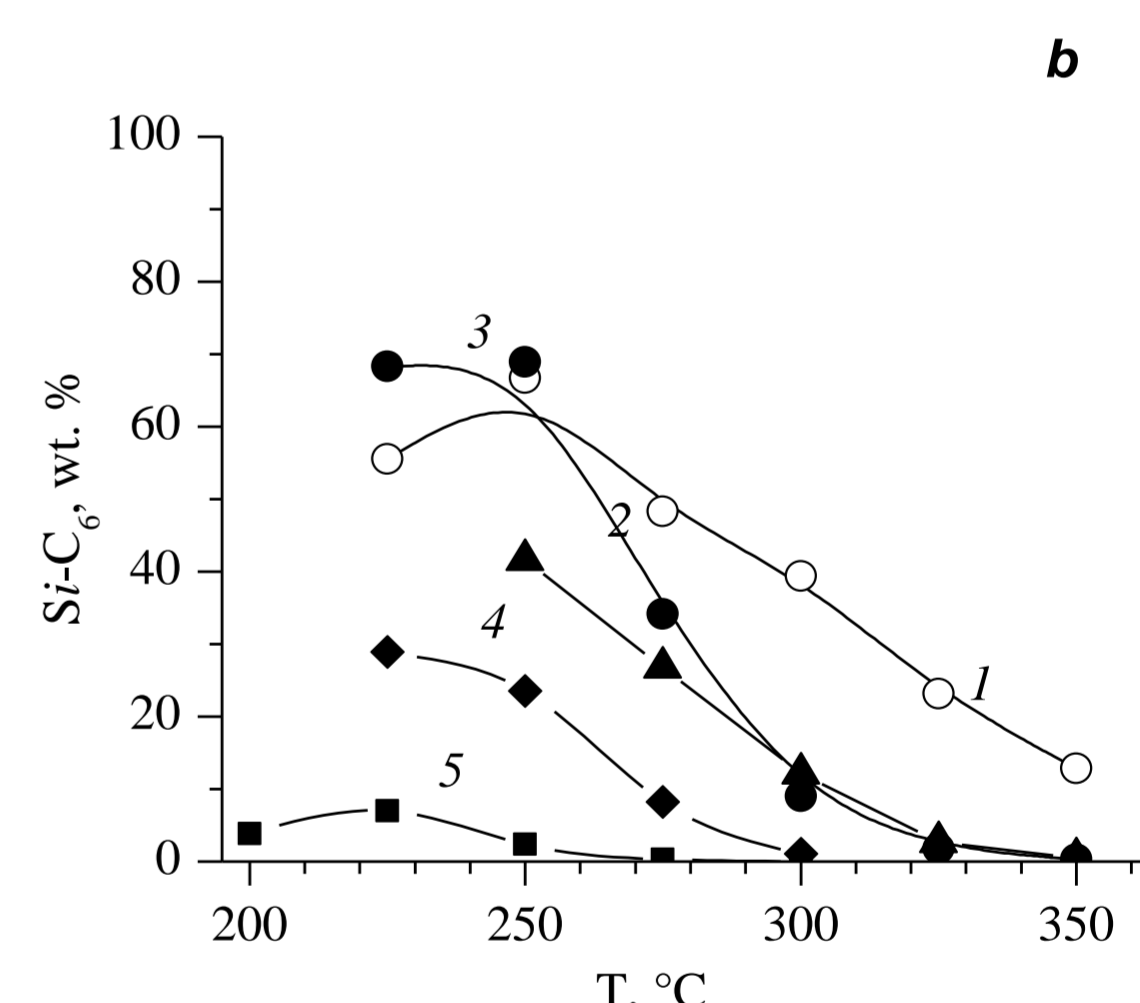
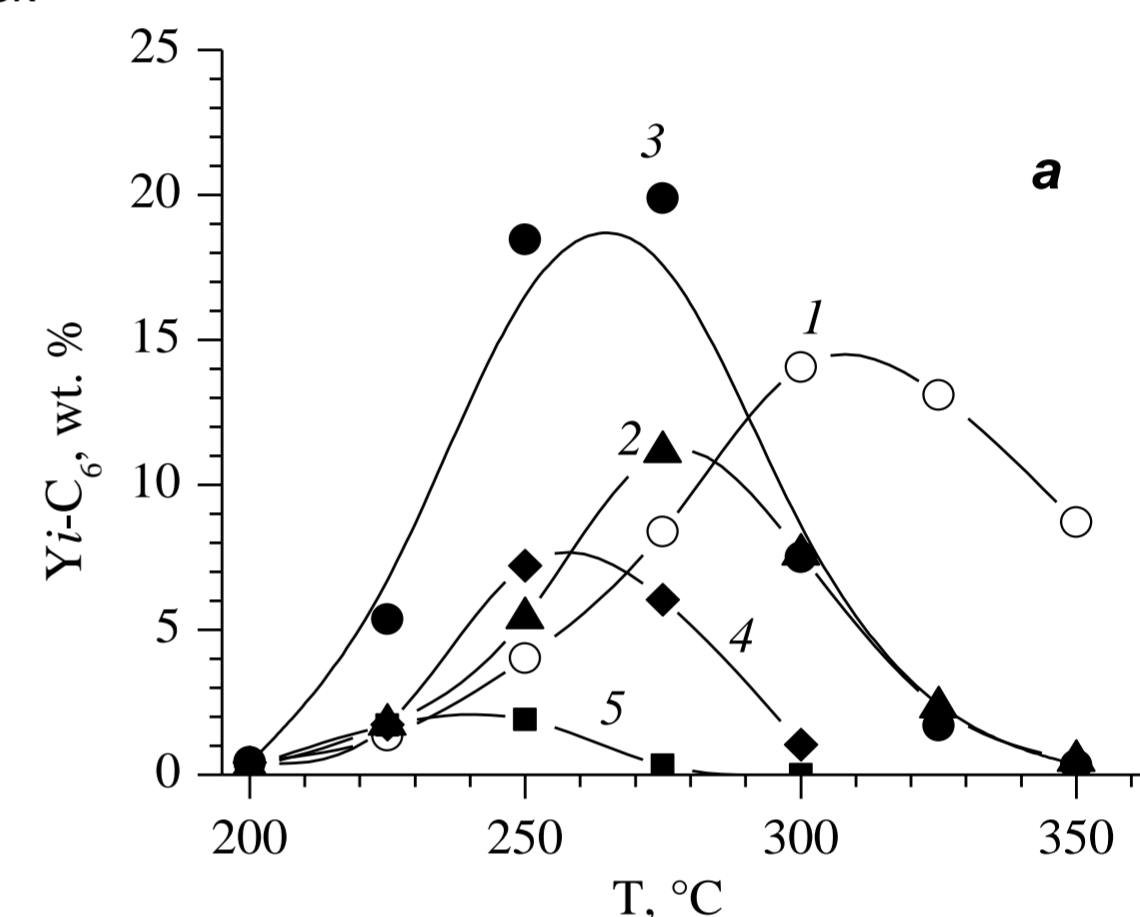
Catalyst	Species size, nm	Description of metal particles
HMLP-1-1Ni	10-60	Significant particle size distribution
HMLP-1-2Ni	5-8, 12, 15	Many small particles 5-8 nm, few 12, 15 nm
HMLP-1-2.5Ni	10-15, 20-40	Many particles 10-15 nm, few 20-40 nm
HMLP-3-1Ni	10-15	Slight variation in particle size
HMLP-5-1Ni	10, 50	Most particles are 10 nm, some are 50 nm

**Table 2** - Adsorption characteristics of nickel-modified samples of acid-treated zeolite rock

Sample	S <sub>BET</sub> , m <sup>2</sup> g <sup>-1</sup>	S <sub>micro</sub> <sup>t</sup> , m <sup>2</sup> g <sup>-1</sup>	V <sub>Z</sub> , cm <sup>3</sup> g <sup>-1</sup>	V <sub>micro</sub> <sup>t</sup> , cm <sup>3</sup> g <sup>-1</sup>	V <sub>meso BJJH</sub> , cm <sup>3</sup> g <sup>-1</sup>
MLP	95	69.9	0.099	0.032	0.020
HMLP-1-1Ni	330	298	0.204	0.133	0.040
HMLP-1-1.5Ni	304	274	0.189	0.121	0.035
HMLP-1-2Ni	287	257	0.182	0.116	0.040
HMLP-1-2.5Ni	278	228	0.215	0.116	0.070
HMLP-1-3Ni	301	261	0.211	0.124	0.050
HMLP-3-1Ni	292	259	0.186	0.117	0.045
HMLP-5-1Ni	322	284	0.212	0.113	0.065
HM-1Ni micropor.	336	319	0.172	0.132	-



**Figure 2** IR-spectra of HMLP (a), HMLP-1-1Ni (b), HMLP-1-2Ni (c) and HMLP-3-1Ni (d) in the region of adsorbed pyridine: 1 – vacuumed samples before adsorption, 2 - after pyridine adsorption at 150 °C, 3 – after pyridine evacuation at 250 °C



**Figure 3** Yield of *i*-C<sub>6</sub> (a) and selectivity to *i*-C<sub>6</sub> (b) for the zeolite samples with different nickel content in conversion of *n*-hexane: HMLP-1-1Ni (1), HMLP-1-1.5Ni (2), HMLP-1-2Ni (3), HMLP-1-2.5Ni (4), HMLP-1-3Ni (5)

## Conclusions

- The low-temperature nitrogen adsorption/desorption has indicated that, despite additional modification by metallic component, acid treatment of natural zeolite rock increases the volume of mesopores by 2-3 times and the volume of micropores up to 4 times;
- X-ray fluorescence analysis and FTIR spectroscopy confirmed the increase of the silica-to-alumina ratio in samples during the process of acidic dealumination of the zeolite structure;
- Pyridine sorption with IR-spectroscopic control shows the presence of Brønsted and Lewis acid sites over catalysts. For the HMLP sample and for the sample treated by 1 mol dm<sup>-3</sup> acid solution the ratio of Brønsted/Lewis acid sites practically equals to 1, but the application of stronger acid solutions leads to the predominance of Lewis acidity;
- The size of metal crystallites deposited on the natural zeolite rock surface after preliminary acid dealumination has been estimated. The latter is 10 nm for most samples, but larger units up to 20-50 nm and smaller particles of about 5 nm were also observed;
- DTA/TG investigations show different peculiarities of physisorbed water removing from pores of the original zeolite rock and from the samples with enlarged cavities after acid treatment. Structural zeolite water in the form of Brønsted acid sites is removed at 500-800 °C;
- Nickel modified catalysts were tested for isomerization of linear hexane in a flow micro-pulse mode in a hydrogen stream. The sample with 2 wt % nickel content and the smallest metal nanoparticles of 5-8 nm showed the best performance (20% yield of C<sub>6</sub> isomers at 250 °C), which is higher than the microporous nickel-containing synthetic mordenite zeolite (12% at 300 °C).

## Acknowledgments

The authors acknowledge the assistance and support of M.G. Kholodny Institute of Botany of National Academy of Sciences in conducting the electron transmission microscopy experiments. The publication contains the results of studies conducted by President's of Ukraine grant for competitive projects F84/147-2019.

## References

- Jordao MH, Simoes V, Cardoso D (2007) Zeolite supported Pt-Ni catalysts in *n*-hexane isomerization. *Appl Catal A: Gen* 319:1-6. <https://doi.org/10.1016/j.apcata.2006.09.039>
- Lima PM, Garetto T, Cavalcante CL Jr et al. (2011) Isomerization of *n*-hexane on Pt-Ni catalysts supported on H-BEA zeolite. *Catal Today* 172:195-202. <https://doi.org/10.1016/j.cattod.2011.02.031>
- Martins GSV, dos Santos ERF, Rodrigues MGF, et al. (2013) *n*-Hexane Isomerization on Ni-Pt/Catalysts Supported on Mordenite. *Modern Res Catal* 2:119-126. <http://dx.doi.org/10.4236/mrc.2013.24017>
- Patrylak LK, Krylova MM, Pertko OP, Voloshyna YuG (2019) Linear hexane isomerization over Ni-containing pentasil. *J Porous Mater* 26(3):861-868. <https://doi.org/10.1007/s10934-018-0685-1>