

UDC 661.183.6, 665.733, 541.128

DOI: 10.15372/CSD2020242

Changes in the Physicochemical Properties of Nickel-Containing ZSM-5 Zeolite under Mechanical Treatment

L. M. VELICHKINA¹, V. I. ZAIKOVSKII^{2,3}, YA. E. BARBASHIN¹, N. V. RYABOVA¹, S. A. PEREVEZENTSEV¹, A. V. VOSMERIKOV¹¹*Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia*

E-mail: mps@ipc.tsc.ru

²*Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia*³*Novosibirsk State University, Novosibirsk, Russia*

(Received November 05, 2019; revised December 23, 2019)

Abstract

Nickel-containing zeolite samples were prepared by dry mechanical mixing of ZSM-5 zeolite (silica modulus 40) and nickel powder with the average particle size of 50 nm in the amount of 0.5 mass %. The samples were mechanically treated in a ball mill for 24–120 h. The crystallinity of the initial zeolite and mechanically treated nickel-containing zeolites was determined by means of IR spectroscopy and XRS. The degree of zeolite crystallinity was revealed to decrease due to loosening of the structure of both the polycrystalline units and primary crystallites as a result of mechanical treatment. The analysis of the state of nanosized nickel in zeolite catalysts by means of UV spectroscopy and XPS revealed almost complete absence of the oxidation of nickel particles. The morphology of the crystals of the initial and mechanically treated zeolites was studied by means of the high resolution transmission electron microscopy. Mechanical treatment was determined to cause a decrease in the particle size of initial ZSM-5 and partial migration of nickel from the surface into zeolite pores. The size of nickel particles decreases during the initial period of mechanical treatment, while a longer mechanical impact, on the contrary, contributes to the agglomeration of nickel particles. The particles of ZSM-5 zeolite in the initial sample look like coarse agglomerates with the overall size of several micrometres. The agglomerates are composed of smaller polycrystalline units 0.5–1.0 μm in size. However, the primary particles are zeolite crystals 50–100 nm in size. Mechanical treatment causes disintegration of coarse zeolite agglomerates into smaller polycrystalline units less than 1 μm in size; primary crystallites comprising the polycrystalline structure are dispersed, too, decreasing in size to ~50 nm. According to the data of low-temperature desorption of nitrogen, mechanical pretreatment of nickel-containing zeolite causes a decrease in its specific surface area and pore volume. The changes in the physicochemical properties of the Ni/ZSM-5 catalyst caused by mechanical treatment should promote selective conversion of feedstock components and flexibility of the regulation of selective formation of target products in oil refining processes.

Keywords: ZSM-5 zeolite, nanosized nickel powder, mechanical treatment

INTRODUCTION

Solid-phase processes initiated by mechanical action serve as the subject of intense investigations for a long time, which is connected with the

outlooks for the development, of new, so-called dry methods of modification, which are rather simple in the instrumental arrangement, ecologically safe and economically profitable [1, 2]. The major part of the studies deal with the optimiza-

tion of the stage of grinding of solids, in particular zeolite catalysts, for the purpose of obtaining the maximal surface area with minimal energy consumption [3–5]. The works dealing with the use of mills for mechanical treatment (MT) for the purpose of catalyst activation are less numerous [1, 6]. More intense MT causes not only changes in the morphology, specific surface area, and the degree of crystallinity, but also improvement of steric conditions for the process, as a consequence of the partial destruction of the large agglomerates of zeolite and the appearance of a larger number of active centres accessible for the molecules of initial raw material. For instance, we established in [6] that preliminary MT of non-modified ZSM-5 zeolite promotes the improvement of catalytic properties, in particular a decrease in the aromatizing activity and an increase in the yield of catalysate from processing the straight-run petroleum fraction of oil, through a decrease in the degree of crystallinity, specific surface area and acidity. The joint MT of the zeolite and nanometre-sized powder (NSP) of nickel causes enhancement of these effects as we demonstrated in [7].

Interaction between the solids occurs at the sites of contacts between particles; their number and area hold decisive importance, so preliminary grinding and mixing under the conditions preventing particle aggregation is necessary, because aggregation leads to a decrease in specific catalytic activity. The dry mechanical mixing of the zeolite support together with the oxides, salts [8] or NSP of transition metals [9, 10] allows one to stabilize isolated cations in the channels and cavities of zeolites and to synthesize metal-containing zeolite systems in one stage without solvents and in the absence of waste waters. In addition, dry mixing is the only method to introduce NSP of metals into zeolite because the addition of metals into zeolite using traditional impregnation methods leads to the loss of their unique properties.

The goal of the present work is to study the effect of additional MT of nickel-containing zeolite obtained by the dry mechanical mixing of ZSM-5 with the NSP of nickel on the properties of its structure, as well as on localization and state of nickel particles.

EXPERIMENTAL

Modification of the pentasil type zeolite (ZSM-5) with the silica modulus (the molar ratio of $\text{SiO}_2/$

Al_2O_3) equal to 40 was carried out by means of dry mechanical mixing of nickel NSP and zeolite in a KM-1 vibratory mill for 2 h. Nickel nanopowder with the average particle size of 50 nm was obtained by the gas-phase method, its content in the zeolite was 0.5 mass %. The synthesized nickel-containing sample was not annealed to conserve the properties of Ni nanopowder and to prevent its oxidation.

The resulting Ni/ZSM-5 catalyst was subjected to MT in the KM-1 vibratory mill for 24, 48, 72, 96 and 120 h. For catalytic tests, the samples were pressed in tablets, which were then ground, and the size fraction of 0.5–1.0 mm was separated with the help of sieves.

The degree of crystallinity of nickel-containing samples before and after MT was determined with the help of IR spectroscopy and X-ray structural analysis (XSA). The IR spectra of the zeolites were recorded with the help of the Fourier transform IR spectrometer with the Raman unit Nicolet 5700 (TermoElectron, USA) within the range of 2000–400 cm^{-1} . The IR Fourier Transform spectrometer was submitted by the Tomsk Regional Shared Equipment Centre, SB RAS, of the Tomsk Scientific Centre of SB RAS. X-ray structural analysis was carried out using a DISCOVER D8 diffractometer (Bruker, Germany) within the angle range $2\theta = 10\text{--}70$ deg.

The electron state of nickel in the zeolite matrix was studied by means of ultraviolet (UV) spectroscopy with the help of a Cary 300 Scan spectrometer (Varian, Australia) with the diffuse reflection attachment, and by means of X-ray photoelectron spectroscopy (XPS) with the Riber-Cameka Mac-3 spectrometer (Riber, France) using AlK_α -radiation ($h\nu = 1486.6$ eV). In both methods, the samples for investigation were deposited on the conducting carbon substrate. The spectra were processed without background subtraction. Investigation of the microstructure of catalysts was carried out by means of high-resolution transmission electron microscopy (HRTEM) with the JEM-2010 electron microscope (JEOL, Japan) with the resolution over lattice 0.14 nm under the accelerating voltage of 200 kV. The samples for electron microscopic analysis were prepared on perforated carbon substrates fixed on copper grinds.

The specific surface area of the catalysts was determined using Brunauer-Emmett-Teller (BET) from the data on low-temperature (-196 °C) nitrogen adsorption with the help of an automatic gas adsorption analyzer Sorbtometer M (KATAKON, Russia). The volume and size of pores in the sam-

ples were calculated using the BJH model (Bartlett–Joyner–Halenda) from the isotherms of adsorption and desorption at the relative pressure of $P/P_0 = 0.99$.

RESULTS AND DISCUSSION

Figure 1 shows the IR spectra (see Fig. 1, *a*) and diffraction patterns (see Fig. 1, *b*) of initial Ni/ZSM-5 and its mechanically treated forms.

It was established according to the data of IR spectroscopy (see Fig. 1, *a*) that all samples have absorption bands characteristic of zeolites with the structure of ZSM-5 [11]. For instance, the absorption band with the maximum within the region $550\text{--}560\text{ cm}^{-1}$, which determines zeolite structure, relates to the vibrations along the outer bonds of SiO_4 and AlO_4 tetrahedrons and is due to the presence of doubled four-, five- and six-membered rings in the framework. The ratio of the intensities of absorption bands at 550 and 450 cm^{-1} allows estimation of the degree of crystallinity of the samples under investigation, which is 90 % for initial zeolite, while after MT for 120 h it decreases to 80 %.

A set of characteristic bands in the diffraction patterns obtained by means of XSA (see Fig. 1, *b*) also provides evidence of the phase purity of the zeolite and corresponds to the ZSM-5 type [12]. The samples subjected to MT have diffraction bands identical to the reflections of pure zeolites, but the intensity of diffraction bands in the region of $2\theta = 23\text{--}25$ deg decreases with an increase in treatment time, which also points to the partial destruction of the structure of zeolite samples and a decrease in the degree of their crystallinity. Thus, it is about 88 % for the initial Ni/ZSM-5 sample, and MT of the zeolite for 24 and 48 h brings practically no changes into this value (87 and 86 %, respectively). With an increase in the time of MT to 72, 96 and 120 h, zeolite crystallinity decreases to 81, 80 and 78 %, respectively.

We demonstrated in [9, 10] that after annealing Ni/ZSM-5 in the air at $550\text{ }^\circ\text{C}$ nickel is transformed into oxidized forms, which promotes undesirable reactions of aromatization during processing the straight-run petroleum fraction. The electron state of nickel on the surface of mechanically treated samples without annealing was determined with the help of UV spectroscopy and XPS. It was established that even after the treat-

ment of Ni/ZSM-5 in the vibratory mill in the air for 120 h the oxidized forms of the metal are almost absent from the catalyst, as the characteristic absorption bands and maxima are not detected in the corresponding regions of the spectra (Fig. 2).

The absorption bands that are to be observed in the UV spectrum in the presence of the oxidized forms (see Fig. 2, *a*) include the following: in the region of 240 nm – the band of charge transfer from O^{2-} to Ni^{2+} ; 320 nm – *d-d*-transition in Ni^{2+} within NiO; 724, 649 and 400 nm – *d-d*-transitions in Ni^{2+} in the octahedral configuration; 400–650 nm – *d-d*-transitions in Ni^+ [13, 14]. Only the presence of low-intensity peaks in the region up to 400 nm may be detected for the studied nickel-containing sample.

The XPS data for the Ni/ZSM-5 sample after MT for 120 h also point to practically complete absence of the transition of nickel particles into the oxidized forms and to the unchanged oxidation degree, which is evidenced by the absence of a shift of the peaks to higher bond energy region in the spectrum and a comparison with the spectrum of metal nickel powder on a substrate (see Fig. 2, *b*). We see the maxima mainly in the region of 852.3–852.8 eV; according to literature data [15], they correspond to Ni^0 bond energy, and substantially smaller maxima in the regions of 853.2–854.2 eV, corresponding to Ni^{2+} bond energy, and 855.8–857.2 eV, characterizing Ni^{3+} .

Thus, after MT nickel particles are present in the zeolite mainly in the form of Ni^0 , which, unlike for the oxidized forms of metals, exhibits higher hydrogenating ability for hydrocarbon transformations, and this allows us to reduce the formation of polycyclic condensed products and to increase in the catalyst cycle length.

The electron microscopic images of the initial Ni/ZSM-5 catalyst (Fig. 3) and mechanically treated samples (Fig. 4, 5) are presented below.

According to the data of HRTEM, the particles of ZSM-5 zeolite in the sample before MT look like coarse agglomerates with the total size of several micrometres (see Fig. 3, *a*). These agglomerates are composed of smaller polycrystalline blocks with a size within the range of 0.5–1.0 μm . However, the primary particles are zeolite crystallites with a size of 50–100 nm (see Fig. 3, *d*). This structure is depicted in the roughness of the surface of zeolite aggregates, which is shown in the insert (see Fig. 3, *a*) and in the images with larger magnification (see Fig. 3, *c*, *d*).

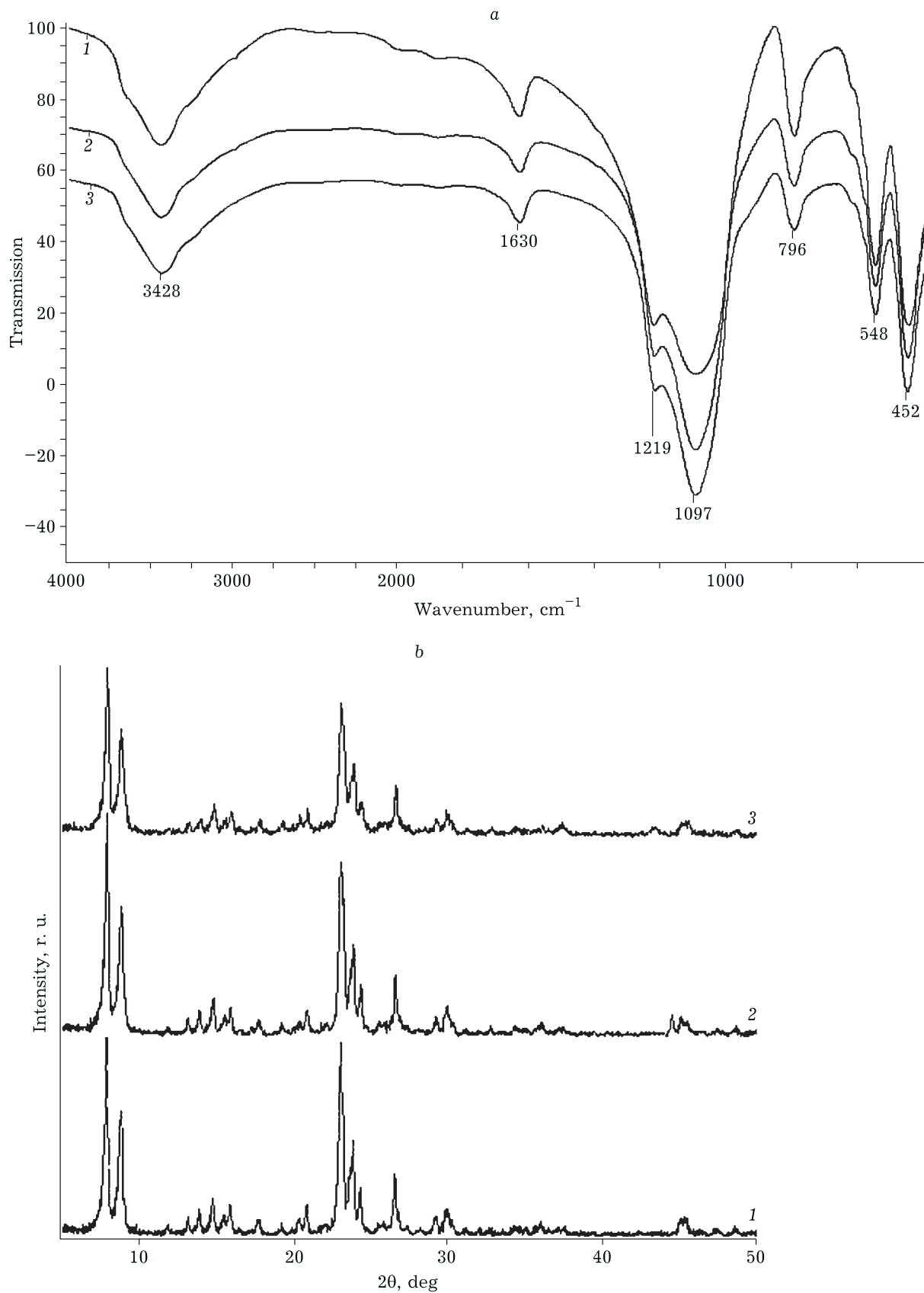


Fig. 1. IR spectra (a) and diffraction patterns (b) of nickel-containing zeolites: 1 - Ni/ZSM-5; 2 - Ni/ZSM-5 (MT for 48 h); 3 - Ni/ZSM-5 (MT for 120 h).

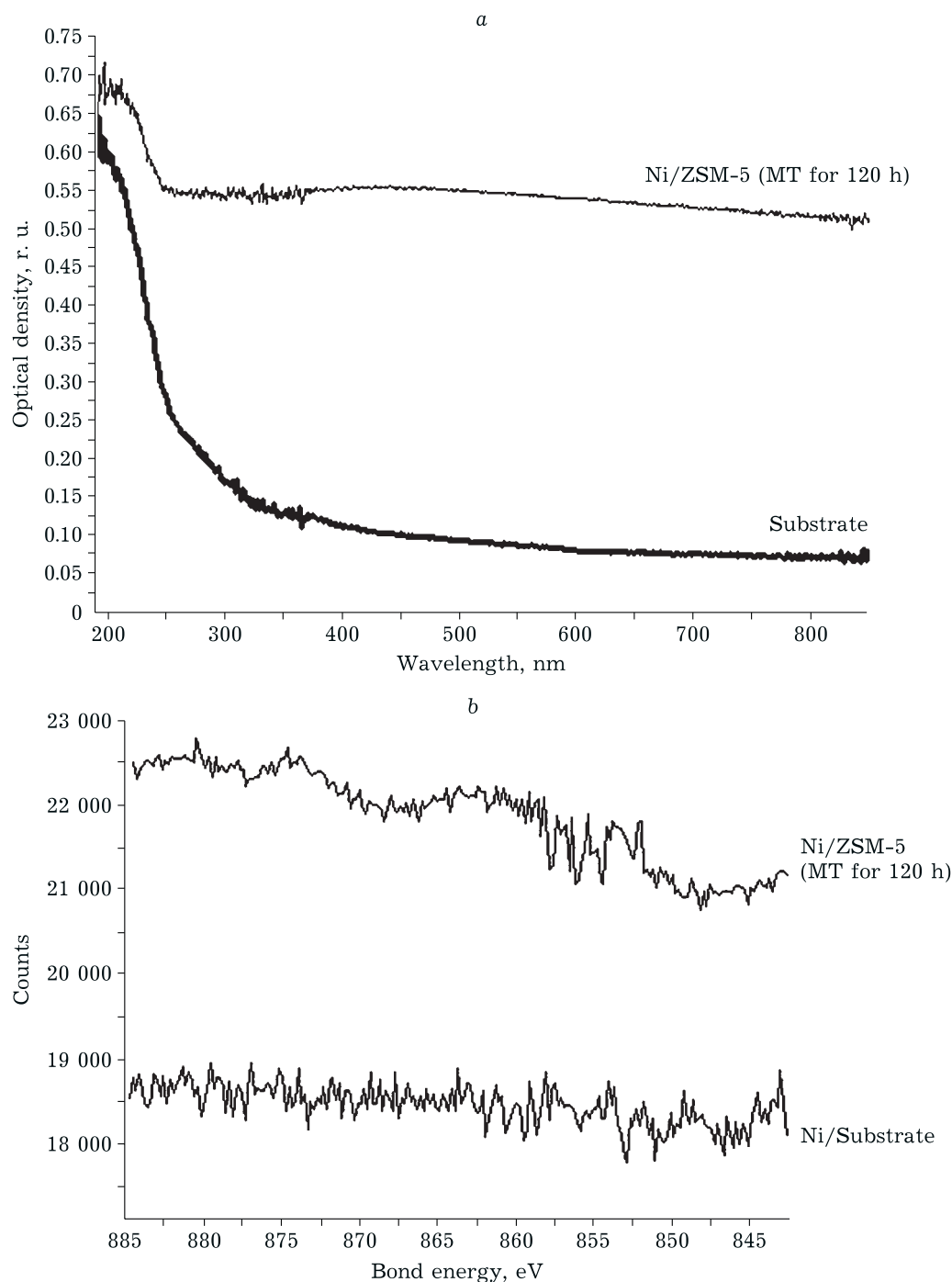


Fig. 2. Spectra of Ni/ZSM-5 after MT in the air for 120 h: UV (a), XPS (b).

Nickel particles in this catalyst sample have the morphology of separate (not bound with zeolite surface) aggregates having the dendritic structure (with a size up to 1 μm), composed of the bound spherical particles 20–200 nm in size (see Fig. 3, b). Electron diffraction from the aggregates unambiguously points to the metal nickel phase; interplane spacings are [16]: 2.03, 1.76, 1.25, 1.05 \AA . It

should be noted that smaller Ni aggregates are bound with zeolite surface and differ by compactness in metal particle packing (see Fig. 3, c, d).

The mechanical treatment of nickel-containing zeolite for 72 h leads to changes in the morphology of its crystals, in nickel particle sizes and in the localization of metal particles on the zeolite surface (see Fig. 4).

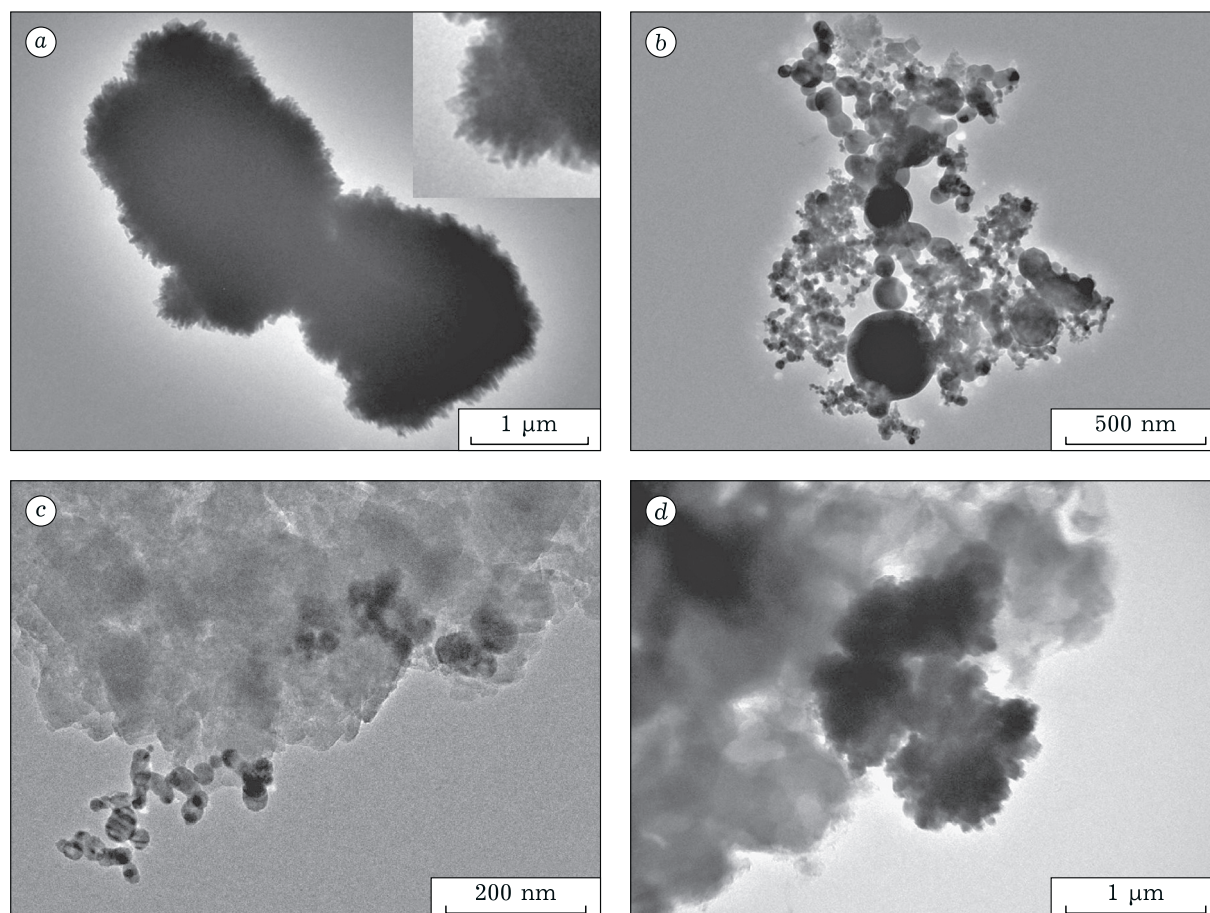


Fig. 3. HRTEM images of initial Ni/ZSM-5 zeolite (before MT): *a* – particles in the form of coarse agglomerates with rough surface (see insert); *b* – nickel particles in the form of aggregates with the dendritic structure not bound with the surface; *c*, *d* – roughness of the surface of zeolite aggregates, zeolite crystallites under different magnification.

The disintegration of large zeolite aggregates into smaller polycrystalline blocks less than 1 μm in size occurs (see Fig. 4, *a*, *b*). Their surface is smoothed out and substantially less rough than for the blocks in the sample before MT. The effect of MT manifests itself also as a decrease in the size of primary crystallites forming the polycrystalline structure: they are dispersed to the size of about 50 nm (see Fig. 4, *c*, *d*).

Mechanical treatment of nickel-containing zeolite leads to substantial changes in the structural arrangement of nickel on the zeolite surface. Nickel dendrites decompose into separate particles 10–30 nm in size, which are located on the surface of zeolite blocks (see Fig. 4, *b*). A selection from the image (see Fig. 4, *b*) is shown in more detail in Fig. 4, *c*: nickel particles are localized in a narrow slit between ZSM-5 crystallites near the surface of the polycrystalline block. However, the effect of metal dispersing is not limited to the decomposition of dendrites into separate particles.

Metal clusters not more than 1 nm in size are observed (see Fig. 4, *d*). Their presence is evidenced by the appearance of a rather large number of dark spots at the background of the bands of the zeolite lattice (period ~ 1 nm). The absence of these clusters on zeolite surface allows us to conclude that nickel clusters are localized in zeolite channels.

An increase in the time of MT of the catalyst to 120 h (see Fig. 5, *a*) does not lead to noticeable changes in the size of zeolite blocks in comparison with the sample subjected to MT for 72 h.

Some loosening of the structure may be observed, both in polycrystalline blocks and in primary zeolite crystallites. For instance, HRTEM images reveal the variation of contrast at the background of lattice images in the form of lighter and darker regions 5–10 nm long (see Fig. 5, *b*, *c*). This is evidently connected with surface loosening and the formation of humps and pits on it, as well as with the formation of cavities (pores) of

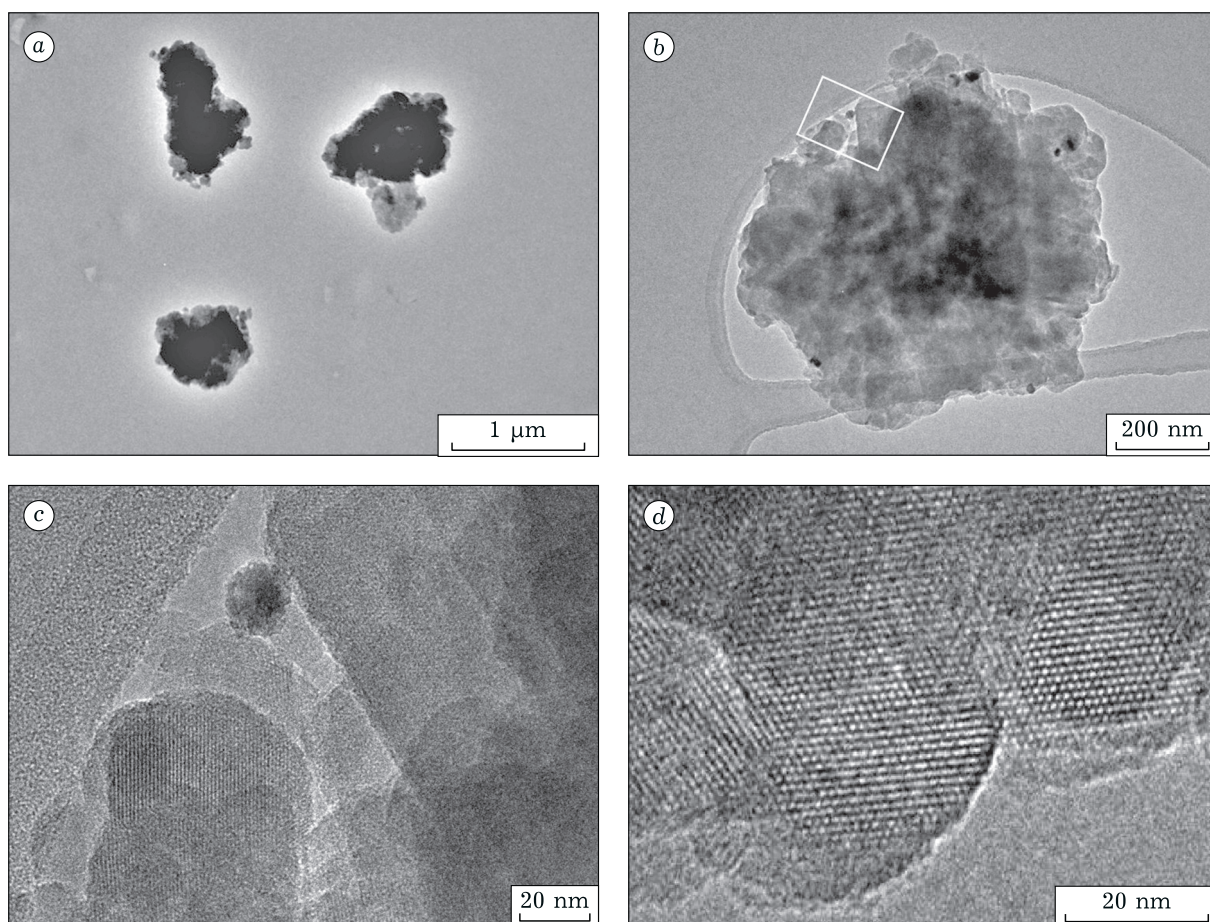


Fig. 4. HRTEM images of Ni/ZSM-5 (MT for 72 h): *a* – disintegration of the coarse zeolite agglomerates into smaller polycrystalline blocks; *b* – decomposition of nickel dendrites into separate particles; *c* (fragment selected from Fig. 4, *b*) – localization of nickel particles in the narrow slits between zeolite crystallites near the surface of the polycrystalline block; *d* – nickel clusters with a size ≤ 1 nm in zeolite channels.

the indicated size within zeolite particles. Thus, longer mechanical action manifests itself as further disintegration of zeolite particles.

The state of nickel localized in Ni/ZSM-5 zeolite changes too. Metal clusters not more than 1 nm in size are observed (see Fig. 5, *b*), similar to those detected in the sample after MT for 72 h. However, larger clusters with a size of about 4 nm are also observed. It may be concluded that MT for 120 h leads to nickel association due to migration along the channels in the zeolite. Associating in the internal cavities (pores) and on the loosened surface of zeolite crystallites leads to the formation of larger clusters (4 nm in size).

One of the main features of high-silica zeolite is its molecular sieve effect, which means that the reagent does not get into the pores of the catalyst (selectivity with respect to reagent), does not form a definite intermediate compound (selectivity with respect to the intermediate), does not un-

dergo a further transformation if the diffusion of the product from the pores is hindered (selectivity with respect to the product). Because of this, the most important characteristics of the catalysts are the parameters of their porous structure.

The specific surface area and porosity of the studied catalysts are presented in Table 1. One can see that the initial Ni/ZSM-5 catalyst is characterized by the largest specific surface area. Mechanical treatment of the catalyst causes a decrease in the specific surface area, so that the longer is treatment, the more substantial this decrease is. The specific pore volume and the volume of micropores are also maximal for the initial Ni/ZSM-5 in comparison with mechanically treated samples. Mechanical treatment does not affect the average pore diameter, which remains unchanged with an increase in the time of treatment. The observed changes are likely to be connected both with partial destruction of zeolite

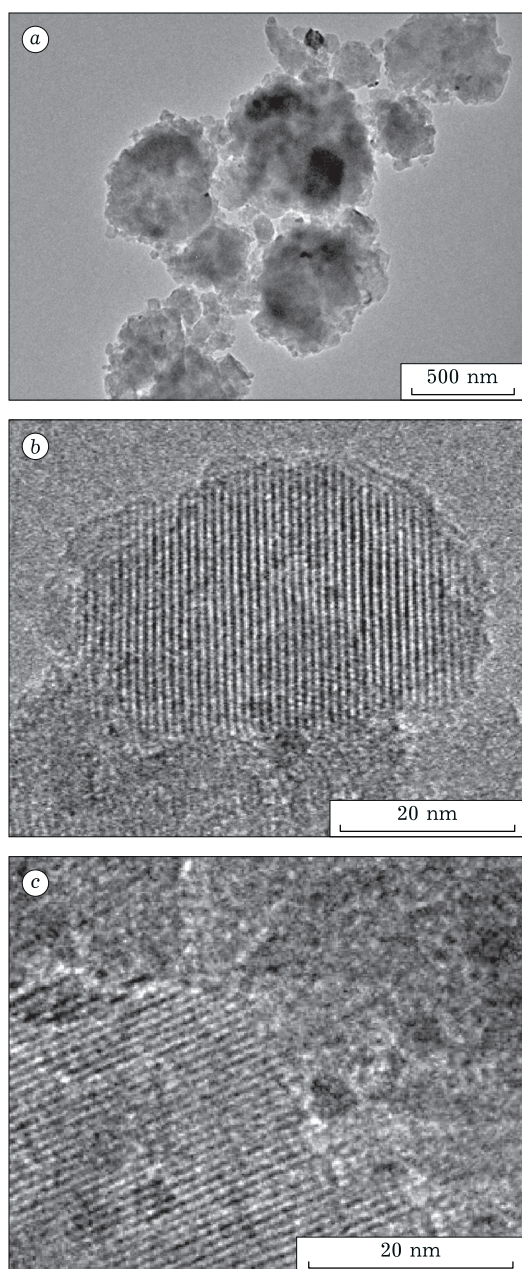


Fig. 5. HRTEM images of Ni/ZSM-5 (MT for 120 h): *a* – zeolite blocks; *b*, *c* – loosening of zeolite surface with the formation of humps and inner cavities, nickel association with the formation of clusters 1–4 nm in size.

TABLE 1

Texture characteristics of zeolite catalysts

Sample	Specific surface area, m ² /g	Specific volume of pores, cm ³ /g	Volume of micropores, cm ³ /g	Average pore diameter, nm
Ni/ZSM-5	389	0.18	0.11	1.9
Ni/ZSM-5 (MT for 24 h)	376	0.18	0.10	1.9
Ni/ZSM-5 (MT for 48 h)	356	0.18	0.09	1.9
Ni/ZSM-5 (MT for 72 h)	318	0.16	0.08	1.9
Ni/ZSM-5 (MT for 96 h)	317	0.14	0.07	1.9
Ni/ZSM-5 (MT for 120 h)	302	0.12	0.05	1.8

lattice during MT and with the changes in the localization of nickel particles.

CONCLUSION

Mechanical treatment of nickel-containing zeolite serves as an efficient method to modify it promoting the changes in the crystal structure, a decrease in the size of zeolite and nickel particles, partial migration of nickel nanopowder from the surface into the pores of zeolite, and a decrease in specific surface and porosity. The absence of the transition of nickel into the oxidized state was established for freshly prepared nickel-containing zeolite and its mechanically treated forms. By varying the time of MT, one may purposefully change the physicochemical properties of Ni/ZSM-5 obtaining the catalyst that allows us to regulate the selective formation of the target product.

Acknowledgements

The work was carried out within the State Assignment to the IPC SB RAS (project No. V.46.2.1), financed by the Ministry of Science and Higher Education of the Russian Federation.

REFERENCES

- 1 Boldyrev V. V., Mechanochemistry and mechanical activation of solids [in Russian], *Uspekhi Khimii*, 2006, Vol. 75, Issue 3, P. 203–216.
- 2 Baklanova O. N., Lavrenov A. V., Vasilevich A. V., Knyazheva O. A., Effect of mechanical activation on the properties of supports and catalysts for oil processing [in Russian], *Ros. Khim. Zhurn.*, 2018, Vol. 62, No. 1–2, P. 131–140.
- 3 Nikashina V. A., Streletskiy A. N., Kolbanev I. V., Meshkova I. N., Grinev V. G., Serova I. B., Yusupov T. S., Shumskaya L. G., Effect of mechanical activation on the properties of natural zeolites [in Russian], *Neorgan. Materialy*, 2011, Vol. 47, No. 12, P. 1470–1475.

- 4 Kucherov A. V., Slinkin A. A., Reaction in the solid phase as a method to introduce the cations of transition metals into high-silica zeolites [in Russian], *Uspelhi Khimii*, 1992, Vol. 61, Issue 9, P. 1687–1719.
- 5 Atyutskaya L. Yu., Bebiya A. G., Milyukova I. V., Control of the specific surface area of zeolite using the Carman-Kozeny method during mechanical activation [in Russian], *Polzun. Almanakh*, 2013, No. 1, P. 95–97.
- 6 Vosmerikov A. V., Velichkina L. M., Vosmerikova L. N., Korobitsyna L. L., Ivanov G. V., The application of mechanochemical technologies in zeolite catalysis, *Chemistry for Sustainable Development*, 2002, Vol. 10, No. 1–2, P. 235–242.
- 7 Velichkina L. M., Vosmerikov A. V., Effect of mechanical treatment on acidic and catalytic properties of nickel-containing zeolite, *Chemistry for Sustainable Development*, 2019, Vol. 27, No. 1, P. 1–7.
- 8 Lapidus A. L., Pavlova V. A., Nekrasov N. V., Dergachev A. A., Ethane aromatization on Ga + Pt/HZSM-5 zeolites obtained by means of solid-phase modification [in Russian], *Neftekhimiya*, 2010, Vol. 50, No. 2, P. 126–131.
- 9 Velichkina L. M., Vosmerikov A. V., Pestryakov A. N., Tuzovskaya I. V., Bogdanchikova N. E., Avalos M., Farias M., Tiznado Kh., Catalytic activity of pentasil containing Pt, Ni, Fe and Zn nanoparticles in the transformations of hydrocarbons (communication 1) [in Russian], *Neftekhimiya*, 2008, Vol. 48, No. 3, P. 201–206.
- 10 Velichkina L. M., Vosmerikov A. V., Pestryakov A. N., Tuzovskaya I. V., Bogdanchikova N. E., Avalos M., Farias M., Tiznado Kh., Catalytic activity of pentasil containing Pt, Ni, Fe and Zn nanoparticles in the transformations of hydrocarbons (communication 1) [in Russian], *Neftekhimiya*, 2008, Vol. 48, No. 5, P. 353–356.
- 11 Shukla D. B., Pandya V. P., Estimation of crystalline phase in ZSM-5 zeolites by infrared spectroscopy, *J. Chem. Technol. Biotechnol.*, 1989, Vol. 44, P. 147–153.
- 12 Collection of Simulated XRD Powder Patterns for Zeolites, M. M. J. Treacy, J. B. Higgins (Eds.), NY: Elsevier, 2001. 586 p.
- 13 Dharmaraj N., Prabu P., Nagarajan S., Kim C. H., Park J. H., Kim H. Y., Synthesis of nickel oxide nanoparticles using nickel acetate and poly (vinyl acetate) precursor, *Mater. Sci. Eng. B.*, 2006, No. 128, P. 111–114.
- 14 Srinivas D., Satyanarayana C. V. V., Potdar H. S., Ratnasamy P., Structural studies on NiO-CeO₂-ZrO₂ catalysts for steam reforming of ethanol, *Appl. Catal. A: Gen.*, 2003, No. 246, P. 323–334.
- 15 Handbook of X-ray Photoelectron Spectroscopy, J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben (Eds.), Minnesota (USA): Perkin-Elmer Corporation Physical Electronics Division, 1993. 235 p.
- 16 PCPDFWIN database, file 04-0850 [electronic resource]. URL: <http://studbooks.net/informatika/bumazhnye/ukazateli> (accessed 06.07.2018).