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FRUCTOSE TRANSFORMATION INTO 5-HYDROXYMETHYLFURFURAL OVER NATURAL TRANSCARPATHIAN ZEOLITES

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Abstract. Based on Transcarpathian zeolite the catalysts in calcium-lanthanum-ammonium form were synthesized and modified by steaming and dealumination with ethylenediaminetetraacetic acid. The samples were characterized by using nitrogen adsorption/desorption, XRD, XRF, and FTIR-spectroscopy. The yield of 5-hydroxymethylfurfural over modified samples at 433 K was found to be 50 and 83 % at a practically full conversion of fructose.

Keywords: fructose, 5-hydroxymethylfurfural, natural zeolites, steaming, dealumination.

1. Introduction

Biomass, being fully renewable, has great potential as an alternative to fossil fuels. It is known that 55–65 % of biomass consist of cellulose and hemicellulose, which, being carbohydrate polymers, can be deconstructed into monomer sugars by biochemical means.[1-5] However, further effective strategies for converting monomers to platform chemicals are still lacking. These processes require the development of active and selective catalysts for the efficient conversion of sugars to valuable chemicals. Among various products that can be obtained when converting sugars, one of the most popular is 5-hydroxymethylfurfural (5-HMF), as it has a considerable versatility as a platform molecule for a new generation of biofuels, renewable polymers, *etc.*[4-8] According to the US Department of Energy, it is considered as one of the best chemicals from biomass with a high added value.[9,10]

The conversion of sugars into 5-HMF requires the development of catalysts capable for selective dehydration. In this regard, the acid-catalyzed conversion of simple carbohydrate molecules is being intensively studied. Despite the fact that firstly 5-HMF obtaining was patented in 1960,[11] its industrial production was established only in 2014 by AVA Biochem.[12]

The loss of three water molecules by glucose or fructose with the formation of 5-HMF is a process complicated by a number of side reactions that lead to the formation of insoluble humins and polymers as a result of cross-polymerization, as well as levulinic and formic acids as a result of 5-HMF rehydration.[13-16]

Traditionally, when dehydrating fructose in aqueous solutions, mineral acids (HCl, H_2SO_4, *etc.*), soluble salts of zinc, niobium, lanthanum, iron, *etc.*, are used as catalysts.[4,5] The process temperature varies from 373 K at atmospheric pressure to 393–543 K at high pressures. The yields of 5-HMF at other equal reaction conditions decrease with increasing concentration of the initial solution of fructose. In homogeneous aqueous systems, the production of 5-HMF with yields of more than 50 % is difficult to achieve due to the rehydration of 5-HMF with the formation of levulinic and formic acids or fructose and 5-HMF co-oligomerization.

Researchers have used various strategies to reduce the formation of by-products. In particular, the use of aprotic solvents, such as dimethyl sulfoxide (DMSO), has been carried out by many scientists in order to minimize side processes.[17-19] Interesting results have been obtained in dehydration of carbohydrates in ionic liquids,[20,21] however, their high cost, limited toxicity data, and 5-HMF separation/purification capabilities still constrain the development of this industrial application.

However, the use of liquid mineral acids as catalysts has several disadvantages. In addition to the general non-selectivity of processes due to 5-HMF degradation as

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a result of rehydration and polymerization reactions, the use of mineral acids causes corrosion of materials, difficulties in separating the acid from the reaction mixture, and, of course, the high toxicity of the acids themselves. Therefore, the development of more environmentally friendly and convenient solid acid catalysts to replace liquid acids is extremely important.

Today the attempts are being made to use oxides, phosphates, heteropolyacids, mesoporous acids, modified silicon dioxide, hydrogen forms of zeolites, and ion exchange resins as green catalysts for 5-HMF obtaining.[4,5,22] The series of works was devoted to the conversion of fructose to ethyl lactate on Sn- and MgO-ZrO_2 oxides catalysts.[23-25] Recently, the efficiency of the calcium-lanthanum-ammonium form of faujasite, previously well established as catalysts for the alkylation of isobutane with butenes,[26-28] has been found in the conversion of glucose into 5-HMF in aqueous and DMSO media.[29] On the other hand, zeolites, especially natural ones, are well-known materials for sorption and purification.[30-32]

Therefore, the aim of the present work was the investigation of the activity of zeolite catalysts based on natural Transcarpathian clinoptilolite for the fructose conversion into 5-HMF.

2. Experimental

2.1. Catalyst preparation

Polycationic form of zeolite (Sh-PC) based on natural Transcarpathian rock (Sh) has been synthesized. To start with, the fraction of the rock with the size of 0.25–0.5 mm was sifted. Ion exchange of native cations for calcium (1.5 mol/L), lanthanum (1.4 mol/L), and ammonium (1 mol/L) cations from aqueous solutions of nitrates of the corresponding salts was carried out. A solid-to-liquid phase ratio was 1:2 for all syntheses. The reaction temperatures were 358–363 or 423 K, so the process was carried out either in flat-bottomed conical flasks heated in a heated shaker, or a rotating autoclave. Firstly, two ion exchanges for calcium were performed at 363 K, and then two more exchanges at 423 K for 2 h in an autoclave under pressure for the maximum introduction of calcium ions in the sample were carried out. Lanthanum nitrate was used twice at 363 K. The last exchange was a one-time exchange for ammonium cations at 363 K. The resulting sample was dried at room temperature for 48 hours. After each exchange, the sample was washed with distilled water from nitrate ions. Peculiarities of exchanges were selected based on previous experience in introducing these cations into faujasite-type zeolites.[26,29]

For comparison, the polycationic sample (M-PC) based on synthetic mordenite (NaM, SiO_2/Al_2O_3=9.7, produced by JS "Sorbent") was obtained similarly. The sequence of exchanges: four exchanges for calcium at 363 K, two exchanges for lanthanum at 363 and 423 K, and one exchange for ammonium at 363 K.

The filtrates were analyzed for calcium, lanthanum, ammonium, and sodium cations using chemical analysis and inductively coupled plasma optical emission spectrometry (Plasma Quant PQ 9000 Elite). The chemical composition of the samples in percent of exchange capacity was following: M-PC – $21Ca47La32NH_4NaM$; Sh-PC – $30Ca41La29NH_4NaSh$.

Sample Sh-10A was obtained after the hydrochloric acid (1 mol/L) treatment of Sh rock for 3 h in a water bath (358–363 K). The degrees of dealumination and decationation were 8 and 13 %, respectively.

The obtained samples M-PC and Sh-PC were subjected to the treatment by a stream of superheated water vapor in a special setup[33] at 473 and 523 K for 2 h.

Samples M-PC and Sh-PC were also subjected to a "soft" dealumination with ethylenediaminetetraacetic acid (EDTA). For this purpose, parts of polycationic samples (7 g) were poured into 105 mL of water, added 0.5–1.0 g of EDTA, and treated at 358–363 K for 11 h. The samples were filtered, washed with distilled water, and dried at 363–373 K. The treatment was repeated three times. The filtrates were analyzed for aluminum. The degree of dealumination of the samples was 10 % in the case of the mordenite sample (M-3Ac) and 22 % for the clinoptilolite sample (Sh-3Ac).

2.2. Catalytic Testing

The transformation of fructose solutions was carried out in stainless steel autoclaves. To start with, a catalyst (0.75 g) was added to a fructose solution in DMSO (10 %, 5 mL) and placed in the reactor. The reaction was carried out at 433 K for 4 h. The reaction temperature was chosen based on the analysis of the literature data and previous investigations. The autoclaves were placed in a special holder in a furnace with electric heating. At the end of the reaction, the autoclaves were cooled to room temperature, depressurized, the liquid layer was filtered under a vacuum on the Büchner funnel through a paper filter. The obtained products were collected and analyzed by using the gas chromatography method (Agilent GC 7890A chromatograph equipped with a flame ionization detector, split/splitless inlet, the capillary column J&W HP-5 (5 %-phenyl-methyl siloxane) of 30 m, inner diameter of 0.32 mm, film thickness of 0.25 μm).

For the gas capillary chromatography analysis, about 0.2 mL of liquid products weighed with an accuracy of 0.0005 g were diluted with 2 mL of H_2O. In the case of precipitation of insoluble humins, the latter was separated by centrifugation. Conditions of analysis were the following: inlet temperature – 453 K; split ratio 20:1; chromatographic column heater temperature – 373 K then 3 K/min to 523 K; flowing rate of carrier gas (He) – 3 mL/min; detector temperature – 533 K; injection volume – 1 μl. The concentration of 5-HMF was calculated using calibration curves from 0.05 to 0.5 wt % of 5-HMF obtained with an analytical standard of 5-HMF sample (Sigma Aldrich, >99 %). The analysis was repeated three times, results were averaged.

To determine the concentration of fructose in liquid products of catalytic transformation, the gas chromatography analysis was carried out with preliminary derivatization of hydroxyl groups using silanization with *bis*(trimethylsilyl)amine and trimethylchlorosilane. About 0.04–0.05 g of the liquid products were placed in a glass vial (10 cm^3). The vial with the sample was weighed and then evacuated (<1 kPa) for 3 h at 293 K and for 1 h at 343–353 K to remove water and volatile products. The residue was dissolved in 2 mL of pyridine, then 100 μL of *bis*(trimethylsilyl)amine and 50 μl of trimethylchlorosilane were added. The vial was closed, shook intensively, and weighted. The obtained precipitate of NH_4Cl was separated by centrifugation. The conditions of analysis were the same as for 5-HMF detection. The reference samples of initial fructose in pyridine (0.05–0.3 wt %) were treated in the same manner for the construction of the calibration curve.

2.3. Catalyst Characterization Methods

Porous characteristics of the synthesized samples were found out *via* low-temperature (77 K) nitrogen adsorption/desorption isotherms measured by using Nova 1200e (Quantochrome) high-speed surface area and pore size analyzer after sample evacuation in vacuum *in situ* at 568 K for 9–12 h. The nitrogen of high purity (99.99 %) was used in these experiments. The specific surface areas (S_{BET}) have been calculated according to the standard Brunauer–Emmett–Teller (BET) method by utilizing the nitrogen adsorption data at p/p_s values between 0.06 and 0.2.[34] The micropores volumes (V^t_{micro}) and micropores surface areas (S^t_{micro}) have been estimated by using the t-plot method. The average pore size R was calculated by using the $R = 2V\Sigma/S_{BET}$ formula, the R_{DFT} is based on the density functional theory, and the R_{BJH} is based on the Barrett-Joiner-Halenda theory.

Lewis and Brønsted acidities of the samples were investigated by using pyridine as a spectral probe with IR-spectroscopic control.[35] The IR-spectra were obtained using the Spectrum One FTIR-spectrometer (Perkin-Elmer) in the range of 1250–4000 cm^{-1}. The samples were pressed into the tablets of 5–9 mg weight and an area of 0.000064 m^2 without a binder and loaded into a special holder. Then, the latter was loaded into a spectral cell and the samples have been activated in a vacuum at 723 K for 1 h. Thereafter, IR-spectra of vacuumed samples were recorded. Adsorption of the spectral probe at a temperature of 423 K was carried out for 30 min. To determine the zeolite acid site strength, the pyridine desorption at 523 K for 30 min was carried out after cooling IR-spectra were recorded.

The elemental composition of synthesized catalysts was investigated on the X-ray fluorescence energy dispersion analyzer Oxford Instruments X-Supreme 8000 (Great Britain).

The diffraction pattern of the original zeolite was recorded on a Rigaku MiniFlex600 diffractometer in CuK_α radiation in the region of 2θ angles 2–80 degrees with a step of 0.02 degrees and a rotation speed of 5 deg/min. The acceleration voltage was 40 kV, anode current – 15 mA. Phase analysis was carried out using the Database of Zeolite Structures.[36]

3. Results and Discussion

3.1. Catalysts Characterization

According to the literature data, the ratio of silicon to aluminum in the rocks of the Sokyrnytsky deposit of Transcarpathia is 3.8–4.5,[37] so this zeolite is classified as a low-silicon clinoptilolite. Obtained by XRF analysis the chemical composition of origin rock was: SiO_2 – 69.9 %; Al_2O_3 – 8.3 %; Na_2O – 0.6 %; MgO – 1.0 %; CaO – 5.5 %; K_2O – 8.1 %; Fe_2O_3 – 6.6 %.

The silica to alumina ratio for the starting rock and the synthesized samples is given in Table 1.

Table 1. Silica to alumina ratio for catalysts based on natural clinoptilolite and synthetic mordenite

Sample	SiO_2/Al_2O_3	Sample	SiO_2/Al_2O_3
Sh	8.4	NaM	9.7
Sh-PC	10.9	M-PC	9.9
Sh-200	11.1	M-200	10.2
Sh-250	11.0	M-250	9.8
Sh-3Ac	13.1	M-3Ac	12.4

Clinoptilolite structure of natural rock was confirmed by using the XRD method. Being one of the most common natural zeolites of the heulandite family, it has some admixtures of quartz.[38] For example, in Fig. 1, the XRD patterns for starting zeolite (a) and for acid-treated sample Sh-10A (b) are shown.

Figs. 2, 3 show the low-temperature nitrogen adsorption/desorption isotherm for the synthesized catalysts. Catalysts based on the natural rock are characterized by isotherms of type 4 IUPAC classification with H4 hysteresis loops, showing the presence of micropores and mesopores. The tendency to increase the verticality of the terminal section of isotherm in the region of p/p_s close to 1 and a certain expansion of the hysteresis loop indicates the development of macroporosity in Sh-250 and Sh-3Ac samples. The total sorption capacity of starting rock is much smaller than that of synthetic powder zeolite. For samples based on synthetic mordenite, hysteresis is observed even at small values of p/p_s and someone can see the excess of desorption branch over the adsorption one. This phenomenon may be due to the presence of subnanosized pores in the structure, from the latter the rate of nitrogen desorption is significantly lower than the rate of adsorption, which causes hysteresis.

Table 2 summarizes the calculated parameters of the adsorption characteristics of the samples.

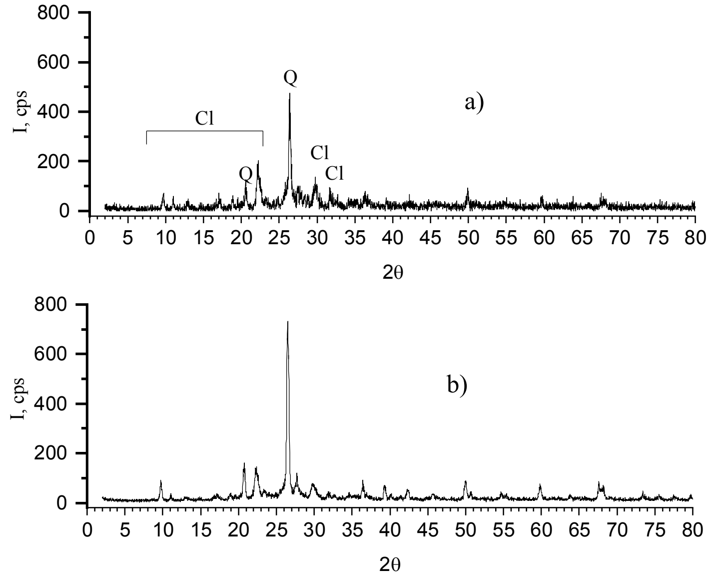

Fig. 1. X-ray diffraction patterns of zeolite rock (Sokyrnytsya deposit).
Cl – clinoptilolite; Q – quartz

Table 2. Textural characteristics of synthesized samples

Sample	S_{BET}, m^2/g	S^t, m^2/g	S^t_{micro}, m^2/g	V^t_{micro}, cm^3/g	V_Σ, cm^3/g	V_{micro}/V_Σ, %	R^{DFT}, nm	$R^{BJH}_{(des)}$, nm	R, nm
M-PC	188	16.6	171	0.070	0.114	61	1.13	1.98	1.22
M-200	161	20.1	141.3	0.061	0.111	55	1.21	1.98	1.38
M-250	157	15.5	141.2	0.059	0.097	61	1.17	1.96	1.24
M-3Ac	282	24.6	257.2	0.108	0.157	69	1.21	1.96	1.11
Sh	9.0	3.9	5.1	0.002	0.018	11	2.6	1.97	3.8
Sh-PC	9.2	2.3	6.9	0.003	0.013	24	2.64	1.96	2.74
Sh-200	7.8	5.2	2.6	0.001	0.013	7.7	2.64	1.96	3.32
Sh-250	9.7	3.9	5.8	0.002	0.028	7.1	2.64	1.96	5.79
Sh-3Ac	89	16.6	72.1	0.031	0.073	42	2.7	1.97	1.65
Sh-10A	63.3	5.4	58.2	0.025	0.037	67	1.3	1.98	1.2

As a result of ion exchange of rock Sh for calcium, lanthanum, and ammonium cations, the Sh-PC sample deteriorated the part of mesoporosity, calculated as the difference between the total pore volume and the volume of micropores from $0.018 - 0.02 = 0.016$ cm^3/g to $0.013 - 0.003 = 0.011$ cm^3/g. The fraction of micropores slightly increased.

Steaming at 473 K further deteriorated the mesoporosity index and the specific surface area of BET, whereas the transition to treatment at 523 K contributed to the increase of mesoporosity by 1.6 times ($0.028 - 0.02 = 0.026$ cm^3/g). It is possible that when treated at lower temperatures there is only a redistribution of cations in the porous structure of the zeolite, and, apparently, larger cations such as calcium and lanthanum move closer to the entrances of the channels, thereby deteriorating the porous characteristics. On the other hand, at 523 K, the effect of structure dealumination, which expands the near-surface entrances to the channels, may increase.

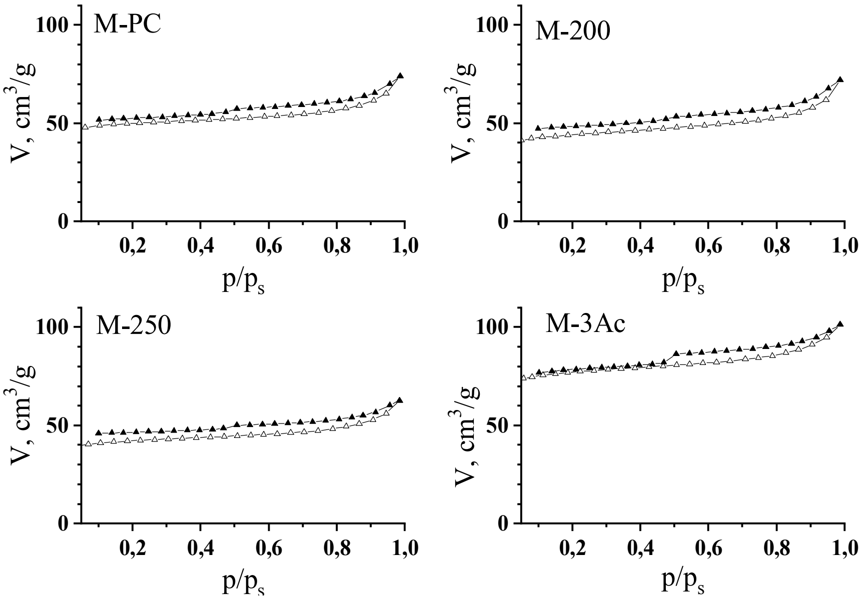

Fig. 2. Low-temperature nitrogen adsorption isotherms for samples of synthetic mordenite origin

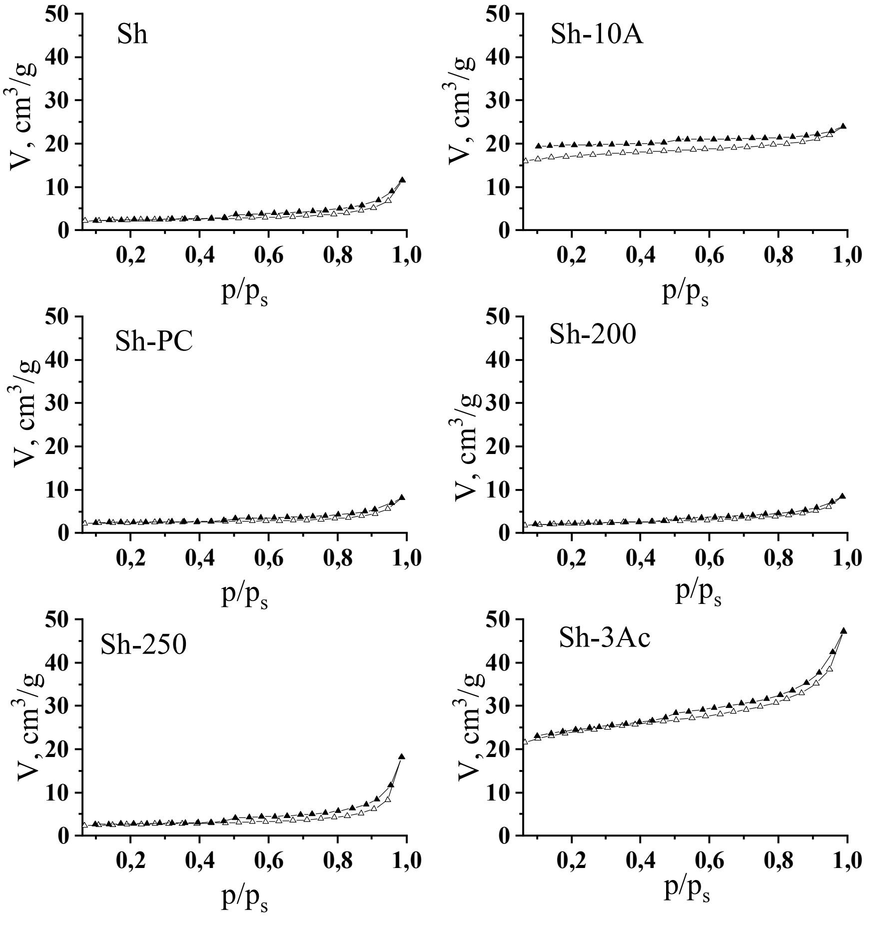

Fig. 3. Low-temperature nitrogen adsorption isotherms for samples of natural zeolite origin

EDTA treatment caused a significant increase (by 10 times) in S_{BET}, micropore, and mesopore volume (2.6 times, $0.073 - 0.031 = 0.042$ cm^3/g). Therefore, the last two samples, because of the narrow porous type of the original zeolite, should have significant advantages in the conversion of carbohydrates. When treated with hydrochloric acid (Sh-10A sample), the volume of micropores in the sample significantly increases. Its surface area increases by one order of magnitude compared to the surface area of the unmodified sample. Accordingly, the BET surface area increases. The area of the external surface increases much less. Thus, modification with hydrochloric acid in contrast to EDTA affects mainly the microporosity of the sample.

The acidity of the catalysts was determined by using pyridine adsorption with IR-spectroscopic control. Figs. 4 and 5 show the IR spectra of adsorbed pyridine on the studied catalysts. The following characteristic bands are observed: 1450 cm^{-1} – pyridine coordinated with Lewis acid sites, 1550 cm^{-1} – pyridine bounded with Brønsted acid sites, and a band at 1490 cm^{-1}, which reflects both Brønsted and Lewis acid sites.

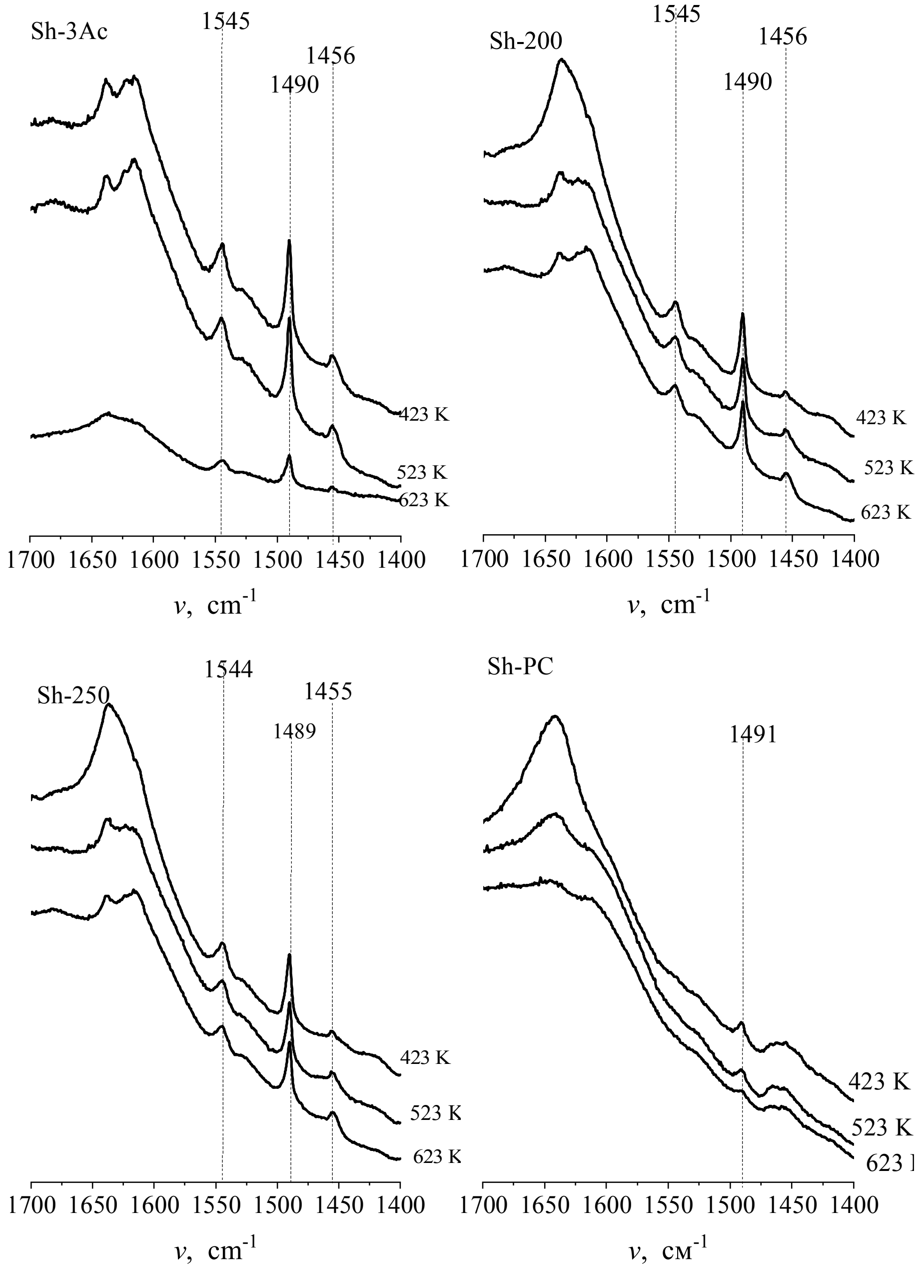

Fig. 4. IR-spectra of natural origin samples in the region of adsorbed pyridine 1400–1700 cm^{-1}

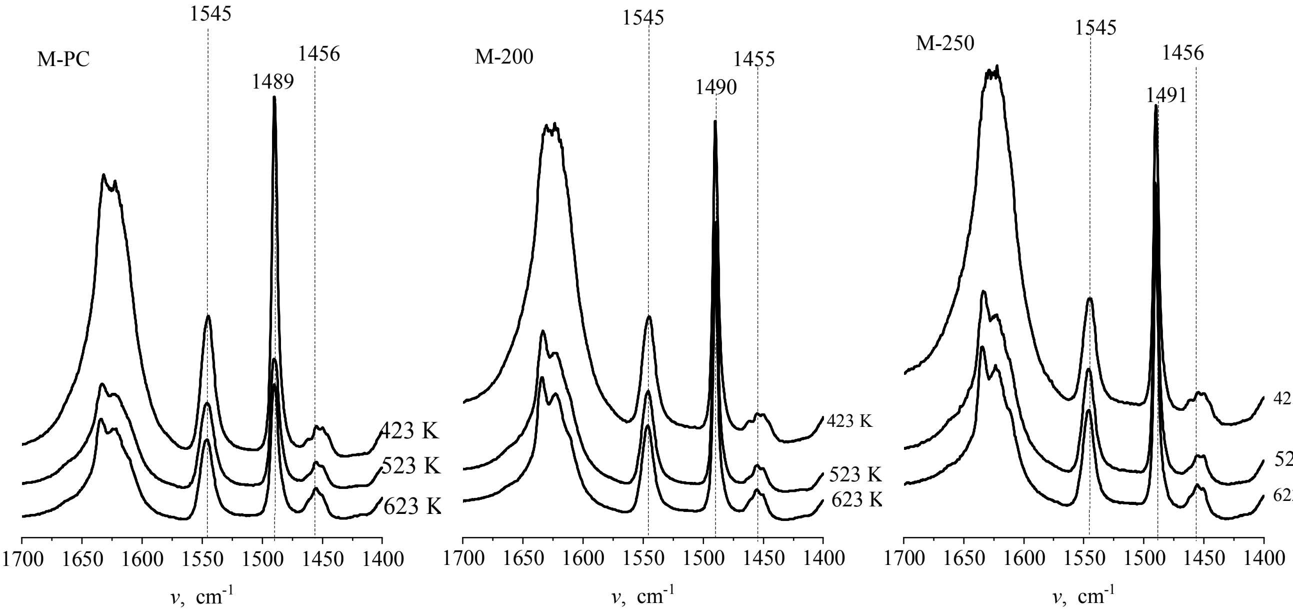

Fig. 5. IR-spectra of mordenite origin samples in the region of adsorbed pyridine 1400–1700 cm^{-1}

As it is known, the clinoptilolite lattice has three open channels A, B, and C. Channel A is ten-membered and has an elliptical shape of 0.44 × 0.72 nm. Channel B is an eight-membered one with the size of 0.41 × 0.47 nm. Channels A and B are parallel, they are crossed at an angle of 50° by an eight-membered channel C measuring 0.40 × 0.55 nm. The effective pore diameter in different sources is indicated from 0.35 nm[39] to 0.44 nm.[40]

Since the kinetic diameter of the pyridine molecule is 0.67 nm, it is difficult to expect its penetration into the micropores of clinoptilolite. Obviously, the determination of acidity will be limited only by the external surface of the crystals. Also, it must be assumed that the same acid centers are present in the internal pores. In the case of mordenite, larger and smaller channels of 0.67 × 0.7 and 0.26 × 0.57 nm are present in the structure, respectively. Therefore, some penetration of pyridine molecules into large channels may occur.

As can be seen in Fig. 6, the total content of acid sites in mordenite samples is one order of magnitude higher than in natural clinoptilolite samples, though, the samples after additional treatment by steaming at 523 K and after dealumination show higher content of both Brønsted and Lewis acid sites. The Brønsted to Lewis acid sites ratio for mordenite and clinoptilolite is also different. It is near 4-6 for mordenite samples and near 2–3 for clinoptilolite ones.

3.2. Catalytic Reaction

Table 3 shows the results of fructose dehydration at 433 K for 4 h and, in Fig. 7, the yields of 5-HMF over the corresponding samples of two series are displayed.

The most effective were samples of clinoptilolite base with improved porous characteristics using steaming at 523 K and "soft" dealumination with EDTA. 5-HMF yields for them are 50 and 83 %, respectively, with practically complete conversion of fructose. The yields were even higher than in the transformation of glucose over polycationic faujasites[29] and hydrogen forms of zeolites modified with nickel.[41]

Table 3. Results of fructose dehydration over synthesized zeolite catalysts

Catalyst	5-HMF yield, % mol.	Fructose conversion, %	Selectivity for 5-HMF, %
Sh	13.7	99.8	13.72
Sh-10A	18.2	99.8	18.20
Sh-Pc	9.1	99.7	9.12
Sh-200	18.0	99.8	18.0
Sh-250	**50.1**	**99.6**	**50.30**
Sh-3Ac	**83.1**	**100.0**	**83.10**
M-PC	28.8	99.6	28.91
M-200	16.1	99.9	16.11
M-250	8.0	99.8	8.01
M-3Ac	14.2	99.8	14.23

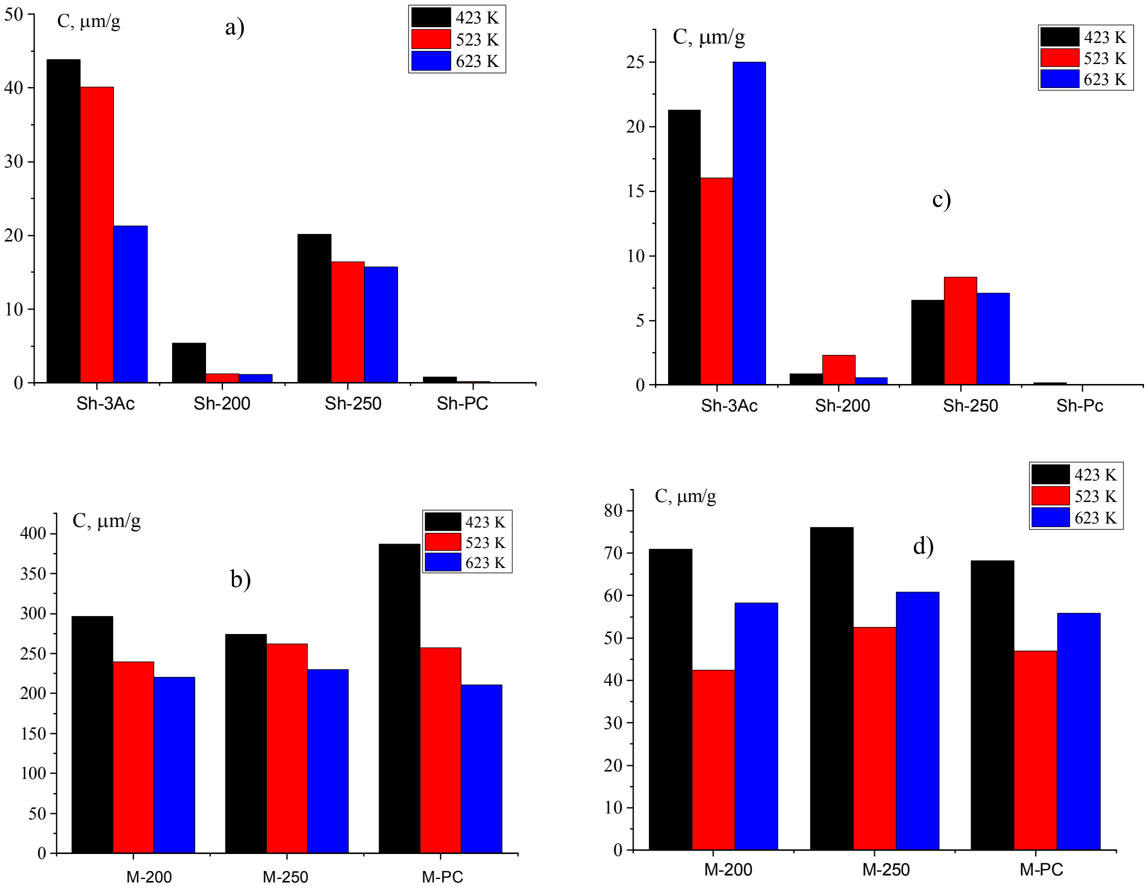

Fig. 6. Distribution of the Brønsted (a, b) and Lewis (c, d) acid sites determined from the pyridine adsorption

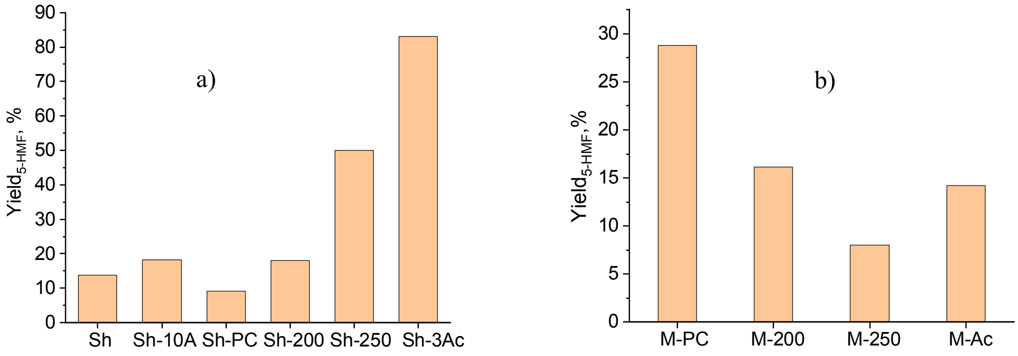

Fig. 7. 5-HMF yields over catalysts based on natural zeolite (a) and synthetic one (b)

As can be seen from Fig. 8, in the case of natural zeolite catalysts, there is a linear increase in the yield of 5-HMF with the increasing volume of mesopores of samples, while in the case of synthetic mordenite even with mesopores volume of 0.04–0.05 cm^3/g yields do not exceed 30 %. This is even though the total acidity of the samples is one order of magnitude higher. This feature is caused, apparently, by the fact that the natural rock had a larger average pore radius (Table 2), ranging from 2.6 to 6 nm. Whereas for samples based on synthetic mordenite, the average pore radius did not exceed 1-2 nm, which significantly complicated the diffusion of fructose molecules in the middle of the zeolite structure.

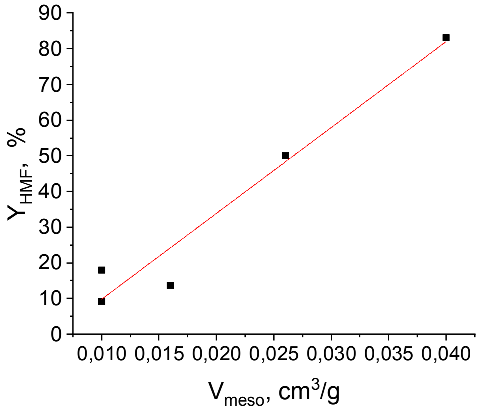

Fig. 8. Dependence of 5-HMF yield on the volume of mesopores for catalysts based on natural zeolite

Therefore, samples based on natural Transcarpathian clinoptilolite rocks have shown high activity and selectivity in the conversion of fructose into 5-HMF. Since during the conversion of carbohydrates over zeolite catalysts two competing processes of the conversion of hexoses into 5-HMF and oligomerization to humins simultaneously proceeds, this reaction is similar to the alkylation of isobutane with butenes over acid catalysts, which also involves two competing reactions of isobutane alkylation and butenes oligomerization.[42] It was previously found that the proceeding of alkylation in the oscillating mode allows increasing the time of effective work of the catalyst. It is possible that similarly with alkylation, in the case of conversion of simple carbohydrates, the proceeding of the reaction in the oscillation regime could also be a promising way to increase the efficiency and selectivity of the target process.

4. Conclusions

1. Acid catalysts in calcium-lanthanum-ammonium forms have been synthesized from natural zeolite rocks of Transcarpathia by hydrothermal ion exchange with additional steaming and dealumination. Several comparison samples based on powdered synthetic mordenite zeolites were obtained.

2. The porosity of the synthesized catalysts was investigated using low-temperature nitrogen adsorption/desorption. Steaming at 523 K and "soft" dealumination with EDTA were found to lead to a significant increase in the volume of mesopores, while the treatment with hydrochloric acid is more conducive to the increase of microporosity.

3. The acidity of catalysts was determined by the chemisorption of pyridine with IR-spectral control. Brønsted and Lewis acid sites have been identified. The total number of acid sites in the case of synthetic mordenite is stated to be one order of magnitude higher than for clinoptilolite samples, despite the close aluminosilicate ratio with natural clinoptilolite.

4. The conversion of fructose into 5-HMF in the presence of synthesized catalysts at 433 K in DMSO was studied. Practically all samples show conversions of 98-100 %, however, high selectivity for 5-HMF has only the natural rock modified by steaming and EDTA treatment. The latter samples provide 5-HMF yields of 50 and 83 %, respectively. On the contrary, for samples based on synthetic mordenite, additional modifications impair the selectivity of the catalysts.

Acknowledgments

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ПЕРЕТВОРЕННЯ ФРУКТОЗИ ДО 5-ГІДРОКСИМЕТИЛФУРФУРОЛУ НА ПРИРОДНИХ ЦЕОЛІТАХ ЗАКАРПАТТЯ

Анотація. *На основі природного цеоліту (Закарпатська обл.) синтезовано каталізатори в кальцій-лантан-амонійній формі, модифіковані парообробкою та деалюмінуванням етилендіамінтетраоцтовою кислотою. Зразки досліджено з використанням адсобрції/десорбції азоту, рентгенофазного, рентгенофлуоресцентного аналізу та ІЧ-спектроскопії з перетворенням Фур'є. Встановлено, що за температури 433 К вихід 5-гідроксиметилфурфуролу на модифікованих зразках становить 50 і 83 % за практично повної конверсії фруктози.*

Ключові слова: *фруктоза, 5-гідроксиметилфурфурол, цеоліти природні, парообробка, деалюмінування.*