UDC 544.473
https://doi.org/10.15407/kataliz2025.36.033

Conversion of glucose into 5-hydroxymethylfurfural on Ukrainian natural zeolites

Lyubov K. Patrylak, Serhiy V. Konovalov, Stepan O. Zubenko, Anzhela V. Yakovenko,
Yuliya G. Voloshyna, Olexandra P. Pertko

V.P Kukhar Institute of Bioorganic Chemistry and Petrochemistry of National Academy of Sciences of Ukraine
1 Academician Kukhar Str., Kyiv, 02094, Ukraine, e-mail: lkpg@ukr.net

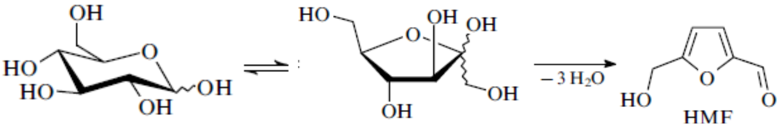
An important product of biomass carbohydrate conversion is 5-hydroxymethylfurfural as a potential raw material component of a wide range of important chemicals. The aim of the work was to study the conversion of glucose into 5-hydroxymethylfurfural in the presence of modified clinoptilolite and mordenite-clinoptilolite zeolite rocks from Transcarpathia. A number of acid catalysts have been synthesized by liquid-phase ion exchange of native cations with calcium, lanthanum, and ammonium cations, as well as by dealumination with hydrochloric and ethylenediaminetetraacetic acid. Their properties were characterized using XRD and XRF analysis, low-temperature nitrogen adsorption/desorption, and FTIR spectroscopy. The acidity of the samples was determined by reverse *n*-butylamine titration. Acid treatment of the samples contributed to an increase in the specific surface area of the samples by an order of magnitude. The samples were tested in the conversion of 9% aqueous glucose solution into 5-hydroxymethylfurfural. The composition of the reaction products was analyzed by gas chromatography. The glucose conversions and the yields of 5-hydroxymethylfurfural, levulinic acid, and fructose were calculated. The glucose conversions ranged from 30 to 70 %. The results were analyzed in accordance with the characteristics of the nature of the active sites of the catalysts and the porous structure of the latter. It was found that the samples with the presence of Lewis acid sites in the form of extra-framework aluminum and multiply charged cations are characterized by the highest 5-hydroxymethylfurfural yields. Due to glucose conversion occurs mainly on the outer surface of zeolite crystals and at the entrances to the cavities, the polycationic form of clinoptilolite, despite its low porous characteristics, demonstrates the highest yield of 5-hydroxymethylfurfural.

***Keywords**:* natural zeolites, acid sites, 5-hydroxymethylfurfural, glucose conversion

Introduction

Carbohydrates of biomass are important natural sources of energy. However, the bulk of the biomass carbohydrates is in the form of cellulose, which, despite its abundance, is little used in the chemical industry due to its low solubility and low reactivity. This natural biopolymer can be hydrolyzed to simple carbohydrates, and the latter can be dehydrated to furan derivatives, in particular, furfural, 5-hydroxymethylfurfural (5-HMF), levulinic, and lactic acids [1-4].

Biomass-derived 5-HMF is a potential feedstock for a wide range of chemicals and biofuels. Its production from monosaccharides involves the isomerization of glucose into fructose, which converts into 5-HMF by losing three water molecules (Scheme 1). Therefore, fructose is considered as a key precursor of 5-HMF.



Scheme 1. Scheme of glucose transformation into 5-HMF

It is believed [5, 6] that in the first stage, Lewis acid sites (LAS) catalyze the isomerization of glucose into fructose by the 1,2-hydride transfer mechanism, while Brønsted acid sites (BAS) contribute to the second stage - the dehydration of fructose into 5-HMF. There is another approach [7], according to which the dehydration of glucose into 5-HMF is possible through the formation of the intermediate 1,2-enediol without involving fructose as an intermediate product.

It is natural that the use of heterogeneous catalysis in the conversion of hexoses is a progressive and promising direction that will contribute to the development of technologically advantageous processes for obtaining platform substances from sugars. Today, the conversion of glucose and fructose is intensively studied in aqueous, alcoholic, or other solvent environments with the involvement of a significant range of solid catalysts. However, cheap natural zeolites have not yet found proper application in this area [8-12].

Therefore, the aim of the work was to study the conversion of glucose into 5-HMF in the presence of modified natural clinoptilolite and mordenite-clinoptilolite zeolite rocks of Transcarpathia.

Experiment

Synthesis of catalysts

As the starting materials, the samples of natural Transcarpathian zeolite rocks of mordenite-clinoptilolite (MC) and clinoptilolite (C) origin were used. The SiO_2/Al_2O_3 ratio for C rock was 8.4, and for MC rock – 9.5. The content of clinoptilolite in the C rock is about 80 % by mass, and the content of mordenite and clinoptilolite in MC rock is 75 % and 25 % by mass. The main impurities are mica and quartz. Sodium, calcium, potassium, and magnesium cations compensate negative charge of aluminum tetrahedrals. Their content was CaO (3 wt. %), Na_2O (1 wt. %), K_2O (2 wt. %) [13] and CaO (5.5 wt. %), Na_2O (0.6 wt. %), MgO (1.0 wt. %), K_2O (8.1 wt. %) [14] for MC and C rocks respectively.

As a result of acid treatment of the corresponding rock with hydrochloric acid (1.5 mol/l and 4 mol/l) at the boiling temperature of a water bath, samples of hydrogen forms C-1 and MC-1 were obtained.

The polycationic form of clinoptilolite (C-3) was obtained by sequential exchange at 90-150 °C for calcium ions (4 exchanges), lanthanum (2 exchanges), and ammonium (1 exchange) from aqueous solutions of the corresponding nitrates with intermediate calcinations at 550 °C for 2 h.

By “soft” dealumination of sample C-3 using ethylenediaminetetraacetic acid (EDTA) in an aqueous medium in three stages, sample C-4 was obtained. The procedure of obtaining these samples is described in more detail in [14, 15].

To obtain the MC-2 sample, silicon atoms in the MC framework were subjected to partial isomorphic substitution with aluminum atoms by high-temperature treatment (600 °C) in $SiCl_4$ vapors, followed by conversion to the hydrogen form by ion exchange with 3 mol/L ammonium nitrate solution and subsequent calcination at 500 °C for 3 h.

Characterization of the catalysts

To determine the total concentration of acid centers in zeolite samples, a reverse titration with *n*-butylamine was performed. To start with, 0.3 g of a natural rock-based sample was placed in a vial of 100 cm^3, weighed with analytical accuracy, and 10 cm^3 of a 0.1 M solution of *n*-butylamine in cyclohexane was added. The vial was sealed, shaken vigorously, and left for 24 hours. After that, the entire liquid phase was collected, transferred to a titration flask, weighed, and titrated with a 0.1 M HCl solution in *i*-propyl alcohol. The concentration of acid sites was determined from the calculated change in *n*-butylamine concentration based on the titration results and the known weight of the sample. This procedure was repeated three times for each studied sample. The results were statistically processed. Confidence level of 95 % was used for calculating confidence intervals.

XRD patterns were recorded using DRON 4-07 equipment. FTIR spectrum was recorded using Affinity-1S spectrometer (Shimadzu Corp.). All samples were also examined by low-temperature nitrogen adsorption/desorption methods (Nova 1200, Quantachrome Instr.). The specific surface areas (S^{BET}) have been calculated according to the standard Brunauer–Emmet–Teller (BET) method utilizing the nitrogen adsorption data at P/P_0 values between 0.06 and 0.2. The micropores volumes (V^{t}_{micro}) and micropores surface areas (S^{t}_{micro}) have been estimated using the de Boer t-plot method. External surface (S^{t}) was calculated as the difference between S^{BET} and S^{t}_{micro}. Silica to alumina ratio in the samples were determined using XRF analysis (X-Supreme8000, Oxford Instruments).

Glucose dehydration

The conversion of glucose on zeolite-based catalysts was carried out in an aqueous medium using glass autoclave reactors of 35 cm^3 with a screw Teflon top. The loading volume of the aqueous reagent solution was 5.0 cm^3, the mass ratio of solid to liquid (S:L) phase was 1:9. The catalyst sample of 0.50 g was poured into the flask, 0.50 g of glucose and 5.00 g of distilled water were added. A magnetic stirrer was placed in the autoclave, then it was sealed and placed in a preheated oil bath. The process was carried out for 4 h with intensive stirring (1000 rpm) at 160 °C. The products were cooled in air and in a stream of cold water. The catalyst and precipitate of insoluble humins as by-products were separated by centrifugation (10 min, 3000 rpm).

Reaction products were analyzed by using an Agilent 7890A gas chromatograph (FID detector, split/splitless inlet, the capillary column J&W HP-5 (5 %-phenyl)-methylsiloxane, 30 m, inner diameter 0.32 mm, film thickness 0.25 μm). For the analysis, about 0.2 cm^3 of liquid products weighed with an accuracy of 0.0001 g were diluted with 2.0 cm^3 of distilled water. The brown sediment of water-insoluble humins was separated using centrifugation (15 min, 4000 min^{-1}). The following conditions were used for the analysis: inlet temperature – 200 °C; split ratio – 20:1; chromatographic column heater temperature – 100 °C, then 5 °C/min to 175 °C and 30 °C/min to 320 °C; carrier gas (N_2) flow rate – 3 cm^3/min; detector temperature – 260 °C; injection volume – 1 μl. The concentrations of 5-HMF and levulinic acid were calculated using calibration curves in range 0.1 to 0.5 wt. % for 5-HMF and 0.05 to 0.2 wt. % for levulinic acid obtained with analytical standards of corresponding pure substances. The analysis was repeated 3–5 times and the results were averaged.

To determine the concentration of glucose in liquid products of catalytic transformation, gas chromatography analysis with D-sorbitol as internal standard (≥ 98.0 %,) was carried out with preliminary derivatization of hydroxyl groups by means of trimethylsilytatation with trimethylchlorosilane (Sigma Aldrich, ≥ 99.0 %, for GC derivatization) and hexamethyldisilazane (Sigma Aldrich, ≥ 99.0 %, for GC derivatization). 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 with an accuracy of 0.0001 g and then evacuated (< 1 kPa) for 3 h at 20 °C and for 1 h at 70-80 °C to remove water and volatile products. The residue was dissolved in 2 cm^3 of D-sorbitol standard solution in pyridine (0.315 wt. %), pyridine, and then 60 μl trimethylchlorosilane and 120 μl of hexamethyldisilazane were added. The vial was closed and shaken intensively followed by centrifugation (10 min, 3000 min^{-1}) in order to remove the sediment of ammonium chloride. The sample for chromatographic analysis was taken from the liquid phase, not disturbing the formed sediment. Varying amounts (about 0.04-0.08 g) of D-glucose (pharmaceutical purity FS 42U-52/37 709 00, Ukraine) standard solution in pyridine (10.00 wt. %) were treated in the same manner in order to calibrate the ratio of FID sensitivity to derivatized forms of D-glucose and D-sorbitol. The conditions of analysis were the same as for 5-HMF and levulinic acid analysis. D-glucose concentration was calculated from chromatographic peaks areas of both anomers of its six-member cyclic form (α- and β-D-glucopyranose).

The conversion of glucose as well as the yields of 5-HMF, levulinic acid, and fructose were calculated from the chromatographic data.

Results and discussion

Starting raw rocks were investigated by using XRD analysis. The diffraction pattern of the MC rock is characterized by 12 lines (2Θ = 6.5; 9.76; 13.44; 13.82; 14.58; 19.6; 22.18; 23.14; 25.6; 26.22; 27.66; 33.12; 35.58), which reflect the presence of mordenite and clinoptilolite phases (Fig. 1). For the C rock, in addition to clinoptilolite lines, intensive lines of impurity quartz have been observed (Fig. 2).

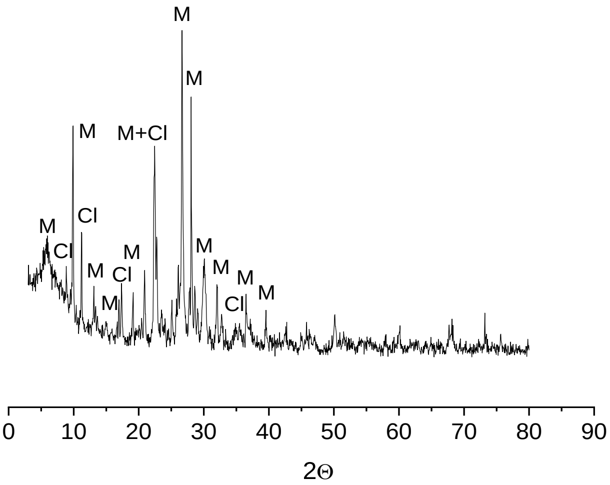


Fig. 1. XRD pattern of MC rock: M – mordenite, Cl - clinoptilolite

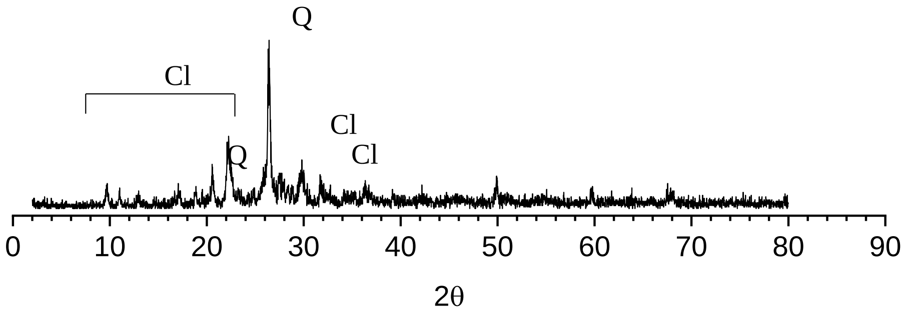


Fig. 2. XRD pattern of C rock: Cl – clinoptilolite, Q – quartz

It is known that ion-exchange cations in the Transcarpatian zeolite rocks are represented predominantly by potassium, sodium, calcium, and magnesium [14, 16]. As a result of modification of the rocks, the silica to alumina ratio of zeolites was changed. Table 1 shows the corresponding values established by using XRF analysis.

Table 2 shows the porous characteristics of the catalyst samples calculated from low-temperature nitrogen adsorption/desorption isotherms. It should be noted that the application of this method for narrow-porous zeolites, such as clinoptilolite (0.31×0.75 nm, 0.36×0.46 nm, and 0.28×0.47 nm) and mordenite (0.67×0.70 nm, 0.29×0.57 nm) [17], is quite limited due to the slow diffusion of nitrogen in their narrow channels.

Table 1. Silica to alumina ratio in the samples

Sample	SiO_2/Al_2O_3	Sample	SiO_2/Al_2O_3
C	8.4	MC	9.5
C1	8.8	MC1	18
C3	10.9	MC2	12
C4	13.1		

Table 2. Adsorption characteristics of the catalysts

Sample	S^{BET}, m^2/g	S^t, m^2/g	S^t_{micro}, m^2/g	V_Σ, cm^3/g	V^t_{micro}, cm^3/g	V_{micro}/V_Σ, %
C	9.6	3.7	5.8	0.016	0.002	13
C-1	131	9.9	121	0.075	0.049	65
C-3	9.2	2.3	6.9	0.013	0.003	24
C-4	89	16.6	72.1	0.031	0.071	42
MC	62	22	40	0.075	0.019	25
MC-1	264	21	243	0.157	0.096	62
MC-2	31	13	18	0.067	0.006	8.8

As can be seen from the data in the table, the specific surface area of the C zeolite and its polycationic form C-3 is quite low (~ 9 m^2/g). Moreover, for C-3 it is even slightly smaller than the value for the original rock, which may be due to an increase in the radius of cations in the polycationic form, in particular, the presence of lanthanum cations. After acid treatments (samples C-1 and C-4), the specific surface area increases by an order of magnitude due to unlocking access to micropores after partial destruction of the zeolite structure, leaching of impurities, and ion exchange of divalent cations for a proton. A similar trend of significant increase in BET surface area is observed after acid treatment of mordenite-clinoptilolite rock. The specific surface area increased from 62 to 264 m^2/g, which is close to the values for synthetic mordenite-type zeolite [18]. At the same time, the content of micropores increases approximately 5 times. The latter can be caused not only by the removal of structural aluminum, but also by the replacement of the original cations of sodium, potassium, calcium with a cation with a smaller radius - a proton [19]. The volume of mesopores also increases.

In the case of modification of MC by isomorphic substitution of framework aluminum atoms with silicon (sample MC-2), the opposite situation is observed - the specific surface area decreases by half, and the volume of meso- and micropores also decreases. This occurs, apparently, as a result of the well-known phenomenon of the formation of extra-framework aluminum structures that remain in the pores of the zeolite [20].

The mesopore content in the samples, calculated using DFT theory, is summarized in Table 3. Dealumination with hydrochloric acid contributed to a slight increase in the mesopore volume in the case of samples MC-1 and C-1, while EDTA treatment (sample C-4) caused a 15-fold increase in the mesopore volume. Obviously during the treatment of the polycationic form of C-3 with EDTA, partial dealumination and decationization of the rock with pore expansion occurs. It is interesting that the use of EDTA contributes to both an increase in microporosity and mesoporosity of the sample, while treatment with mineral acid only leads to an increase in microporosity (Tables 1 and 3).

Table 3. Volume of pores (V) with a diameter bigger than 2 nm for unmodified and modified samples calculated using DFT approaches

Sample	V, cm^3/g	Sample	V, cm^3/g
C	0.003	MC	0.062
C1	0.015	MC1	0.073
C3	0.008	MC2	0.051
C4	0.045		

Table 4 shows the concentration of acid centers in the zeolite catalyst samples, measured by reverse titration with *n*-butylamine. Obviously, the molecules of the latter (kinetic diameter ~ 0.5 nm) cannot access the acid sites inside the zeolite micropores of clinoptilolite. Therefore, the values given refer only to the centers on the outer surface of the catalysts. One can be absolutely sure that glucose molecules (kinetic diameter about 1 nm [21]) cannot access the centers located deep in the clinoptilolite structure, to which *n*-butylamine does not have access. As might be seen from the data in Table 4, the concentration of acid sites available for the latter in the original C rock and its polycationic form, C-3, is extremely low. A noticeable increase in the number of acid sites in the C-4 sample is observed after EDTA treatment. As shown above, the surface area of the sample also increased significantly (Table 2). The start MC rock contains slightly more acid centers than the C rock. The acid treatment resulted in a threefold increase in their concentration (sample MC-1), while dealumination by isomorphic substitution of aluminum (sample MC-2) for silicon reduced it, which is apparently due to the removal of aluminum necessary for the formation of bridged BAS. But when treating the sample with silicon tetrachloride under static conditions, aluminum compounds are not removed, and therefore they can be LAS. However, access to them is difficult, which is confirmed by a decrease in the BET specific surface area of the sample.

Table 4. Experimental (C_{ac}) and reduced cconcentration (CR_{ac}) of acid sites in zeolite samples according to the results of titration with *n*-butylamine

Catalyst	C_{ac}, mmol/g	CR_{ac}, mmol/m^2	Potential LAS	Potential BAS
C	0.07±0.06	0.0184*	Na^+, K^+, Ca^{2+}	Weak BAS
C-1	-		-	Bridge OH-groups
C-3	0.04±0.04	0.0173*	Ca^{2+}, La^{3+}	Weak BAS Bridge OH-groups
C-4	0.28±0.04	0.031**	Ca^{2+}, La^{3+}	Weak BAS Bridge OH-groups
MC	0.18±0.1	0.0082*	Na^+, K^+, Ca^{2+}	Weak BAS
MC-1	0.53±0.02	0.002**	-	Bridge OH-groups
MC-2	0.11±0.04	0.085*	Ca^{2+}, La^{3+}, extraframework Al species	Weak BAS Bridge OH-groups

* experimental number of sites divided by external surface area, which is accessible for glucose molecules

** experimental number of sites divided by BET surface area, which is accessible for *n*-butylamine molecules

In the third column of Table 4, the reduced concentration of acid sites of the samples and lists of potential sources of LAS and BAS were also indicated. The initial forms contain calcium, sodium, and potassium cations, which compensate the negative charges on the aluminum-oxide tetrahedra. In the field of polyvalent cations, in this case calcium, the decomposition of a water molecule is possible with the formation of a cation $(CaOH)^+$ and an acid-bridging OH-group - BAS. Therefore, the original form uniquely contains both Brønsted acid sites and weak Lewis acid sites in the form of mono- and divalent cations of sodium, potassium, and calcium.

During acid treatment with 4 mol/L hydrochloric acid (sample MC-1), partial dealumination of the rock and simultaneous decationization with the formation of new BAS occur. Aluminum was mainly removed from the sample in this case. When treating the C rock with 1.5 mol/l hydrochloric acid, no significant dealumination occurred. This is confirmed by the small change in silica to alumina ratio (Table 1), which is apparently caused by the low acid concentration.

When performing isomorphic substitution of aluminum for silicon, the silica to alumina ratio increases, which, as is known, contributes to an increase in the acidity strength of Brønsted sites, which are formed during ion exchange of native cations for ammonium and followed by thermal decomposition of the latter. However, further thermal treatment of ammonium forms is accompanied by partial dehydroxylation and destruction of the zeolite lattice with the formation of extra-framework aluminum, which acts as a Lewis acid site. In addition, extra-framework aluminum compounds are formed during the isomorphic substitution procedure itself [20]. This is confirmed by the presence of an absorption band at 3650 cm^{-1} in the FTIR spectrum (Fig. 3), which is associated with the formation of Al-OH-Al groups [22].

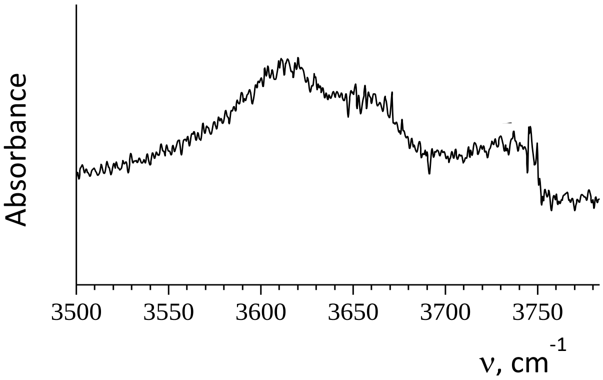


Fig. 3. FTIR spectrum of MC-2 sample in the region of valence vibration of OH-groups

Therefore, when determining the acidity in MC-1 sample by titration with *n*-butylamine, it is quite natural that the number of acid sites is significantly greater than in the original rock. And these centers, which are located in the mesopores, can be partly accessible for glucose molecules, which are bigger than *n*-buthylamine molecules. Whereas in the raw rock MC and in MC-2 sample, only the centers of the external surface of the zeolite and the entrances to the channels are available for glucose conversion.

The polycationic form of C-3 contains about 80 % of the exchange capacity of lanthanum. However, the significant kinetic radius of the lanthanum cation allows it to enter into the narrow pores of clinoptilolite-type zeolites only upon destruction of the hydration shell at high temperatures of hydrothermal ion exchange. At the same time, the entrances to the channels become even narrower, and the BET surface becomes even smaller (Table 2).

The results of glucose catalytic transformations are presented in Table 5. It is quite natural that the process of glucose transformation in aqueous medium proceeds worse than, for example, in DMSO [23], and the obtained yields of 5-HMF are significantly lower.

In relation to the number of acid centers and their nature, the obtained data can be interpreted as follows. In the raw MC rock, there are weaker LAS (sodium, potassium, calcium, and magnesium cations) than BAS, since the latter are formed only in the interaction with divalent cations.

Table 5. Glucose conversion (X), 5-HMF yield (Y_{HMF}), levulinic acid yield (Y_{LA}), and fructose yield (Y_{FR}) on the zeolite samples

Catalyst	X, %	Y_{HMF},% mol	Y_{LA}, % mol	Y_{FR}, % mol
MC	30	10.5	4.4	10.6
MC-1	51	12.0	4.1	4.4
MC-2	60	14.7	4.2	11.9
C	68	13.3	4.0	8.0
C-1	50	11.0	4.1	3.3
C-3	70	18.7	4.3	3.4
C-4	39	13.4	<3.2	9.3

Therefore, part of fructose as an intermediate product of the conversion of glucose into 5-HMF remains in the products. Weak BAS predominantly convert glucose into humins, as was found in [23].

The MC-1 sample has a lot of BAS, while the number of LAS has decreased because the cations have been replaced by protons using mineral acid. The extra-framework aluminum is simultaneously mainly removed from the sample in the form of aluminum chloride. As a result, the degree of glucose conversion has increased, but the yield of 5-HMF has increased insignificantly (only by 2 %). Therefore, the main contribution to increase in glucose conversion was made by the formation of humins as by-products.

On the MC-2 sample, the increase in the BAS strength contributed to an increase in the yield of HMF by 4 %. However, in this case, the hydrogen form was obtained through the decomposition of the ammonium form, which caused the formation of extra-framework aluminum, which acts as LAS. In addition, strong LAS in the form of extra-framework aluminum structures were formed during the isomorphic substitution procedure itself. Therefore, the fructose yield increased again compared to the previous sample. However, the contribution of humins is still significant in this case.

The degrees of glucose conversion on the C and C-3 samples are close. However, in the second sample, the presence of lanthanum increases the contribution of LAS and weak BAS, which are formed during the decomposition of a water molecule in the La^{3+} force field. As a result, the yield of 5-HMF increases up to 19 %. On the other hand, in C-1 sample treated with hydrochloric acid, almost all metal cations were removed, which leads to the depletion of the sample in the LAS. While dealumination occurred to a small extent, the acidity strength did not change significantly. As a result, it naturally demonstrates both lower conversion and lower selectivity for 5-HMF.

In the case of C-4 sample with a higher total acidity according to butylamine titration, the same fructose yield is observed as on the original rock form, which may be due to the potentially larger number of LAS compared to BAS. However, glucose access to them is limited, so the overall conversion is low.

Taking into account the approximately comparable yields of levulinic acid on all catalysts, strong BAS are represented to a negligible extent in the above samples [23].

Therefore, in general, there is a certain correlation between the reduced number of acid sites titrated with *n*-butylamine and the activity of the samples in glucose conversion. There is a clear agreement with the nature of the acid sites caused by different stages of sample modification. The clearly higher content of 5-HMF yields in samples with the presence of lanthanum and extra-framework aluminum as strong LAS indicates the implementation of a two-stage scheme of glucose conversion through its initial isomerization into fructose. The highest yield of humins is observed on samples modified with hydrochloric acid with a minimum amount of LAS. It is 85 and 86.4 wt. % for MC-1 and C-1 samples respectively.

The glucose conversions obtained in this work are not very high (30-70 %). They are lower than fructose conversions on natural clinoptilolite samples [14] obtained in DMSO medium. However, the obtained yields of 5-HMF are comparable and even slightly higher than the yields of 5-HMF on synthetic hydrogen and nickel-containing forms of zeolites Y, M, and ZSM-5 [23], which did not exceed 10-12 %.

Conclusions

Thus, in view of the large size of the glucose molecule compared to the pore size of narrow-pore natural zeolites, the transformations are realized mainly on the outer surface of the zeolites and at the entrances to the channels. The degree of glucose conversion and the yield of 5-HMF correlate with the acidity of the samples, determined by *n*-butylamine titration, referred to the sample surface area accessible to glucose molecules. The features of the catalytic conversion of glucose into 5-HMF are in accordance with the nature of the active sites of the samples and their porous structure. The efficiency of glucose conversion is significantly influenced by the nature of Lewis acidity, which is represented in the samples by metal cations and extra-framework aluminum species. The presence of multiply charged cations, in particular, lanthanum, contributes to a more efficient course of glucose conversion compared to the raw rocks, in which Lewis acidity is provided by singly and doubly charged cations. The highest yield of 5-HMF of about 19 % was obtained on the polycationic form of the clinoptilolite with high lanthanum content. The obtained data confirm the two-stage conversion scheme of glucose on natural zeolites with the intermediate formation of fructose.

Acknowledgements

The authors would like to thank the organizers of the II European Chemical School for Ukrainians (https://acmin.agh.edu.pl/en/detail/s/ii-european-chemistry-school-for-ukrainians) for their support and helpful educational information.

References

1. Esteban J., Yustos P., Ladero M. Catalytic processes from biomass-derived hexoses and pentoses: a recent literature overview. *Catalysts.*, 2018, **8,** 637–678.
2. Chen N., Zhu Z., Ma H., Liao W., Lü H. Catalytic upgrading of biomass-derived 5-hydroxymethylfurfural to biofuel 2,5-dimethylfuran over Beta zeolite supported non-noble Co catalyst. *Mol. Catal.*, 2020, **486**, 110882.
3. Xu H., Wang Z., Huang J., Jiang Y. Thermal Catalytic Conversion of Biomass-Derived Glucose to Fine Chemicals. *Energy Fuels,* 2021, **35**(10), 8602–8616.
4. Tomishige K., Yabushita M., Cao J., Nakagawa Y. Hydrodeoxygenation of potential platform chemicals derived from biomass to fuels and chemicals. *Green Chem.*, 2022, **24**, 5652–5690.
5. Choudhary V., Mushrif S.H., Ho C., Anderko A., Nikolakis V. et al. Insights into the interplay of Lewis and Brønsted acid catalysts in glucose and fructose conversion to 5-(hydroxymethyl)furfural and levulinic acid in aqueous media. *J. Am. Soc.,* **2013**, 135, 3997–4006.
6. Bhaumik P., Dhepe P.L. Solid Acid Catalyzed Synthesis of Furans from Carbohydrates. *Catal. Rev.,* 2016, **58**(1), 36–112.
7. Li J., Li J., Zhang D., Liu C. Theoretical elucidation of glucose dehydration to 5-hydroxymethylfurfural catalyzed by a SO_3H-functionalized ionic liquid. *J. Phys. Chem. B*, 2015, **119**, 13398–13406.

8. Barbosa S.L., de S. Freitas M., dos Santos W.T.P. et al. Dehydration of d-fructose to 5-hydroxymethyl-2-furfural in DMSO using a hydrophilic sulfonated silica catalyst in a process promoted by microwave irradiation. *Sci. Rep.,* 2021, **11**, 1919.
9. Pande A., Niphadkar P., Pandare K., Bokade V. Acid modified H-USY zeolite for efficient catalytic transformation of fructose to 5-hydroxymethylfurfural (biofuel precursor) in methyl isobutyl ketone─water biphasic system. *Energy Fuels.,* 2018, **32**(3), 3783–3791.
10. Levytska S.I. Investigation of glucose isomerization into fructose on MgO-ZrO$_2$ catalyst in flow mode. *Catalysis and Petrochemistry,* 2017, **26**, 46–52. [in Ukrainian].
11. Huang F., Jiang T., Dai H., Xu X., Jiang S., Xhen L., Fei Z., Dyson P.J. Transformation of glucose to 5-hydroxymethylfurfural over regenerated cellulose supported Nb$_2$O$_5$ center dot nH$_2$O in aqueous solution. *Catal. Letters.,* 2020, **10**, 13489–13495.
12. Wei W.Q., Wu S.B. Experimental and kinetic study of glucose conversion to levulinic acid in aqueous medium over Cr/HZSM-5 catalyst. *Fuel,* 2018, **225**, 311–321.
13. Patrylak K., Bobonych F., Voloshyna Yu. et al. Ukrainian mordenite-clinoptilolite rocks as a base for linear hexane isomerization catalyst. *Appl. Catal. A Gen.,* 1998, **174**(1–2), 187–198.
14. Patrylak L., Konovalov S., Yakovenko A., Pertko O., Povazhnyi V. et al. Fructose transformation into 5-hydroxymethylfurfural over natural transcarpathian zeolites. *Chem. Chem. Technol.*, 2022, **16**(4), 521–531.
15. Patrylak L., Konovalov S., Zubenko S., Yakovenko A. Transformation of hexoses on natural and synthetic zeolites. *Chem. Chem. Technol*., 2023, **17**(2), 287–293.
16. Vasylechko V., Sydorchuk V., Manko N., Kostiv O., Klyuchivska O., Ilkov O., Bagday S., Zelinskiy A., Gromyko A., Stoika R., Kalychak Ya. Effect of physico-chemical modification of clinoptilolite composites on their antimicrobial activity. *Chem. Chem. Technol.,* 2025, **19**(2), 183–195.
17. Breck D.W. Zeolite molecular sieves: structure, chemistry and use. – John Wiley, New York, 1974.
18. Ahmed A.M., Jarullah A.T., Hussein H.M., Ahmed A.N. Mordenite-Type Zeolite from Iraq Sand: Synthesis and Characterization. *J. Petrol. Research and Studies*, 2023, **13**(3), 126–142.
19. Voloshyna Yu., Pertko O., Pavazhnyi V., Yakovenko A. Effect of modifying the clinoptilolite-containing rocks of Transcarpathia on their porous characteristicss and catalytic properties in the conversation of C$_6$-hydrocarbons. *Chem. Chem. Technol.,* 2023, **17**(2), 373–385.
20. Anderson M.W., Klinowski J. Zeolites treated with silicon tetrachloride vapour. Part 1 – Preparation and characterization. *J. Chem. Soc., Faraday Trans.1,* 1986, **82**, 1449–1496.
21. Mahala S., Arumugam S.M., Kumar S., Devi B., Elumalai S. Tuning of MgO's base characteristics by blending it with amphoteric ZnO facilitating the selective glucose isomerization to fructose for bioenergy development. *Nanoscale Adv.,* 2023, **5**(9), 2470–2486.
22. Khivantsev K., Jaegers N.R., Kovarik L., Derewinski M.A., Kwak J.-H., Szanyi J. On the nature of extra-framework aluminum species and improved catalytic properties in steamed zeolites. *Molecules,* 2022, **27**(7), 2352.
23. Patrylak L.K., Konovalov S.V., Yakovenko A.V., Pertko O.P., Povazhnyi V.A., Voloshyna Yu.G., Melnychuk O.V., Filonenko M.M. Micro–mesoporous kaolin-based zeolites as catalysts for glucose transformation into 5-hydroxymethylfurfural. *Appl. Nanosci.,* 2023, **13**(7), 4795–4808.
24. Patrylak L.K., Pertko O.P., Povazhnyi V.A., Yakovenko A.V., Konovalov S.V. Evaluation of nickel-contaning zeolites in the catalytic transformation of glucose in an aqueous medium. *Appl. Nanosci.,* 2022, **12**(4), 869–882.

Надійшла до редакції 11.09.2025

Перетворення глюкози до 5-гідроксиметилфурфуролу на українських природних цеолітах

Любов К. Патриляк, Сергій В. Коновалов, Степан О. Зубенко, Анжела В. Яковенко, Юлія Г. Волошина, Олександра П. Пертко

Інститут біоорганічної хімії та нафтохімії ім. В.П.Кухаря Національної академії наук України
вул. Академіка Кухаря, 1, Київ, 02094, Україна, e-mail: lkpg@ukr.net

Важливим продуктом перетворення вуглеводів біомаси є 5-гідроксиметилфурфурол як потенційний сировинний компонент широкого ряду важливих хімічних речовин. Метою роботи було дослідження конверсії глюкози до 5-гідроксиметилфурфуролу в присутності модифікованих клиноптилолітової та морденіт-клиноптилолітової цеолітових порід Закарпаття. Синтезовано ряд кислотних каталізаторів шляхом рідкофазного іонного обміну нативних катіонів на катіони кальцію, лантану та амонію, а також шляхом деалюмінування хлоридною та етилендіамінтетраоцтвою кислотою. Охарактеризовано їх властивості за допомогою рентгено-фазового та рентгенофлуорисцентного аналізу, низькотемпературної адсорбції/десорбції азоту та ІЧ-спектроскопії. Здійснено оцінку кислотності зразків за титруванням з *н*-бутиламіном. Кислотна обробка зразків сприяла зростанню питомої поверхні зразків на порядок. Зразки випробувано у перетворенні 9 % водного розчину глюкози до 5-гідроксиметилфурфуролу. Склад продуктів реакції аналізували за допомогою газової хроматографії. Було розраховано конверсії глюкози та виходи 5-гідроксиметилфурфуролу, левулінової кислоти та фруктози. Конверсії глюкози склали від 30 до 70 %. Результати проаналізовано у відповідності до особливостей природи активних центрів та пористої структури каталізаторів. Встановлено, що найкращі виходи 5-гідроксиметилфурфуролу характерні для зразків із наявністю льюїсових кислотних центрів у вигляді позакаркасного алюмінію та багатозарядних катіонів. Оскільки перетворення глюкози перебігає переважно на зовнішній поверхні цеолітних кристалів та у входах у порожнини, то полікатіонна форма клиноптилоліту, незважаючи на її низьку пористість, демонструє найвищий вихід 5-гідроксиметилфурфуролу.

Ключові слова: природні цеоліти, кислотні центри, 5-гідроксиметилфурфурол, конверсія глюкози