INVESTIGATION OF THE FEATURES OF NICKEL-MODIFIED MORDENITE ZEOLITES

L. K. Patrylak[1], *Yu. G. Voloshyna*[1], *O. P. Pertko*[1], *A. V. Yakovenko*[1], *V. A. Povazhnyi*[1],
O. V. Melnychuk[1]
[1] V. P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry of National Academy of Sciences of Ukraine, lkpg@ukr.net

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Zeolites are wide used materials in a range of processes of chemical, petrochemical, and nutritional industry. They are the active catalysts and sorbents, in particular, zeolites are characterized by high efficiency towards extraction of heavy and radioactive metals from the aqua medium. An important factor of high zeolite catalyst activity is preserving the integrity of the crystal structure. The purpose of this research was to check out the features of MOR zeolite modifications with nickel by means of low temperature nitrogen adsorption/desorption, IR-spectroscopy, and X-Ray Diffraction (XRD). Using ion exchange and following calcination the hydrogen form of zeolite was obtained. The last was impregnated by nickel in quantity of 1, 5, and 15 wt. %. The investigations of nickel-modified samples demonstrated that MOR-type zeolite was relatively resistant to the used manipulations. However, the hysteresis loops of their isotherms are observed. The last can be connected with mesoporosity appearance. The degree of zeolite destruction is found out to increase with rise of nickel content in the samples. Based on IR spectra analysis by means of checking out the ratio between intensity of bands at 560 and 440 cm^{-1} using Gaussian function in Origin medium the same conclusions were drawn. Crystalline structure of mordenite was confirmed by using XRD method, but minor quantitative destruction cannot be recognized without application of methods of the internal and external standards.

Keywords: *impregnation, zeolite modification, mordenite, nickel, zeolite, zeolite structure.*

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1. Introduction

Today zeolites are wide used materials in a range of processes of chemical, petrochemical, nutritional industry, etc. [1-4]. Being the materials with unique properties [5-7] they are the effective catalysts and sorbents, in particular, they have high efficiency towards extraction of heavy and radioactive metals from the aqua medium [8-11]. The most used in industry are LTA, FAU, MFI, and MOR-type zeolites. The latter two modified with nickel demonstrated high activity in hydroisomerization of linear hexane [12-14]. An important factor of high catalyst activity in target reaction is preserving the integrity of the zeolite structure, which will promote the presence of the maximum number of active sites in the samples. The most widely used method for assessing the crystallinity of zeolites is X-ray diffraction analysis [15, 16]. The investigations of the features of the absorptions in the region of crystalline lattice vibrations by using IR spectroscopy also give substantial information concerning the peculiarities of zeolite structure [17]. Another method that can provide the information on the integrity of the zeolite structure is the adsorption of gases [5, 18, 19].

Therefore, the purpose of this research was to check out the features of MOR zeolite modifications with nickel by means of low temperature nitrogen adsorption/desorption, IR-spectroscopy, and XRD methods.

2. Materials and Methods

As a starting material the powder NaMOR zeolite (SiO_2/Al_2O_3=9.8) produced by JS “Sorbent” (Nizhnii Novgorod, Russia) was used. The static capacity to water vapor was 0.12 cm^3/g.

Ammonium form of MOR-type zeolite (fraction 1-2 mm) was obtained from Na-form by means of 3-fold ion exchange of native sodium cations on ammonium ones using 3 mol/dm^3 aqueous solution of ammonium nitrate. Conditions of ion exchange: temperature – 358 K, solid to liquid phases ratio – 1:2, time – 2 h. Each exchange was followed with zeolite calcination for 2 h at 823-833 K for ammonium decomposition and hydrogen form of zeolite obtaining. In the result HMOR sample was synthesized for nickel impregnation.

Air-dry hydrogen form of zeolite was poured with 0.6 or 0.12 mol/dm^3 solution of nickel nitrate hexahydrate $Ni(NO_3)_2 \cdot 6H_2O$ in the required amount to obtain samples containing 1, 5, and 15 wt % of nickel per metal. It was believed that the use of nickel is 100%. The solution was evaporated at a sand bath for 3 hours. After that, the sample was dried for 2 h at 373 K. In the result samples HMOR-Im1Ni, HMOR-Im5Ni, and HMOR-Im15Ni were obtained. Metallic component were reduced in hydrogen flow at 653 K for 6 h.

IR spectra of the catalysts in the region of lattice vibrations 400-1400 cm^{-1} were recorded by using FTIR spectrometer IRAffiniti-1s (Shimadzu, Japan) with the prefix of the broken full internal reflection (ATR) Specac Quest GS 10801. The sample was applied to the surface of the diamond prism of the accessory ATR and the spectrum was recorded.

Low temperature nitrogen adsorption/desorption (77 K) isotherms for zeolite catalysts were taken on a Quantachrome Autosorb NOVA 1200e® automatic sorbometer after thermal dehydration of the sample in the muffle furnance at 653 K for 2 h and additional in situ evacuation at 250 °C for 1 h. The parameters of the porous structure of the catalysts were calculated by using NOVAWin software™: specific surface area S_{BET} – by using the multipoint BET method (it should be noted that the presence of micropores in the studied objects causes an error in the absolute values calculated by BET); the specific surface area excluding micropores St and the volume of micropores V_{tmicro} - t-method, the surface of micropores - by the formulae $S_{micro} = S_{BET} - S_t$; the total pore volume V_Σ - by the volume of adsorbed nitrogen at $p/p_s > 0.99$.

The diffraction patterns were recorded on a DRON-4-07 diffractometer in filtered (Ni) CuKα radiation in a reflected beam in the Bragg-Brentano survey geometry in the angular range of 5–80 deg with a step of 0.05, exposure time - 1 s. Individual intervals were recorded with a step of 0.02 deg and exposure time - 4 s. The phase composition of the samples was determined using the X-ray diffraction database PDF-2, ICDD, Newton Square, PA.

3. Results and Discussion

Figure 1 illustrates the isotherms of low-temperature nitrogen adsorption for zeolite samples. Adsorption isotherms for MOR zeolite-based catalysts with introduced nickel by impregnation method, in contrast to MFI-based catalysts [12], have pronounced hysteresises, which are a confirmation of the partial destruction of zeolite and the emergence of mesoporosity. Isotherms are typical for micro/mesoporous sorbents. They are characterized by a steep rise at low values of relative pressure caused by microporosity and the presence of a hysteresis loop at higher values of p/p_s [19]. The cause of the latter, considering the presence of hysteresis for sample of hydrogen form, may be not so much in the modification of nickel, as in the partial destruction of the structure of the zeolite during the obtaining of its hydrogen form. The observed hysteresis loops can be classified as H4 according to the IUPAC classification. A moderate rise near p/p_s=1 may indicate that capillary condensation occurs in meso- and macropores within the crystallite and follows the mechanism of multiple condensation-evaporation processes, as a result of which the condensed adsorbate is blocked by micropores and can only be partially desorbed. Occurrence of meso- and macropores inside the crystallite is most likely during heat treatment.

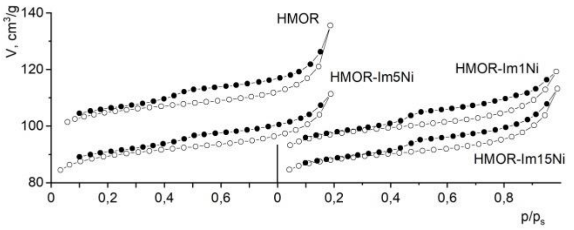

Fig. 1 *Low temperature nitrogen adsorption/desorption isotherms for H-form and nickel-containing samples*

Table 1 shows the main porous characteristics of the samples obtained from isotherms. In the process of modification by nickel, there is a certain decrease in the specific surface area of the samples and in the pore volume. Analyzing the quantitative indicators of loss of the specific surface of micropores S_{micro} for the samples, it should be noted that the increase in nickel content from 1 to 5 and 15 wt. % leads to a 12-15 % decrease in the surface area, which obviously indicates a certain additional destruction of the zeolite structure during the introduction of nickel. It is possible that when nickel oxide is reduced in the hydrogen atmosphere at 653 K, the metal component aggregates into larger metal particles, which can also partially destroy the microporosity of the zeolite. This destroy is higher for higher content of nickel in the sample.

As is known, some important information on the peculiarities of the structure of zeolites can be obtained from the IR absorption spectra in the region of the lattice valence vibrations 400-1400 cm^{-1} [17]. There are bands near 500–700 cm^{-1} due to pseudo-lattice vibrations of structural units in the spectra of synthesized samples (Fig. 2).

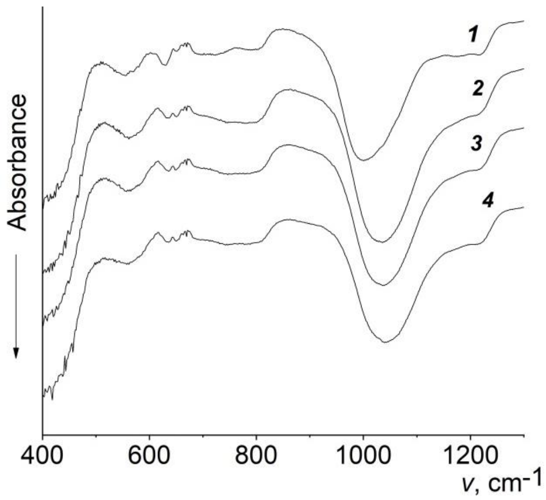

Fig. 2 *IR spectra of catalysts on mordenite base: 1 – NaMOR; 2 – HMOR-Im1Ni; 3 – HMOR-Im5Ni; 4 – HMOR-Im15Ni*

Table 1. *Adsorption properties of nickel-containing catalysts*

Sample	S_{BET}, m^2/g	S_t, m^2/g	S_{micro}, m^2/g	V_Σ, cm^3/g	V^t_{micro}, cm^3/g	S/S_{HMOR}, %
HMOR	382	17,1	365	0,21	0,16	100
HMOR-Im1Ni	360	18,2	342	0,19	0,14	94
HMOR-Im5Ni	336	16,5	319	0,17	0,13	88
HMOR-Im15Ni	328	17,9	310	0,18	0,13	85

According to the literature data, the spectra of zeolites such as mordenite in this region contain the following characteristic absorption bands [20]: 440 cm^{-1} – band, which is attributed to deformation vibration of tetrahedra bonds; 560 cm^{-1} – vibrations of double five-membered rings; 910 cm^{-1} – antisymmetrical valance vibrations of bonds in tetrathedra T–O (T = Si, Al); 705, 780 cm^{-1} – bands caused by symmetric valence vibrations of bonds Si (Al)–O; 1210 cm^{-1} – external antisymmetrical valence vibrations of bonds between tetrathedra (chain of five-membered rings); 660 cm^{-1} – vibrations of oxygen rings of entrance windows of lattice.

In general, the character of the IR spectra of the synthesized zeolite catalysts with different nickel contents indicates the presence of the characteristic absorption bands of MOR-type zeolites (Fig. 2). The possible band of Ni-O-Ni valence vibrations (at 1100 cm^{-1}) [21] may be overlapped with a broad zeolite lattice band near 1000 cm^{-1}.

It is known [22] that the ratio of the intensities of the bands at 550 and 450 cm^{-1} in the IR spectrum of zeolite MFI-type can assess the crystallinity of its samples. Since band at 550 and 450 cm^{-1} in the IR spectrum of MFI zeolite correspond to the bands at 560 and 440 cm^{-1} for MOR zeolite [23], for the last preservation of the crystallinity of the synthesized samples on its basis were evaluated in the same way. IR spectra analysis by means of checking out the ratio between intensity of band at 560 and 440 cm^{-1} using Gaussian function in Origin medium was carried out (Fig. 3, Table 2).

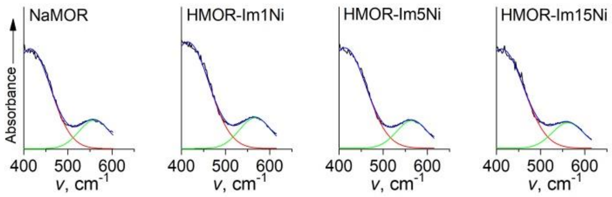

***Fig. 3** Bands at 440 i 560 cm^{-1} of IR spectra of MOR zeolites processed using Gaussian function*

Table 2 *Areas of the bands at 440 i 560 cm^{-1} calculated with Gaussian function using and their ratio*

Sample	Area, a.u.		Ratio	
	440 cm^{-1}	560 cm^{-1}	$R^{560/440}$	Δ, %
NaMOR	8111	1750	0.22	100
HMOR-Im1Ni	9149	1942	0.21	98
HMOR-Im5Ni	8611	1698	0.20	91
HMOR-Im15Ni	8782	1603	0.18	85

The ratio of $R^{560/440}$ of band intensities for samples synthesized from MOR zeolite decreases monotonically with increasing content of nickel in the samples compared to the original NaMOR from 100 % to 85%, which obviously indicates a slight destruction of the crystal structure (up to 15%) in the process of applying a large amount of metal component (5–15 wt. %) on zeolite of this structural type.

Figure 4 demonstrates the diffraction patterns of the synthesized samples. According to the positions of the characteristic lines known from the JCPDS card, the crystal structure corresponding to the MOR zeolite structure (JCPDS card 011-0155) was confirmed. Lines at 44.5, 51.8, 76.4 correspond to nickel crystallites (111), (200), and (220).

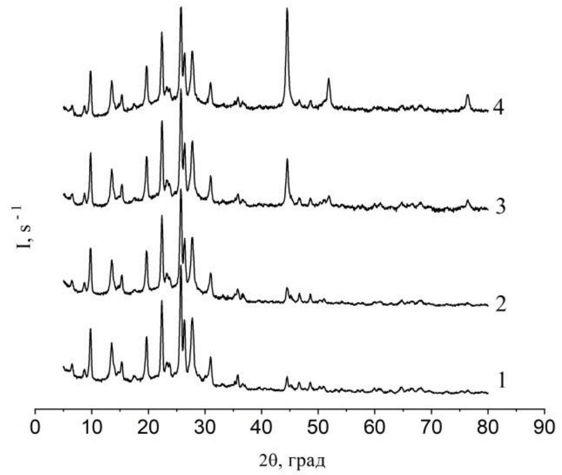

Fig. 4. *XRD patterns for mordenire zeolite samples: HMOR (1), HMOR-Im1Ni (2), HMOR-Im5Ni (3), HMOR-Im15Ni (4)*

However, it should not be forgotten that in the presence of a phase in a small quantity the lines will be correspondingly weak, and the least intensity ones may disappear altogether. Therefore, it is necessary to take into account the presence of the most intensive lines. It is known, in particular, that the sensitivity of quantitative XRD analysis in different cases is significantly different and depends on the reflectivity of the substance, its dispersion, the characteristics of the equipment. The ratio of the absorption coefficients of the whole mixture and the individual phase is of particular importance too. Thus, the accuracy of XRD phase analysis can be from 2 to 10% of the determined value [24]. Methods of quantitative phase analysis have been developing intensively in recent years, mainly due to the automation of X-ray diffractometers and the ability to improve the processing of diffraction patterns using personal computers. In our case, it is difficult to identify their quantitative destruction of the zeolite phase based on the intensity of the corresponding reflexes without resorting to the use of long and difficult complex methods of internal and external standards [24].

4. Conclusions

Therefore, studies of nickel-modified zeolites showed that the MOR zeolite samples were relatively stable under the used synthesis conditions. They are characterized by the occurrence of mesoporosity, which is reflected by the appearance of a hysteresis loop in the isotherm of low-temperature nitrogen adsorption/desorption.

The degree of destruction of zeolite was found to increase with nickel content increasing in the samples. IR spectroscopic spectra in the region of crystal lattice vibrations, obtained on the basis of estimating the ratio of band intensities at 560 and 440 cm^{-1} confirm the following conclusions.

The crystallinity of the samples structure was confirmed by X-ray diffraction and the mordenite-type zeolite phase composition was identified, but quantitatively insignificant destructions could not be determined without the use of difficult and long studies utilizing internal and external standards.

Acknowledgments

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ДОСЛІДЖЕННЯ ОСОБЛИВОСТЕЙ МОДИФІКОВАНИХ НІКЕЛЕМ ЦЕОЛІТІВ ТИПУ МОРДЕНІТУ

Л. К. Патриляк[1]*, Ю. Г. Волошина*[1]*, О. П. Пертко*[1]*, А. В. Яковенко*[1]*, В. А. Поважний*[1]*,*
О. В. Мельничук[1]

[1] Інститут біоорганічної хімії та нафтохімії ім. В. П. Кухаря НАН України, lkpg@ukr.net

DOI:

Цеоліти широко використовують у ряді процесів хімічної, нафтохімічної, харчової промисловості. Вони є ефективними каталізаторами та сорбентами, зокрема, відзначаються високою ефективністю щодо вилучення важких та радіоактивних металів із водного середовища. Важливим фактором високої активності цеолітних каталізаторів є збереження цілісності кристалічної структури. Метою даної роботи була оцінка особливостей модифікування нікелем цеолітів типу MOR методами РФА, ІЧ-спектроскопії та низькотемпературної адсорбції/десорбції азоту. Методом іонного обміну одержано водневу форму цеоліту, на яку просочуванням нанесено нікель у кількості 1, 5 та 15 % мас. Вивчення модифікованих нікелем зразків показали, що цеоліт типу MOR виявився відносно стійким до використаних маніпуляцій. Однак, для нього спостерігається петля гістерезису на ізотермі низькотемпературної адсорбції/десорбції азоту, що свідчить про утворення мезопористості. Знайдено, що ступінь руйнування цеоліту зростає зі збільшенням вмісту нікелю у зразках. Аналогічні висновки зроблено на основі аналізу ІЧ-спектрів шляхом оцінки співвідношення інтенсивності смуг поглинання при 560 та 440 см$^{-1}$ *за допомогою функції Гауса в середовищі Origin. Методом РФА підтверджено кристалічну структуру типу морденіту, однак незначні кількісні руйнування визначити не вдалося без застосування методів внутрішнього стандарту та зовнішнього еталону.*

Ключові слова: *імпрегнування, модифікація цеоліту, морденіт, нікель, цеоліт, цеолітна структура*
