TRANSFORMATION OF HEXOSES
ON NATURAL AND SYNTHETIC ZEOLITES

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Abstract. A number of zeolite catalysts based on synthetic powder zeolites and natural Ukrainian clinoptilolite as well as mordenite-clinoptilolite zeolite rocks were synthesized. The activity and selectivity of the prepared samples were compared in glucose and fructose dehydration into 5-hydroxymethylfurfural in a dimethyl sulfoxide environment.

Keywords: natural zeolite, synthetic zeolite, glucose dehydration, fructose dehydration, 5-hydroxymethylfurfural.

1. Introduction

The depletion of fossil resources and the continuous deterioration of the environment contribute to the intensive development of "green" chemical processes and the active use of renewable resources. Therefore, recently, more and more attention is being paid by investigators around the world to the study and implementation of so-called biorefining processes,[1,2] designed to provide the industry with chemicals that are products of biomass conversion.

Biomass carbohydrates are really an inexhaustible source of carbon. However, most of them are composed of insoluble and low-reactive cellulose. These can be hydrolyzed to simple carbohydrates, from which 5-hydroxymethylfurfural (5-HMF) or other platform substances (furfural, furan derivatives, lactic acid, *etc.*) can be obtained by dehydration.[1-3] Platform substances are the raw materials for hundreds of new syntheses to prepare a new generation of biopolymer materials, fuels, pharmaceuticals, pesticides, food additives, and a number of other important chemicals.

Hydrolysis of cellulose into soluble mono- and oligosaccharides can be accomplished using homogeneous, heterogeneous, and enzymatic catalysis.[4,5] Firstly, polysaccharides are converted to glucose, which is isomerized to fructose, and the latter, losing three water molecules, is converted into 5-HMF (Fig. 1). That is why fructose, as a rule, is considered a key precursor of HMF.

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Until the 1980s, most methods of HMF synthesis were based on homogeneous acid-catalyzed processes implemented in aqueous systems. Today, these processes differ significantly depending on the solvents involved.

The best-developed methods of HMF synthesis are on the basis of fructose, which is already used as a raw material in existing production.[6] When dehydrating fructose in aqueous solutions, mineral acids (HCl, H_2SO_4, *etc.*), soluble salts of zinc, niobium, lanthanum, iron, *etc.*, are usually utilized as catalysts. The process temperature varies from 373 K at atmospheric pressure to 393-543 K at elevated pressures. Under other conditions being equal, HMF yields decrease with an increasing concentration of the initial fructose solution. It is believed that in homogeneous aqueous systems, the production of HMF with yields of more than 50 % is difficult to achieve due to the hydrolysis of 5-HMF with the formation of levulinic and formic acids.

Isomerization of glucose to fructose or methyl/ ethyl fructosides is the simplest way for its conversion. In the transformation of glucose in aqueous solutions, mineral acids, soluble salts, as well as solid acid catalysts such as cation exchange resins, oxides, and aluminosilicates are used as catalysts.[7-10] So far, solid catalysts are significantly inferior to enzymes for selectivity in the process of isomerization of glucose to fructose, so the search for new effective solid catalysts remains an urgent task.

Vieira *et al.*[11] investigated niobium oxide Nb_2O_5 in glucose conversion as an effective Lewis acid and a weak Brønsted acid. It was found, in particular, that in combination with strong Brønsted acidity (HCl or Amberlyst), selectivity for HMF can reach up to 50 % when using the binary tetrahydrofuran/water system at 403 K in conversion of 2 % glucose solution. Unlike the application of niobium on silica or MCM-41, the yield of HMF does not exceed 5 %.

Since the direct conversion of glucose into HMF in the aqueous medium is not an easy task, organic solvents are often used. Their role is not only to ensure access of reactants to active catalyst centers but also to suppress side processes and prevent quick catalyst deactivation. Among them, there are methanol, ethanol, dimethyl sulfoxide (DMSO), dimethylacetamide, gamma-valerolactone, acetone, *etc.*[8,9,12-17]
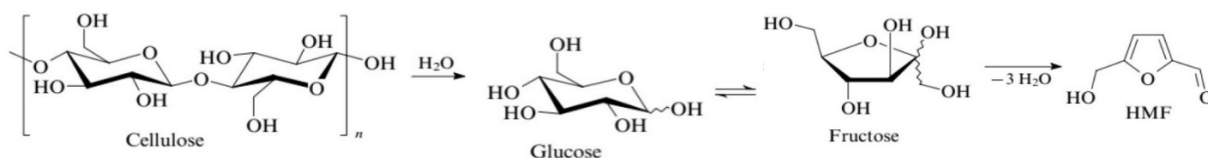
Fig. 1. Scheme of cellulose transformation into 5-HMF

The effect of salt addition on the efficiency of glucose conversion in the water/methyl isobutyl ketone binary system was studied.[18] The best results were obtained using a 20 % solution of sodium chloride in water: 80 % conversion with a 42 % yield of HMF at 468 K on HZSM-5, while without NaCl the yield was 1.6 % with 52 % conversion. And the volume of methyl isobutyl ketone should be twice as large as the aqueous phase because at equal volumes the yield drops to 15 %.

Heterogeneous catalysis utilization in the transformation of hexoses is a progressive and promising direction that will contribute to the development of technologically convenient processes for obtaining platform substances from sugars. Well known that a significant advantage of solid catalysts *vs.* liquid ones is the simple separation of the reaction products, the ability to regenerate catalysts and their reuse as well as the ability to use them in a wide range of reaction conditions. Up to date, a significant number of solid catalysts have been tested in the conversion of glucose and fructose in aqueous or alcohol media. However, zeolites in this area have not been properly used yet.[2,19] While the structure of zeolites, which contain numerous pores and channels ranging from nano- to micrometers, as well as the strong crystalline order of the pores, makes them nanostructured materials with unique properties. Ukraine has significant deposits of natural zeolites, which can be used in a range of adsorption and catalytic processes.[20-22]

Therefore, the aim of this work was to compare the effectiveness of natural and synthetic zeolites in the conversion of hexoses into 5-HMF in a DMSO environment.

2. Experimental

2.1. Materials

For synthesis of catalysts, clinoptilolite (Sokyrnytsia deposit, Transcarpathian region, Ukraine) and mordenite-clinoptilolite (Lipcha village, Transcarpathian region, Ukraine) rocks as well as powder X, Y (faujasite) and M (mordenite) (SiO_2/Al_2O_3 ratios of 2.3, 4.7, and 9.0, JS "Sorbent") were utilized.

The analytical grade reagents used in this study ($Ca(NO_3)_2 \cdot 4H_2O$, $La(NO_3)_3 \cdot 6H_2O$, NH_4NO_3) were purchased commercially in Ukraine. They were utilized as received without further purification. In the measure-

ments, nitrogen and helium of high purity (99.99 %) were applied. In the experiments, 5-HMF and *N*-methyl-*N*-(trimethylsilyl)-trifluoroacetamide (Sigma Aldrich, >99 %), glucose and fructose (pharm. purity, Ukraine), as well as DMSO (pharm. purity, USA) were used.

2.2. Samples Synthesis

Calcium and calcium-lanthanum-ammonium forms of clinoptilolite zeolite (CaClin, CaLaNH4Clin) have been synthesized. To start with, ion exchange (fraction 0.25-0.5 mm) of native cations for calcium (1.5 mol/L) was carried out. The sodium for lanthanum (1.4 mol/L) and then ammonium (1 mol/L) cations were exchanged using aqueous nitrate solutions of salts. The solid-to-liquid phase ratio was 1:2. The reaction temperatures were 363 or 423 K. The resulting samples were dried at 373 K for 2 h. After each exchange, the samples were washed with distilled water. Conditions of ion exchange were selected based on the results of previous works.[23,24]

For comparison, a range of samples was used. Ammonium and hydrogen forms of zeolite Y and M were synthesized from sodium forms of powder zeolites. Firstly, sodium cations were exchanged at 353 K for 3 h for ammonium ones using a 3 mol/L ammonium nitrate solution. Thus, the obtained ammonium forms of zeolites were filtrated and washed with distilled water. The exchange procedures were repeated three times. The NH4-forms of zeolites were calcined in a muffle furnace at 823 K in the presence of air for 2 h afterward, and the hydrogen forms of zeolites HUSY and HM were obtained. The last one was impregnated with the aqueous solution of tin chloride (1 mol/L). A catalyst with 10 wt.% of tin was heated at 323 K for 5 h and then calcined at 673 K for 2 h before further investigations. Thus, samples NH4Y, HUSY, and HM-Sn were obtained.

The preparation of samples based on a mordenite-clinoptilolite rock was described in detail earlier.[20] The HMLP-1Ni and HMLP-2Ni catalysts contain 1 and 2 wt.% of Ni. Previously, a CaLaNH4X catalyst was synthesized and tested in glucose conversion.[23]

2.3. Catalyst Characterization

The textural properties of the synthesized catalysts have been investigated using low-temperature (77 K) nitrogen adsorption/desorption measured by the Nova

1200e (Quantochrome) porometer. High purity nitrogen (99.9 %) was used in adsorption experiments. The specific surface areas have been calculated from nitrogen adsorption data at $P/P_s = 0.06$-0.2 utilizing the Brunauer–Emmet–Teller (BET) equation.[25] Using the "t-plot" statistical thickness method (de-Boer equation), micropore volumes and micropore surface areas have been estimated. Barret-Joyner-Halenda (BJH) analysis and density functional theory (DFT) were used for calculations of the average diameter of pores.

The zeolite silica-to-alumina ratios and nickel content in the synthesized samples have been determined using X-ray fluorescence analysis (Oxford Instruments X-Supreme 8000 analyzer, Great Britain).

2.4. Catalytic Testing

The reaction was carried out in a round bottom flask (50 mL) under reflux and stirred with a magnetic stirrer. A catalyst (1.3 g) was added to the glucose solution in DMSO (20 % by weight, 20 g). The reaction temperature was 433 K and was chosen based on the results of previous studies.[26] Samples of liquid products for analysis were taken every hour. In the case of experiments without a catalyst, 23 g of 20 % glucose solution in DMSO was used. Other conditions were the same.

The transformation of fructose/DMSO solutions was carried out in autoclaves (25 cm^3). Weighted zeolite catalyst samples (0.25 g) were poured with 5 g of 10 % fructose solution. The reaction was carried out at 433 K for 4 h. The autoclaves were placed in a special holder in a furnace with electric heating. Then the autoclaves were cooled to an ambient temperature and the liquid products were separated under a vacuum through a Büchner funnel with a paper filter. In order to collect the residues of the catalyst and reaction mixture, the reactors and catalyst samples were additionally washed with DMSO.

2.5. Analysis of Reaction Products

Reaction products were analyzed by using gas chromatography (Agilent 7890A gas chromatograph, FID detector, the capillary column J&W HP-5, 30 m, 0.32 mm, 0.25 μm). For the analysis, about 0.2 mL of liquid products weighed with an accuracy of 0.0001 g was diluted with 1.8 mL of DMSO. 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.

To determine the concentration of glucose in liquid products of catalytic transformation, the gas chromatography analysis was carried out with preliminary derivatization of hydroxyl groups by means of silanization with *N*-methyl-*N*-(trimethylsilyl)-trifluoroacetamide (MSTFA). 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 weighted 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 1 mL of pyridine, then 150 μL of MSTFA was added. The vial was closed, shacked intensively, and kept at 303 K for 2 h. The reference samples of initial glucose were treated in the same manner for the construction of the calibration curve. The conditions of analysis were the same as for a 5-HMF detection.

3. Results and Discussion

3.1. Catalysts Characterization

The silica-to-alumina ratios from XRF analysis and adsorption properties of the samples based on Ukrainian natural and synthetic powder zeolite catalysts are shown in Table 1.

The highest BET surface areas (570-650 m^2/g) are demonstrated by powder samples of X and Y zeolites. Intermediate values of the specific surface areas (160 and 287 m^2/g) show samples of the mordenite-clinoptilolite base, while for clinoptilolite samples they are minimal (9 m^2/g). The latter can be caused by a narrow-porous clinoptilolite structure. Sprynskyy and co-workers[27] show that considering the large size of the N$_2$ molecule, the nitrogen adsorption/desorption method cannot provide true information about the microporosity of the clinoptilolite micropores. The N$_2$ molecule has a kinetic diameter of 3.7 Å, thus it is not accessible to the clinoptilolite framework with window dimensions of channels 3.1–7.5 Å and 3.6–4.6 Å or 2.8–4.7 Å.[28] Total pore volume for faujasite samples (0.22-0.26 cm^3/g) is twice as high as for mordenite-clinoptilolite samples (0.12-0.18 cm^3/g).

3.2. Glucose Transformation

Synthesis of 5-HMF from glucose was carried out in the presence of the original clinoptilolite rock, rock modified with calcium (CaClin), on the polycationic sample (CaLaNH$_4$Clin), and without catalyst.

Fig. 2 depicts the yields of 5-HMF and glucose conversion on clinoptilolite-based samples as well as the yield of 5-HMF without the catalyst when the process is non-selective for HMF. In the last case, glucose is spent almost entirely on the formation of humins. Their structure appears to be comparable to that proposed in the paper[26] on Ni-containing synthetic zeolites, but in the experiments without the catalyst glucose-ring fragments are predominant in the

humin structures with lower content of furan rings (Fig. 3). Such glucose transformation can proceed in DMSO medium without catalysts because it is known that in the latter cyclization, dehydrohalogenation and dehydration processes occur. DMSO possesses some basic (donor number 29.8) and acid properties (acceptor number 19.3) and works like a catalytic medium in glucose oligomerization with the inclusion of some furan fragments.

Table 1. The zeolite silica-to-alumina ratios and adsorption properties of the synthesized catalysts

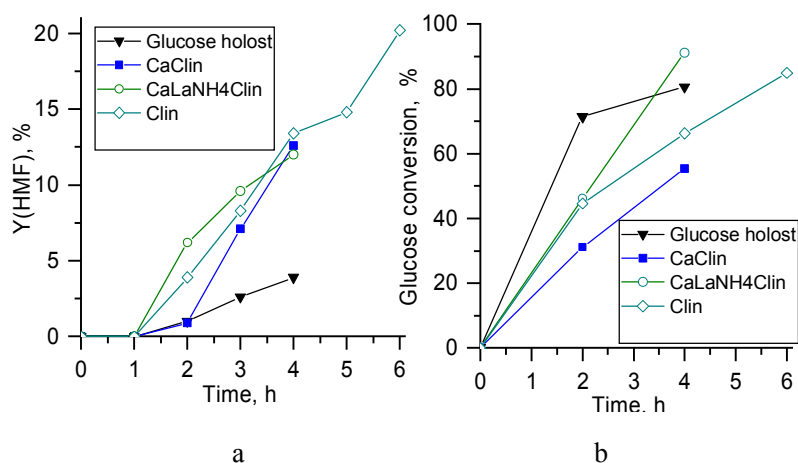| Sample	SiO_2/Al_2O_3	S^{BET}, m²/g	S^t, m²/g	S^t_{micro}, m²/g	V_{Σ}, cm³/g	V^t_{micro}, cm³/g	R^{DFT}, nm	R, nm	R^{BJH}, nm
NH_4Y	4.8	650	40	610	0.262	0.280	–	3.5	–
HUSY	4.9	645	87	558	0.220	0.248	–	3.8	–
$CaLaNH_4X$	2.4	572	7.2	565	0.257	0.240	2.64	0.9	3.1
Clin	8.4	9.0	3.9	5.1	0.002	0.018	2.60	1.9	3.8
$CaLaNH_4Clin$	10.8	9.2	2.3	6.9	0.003	0.013	2.64	1.9	2.7
HMLP-1Ni	12.3	160	30.0	130	0.125	0.062	0.92	1.6	-
HMLP-2Ni	12.3	287	30.0	257	0.182	0.116	1.17	1.3	-

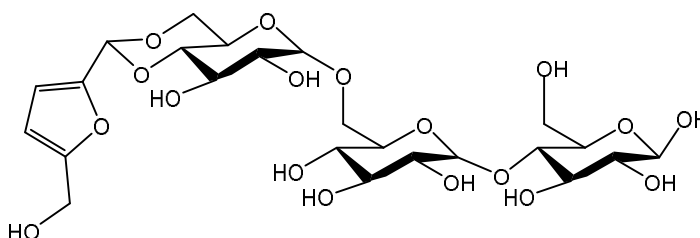**Fig. 2.** The 5-HMF yields (a) and glucose conversion (b) *vs.* reaction time

Fig. 3. Hypothetical humin structure in the case of low 5-HMF yield

The original clinoptilolite rock, calcium form, and polycation form are very similar in HMF yields. However, the calcium rock develops more slowly and polycation – faster. At the fourth hour of operation, the samples are almost equal to the yields of HMF, which is 12–14 %. However, the difference in conversion is significant: 50, 60, and 90 %. According to the conversion curves, the calcium form would also reach 20 % of HMF yields after about 6 h of operation, which is not the case with the polycation form because 90 % of glucose was converted at the 4th hour.

Fig. 4 shows typical chromatograms of glucose and fructose conversion products on synthesized catalysts before and after derivatization. There are two peaks on the

original chromatogram and on the chromatogram of derivatized glucose conversion products, which obviously correspond to the intermediates of this conversion. In the first case, they are quite wide asymmetric peaks, which after processing become narrow. At about the same time of retention (> 15 min), heavier humin precursor products are observed, probably with three or four cycles. If before derivatization they can be seen only in the form of zero-line drift, then after derivatization they are quite clearly separated.

3.3. Fructose Transformation

The results of the dehydration of fructose at 433 K for 4 h on natural-based zeolite catalysts as well as synthetic-based samples are summarized in Table 2.
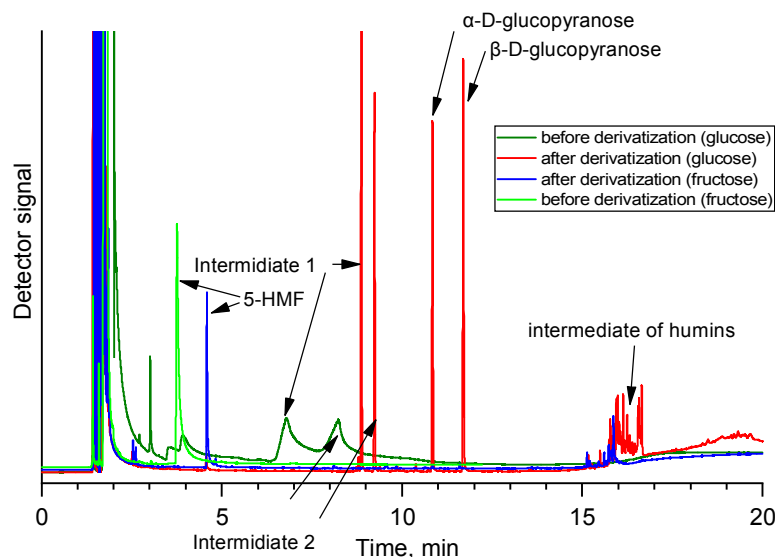

Fig. 4. Glucose/fructose conversion product chromatograms before and after derivatization

Table 2. Results of fructose dehydration on synthesized zeolite catalysts

Sample	5-HMF yield, % mol.	Fructose conversion, %	Selectivity for 5-HMF, %
Clin	13.7	99.8	13.72
CaClin	11.2	99.5	11.1
CaLaNH$_4$Clin	9.1	99.7	9.12
HMLP-1Ni	23.3	99.6	23.39
HMLP-2Ni	6.1	99.5	6.13
CaLaNH$_4$X	62.5	99.9	62.56
HUSY	43.7	99.9	43.74
HM-Sn	26.0	99.8	26.05
NH$_4$Y	26.3	99.6	26.41

As can be seen from the data in Table 2, samples of clinoptilolite base are inferior to synthetic zeolites in the conversion of fructose. Nickel-containing mordenite-clinoptilolite rock demonstrates a slightly better performance, which is comparable to the results on tin-containing powder mordenite and the ammonium form of zeolite Y. Ultrastabilized Y and the polycationic form of zeolite X show significantly higher yields of 44 and 62 %, respectively.

Thus, natural Ukrainian zeolites are clearly less efficient than synthetic zeolite catalysts in the transformation of hexoses.

4. Conclusions

Zeolite catalysts based on Ukrainian natural zeolite rocks and synthetic powder zeolites with different porous structures and different specific surface areas of 9 to 650 m^2/g were synthesized. Prepared catalysts have been tested and compared in glucose and fructose transformation in the DMSO medium. All samples show a high amount of fructose conversion, but a lower amount of glucose conversion.

Narrow-porous clinoptilolite is clearly inferior to mordenite-clinoptilolite rock in fructose dehydration. On

the latter, the 5-HMF yields are up to 23 %, which is only slightly worse than the results on synthetic mordenite and zeolite Y. The calcium-lanthanum-ammonium form of synthetic X-type zeolite produced the highest yield of 5-HMF (62 %) and demonstrates the best selectivity for 5-HMF.

It was found that at high temperatures, glucose in DMSO without a catalyst also undergoes significant conversion but primarily to humin compounds with low furan ring content. A hypothetical structure of the latter was proposed.

Acknowledgments

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ПЕРЕТВОРЕННЯ ГЕКСОЗ НА ПРИРОДНИХ І СИНТЕТИЧНИХ ЦЕОЛІТАХ

Анотація. Синтезовано низку каталізаторів на основі синтетичних порошкоподібних цеолітів, природних українських клиноптилолітових і морденіт-клиноптилолітових порід. Активність і селективність приготованих зразків було порівняно в дегідратації глюкози та фруктози до 5-гідроксиметилфурфуролу в середовищі диметилсульфоксиду.

Ключові слова: цеоліти природні, цеоліти синтетичні, глюкози дегідратація, фруктози дегідратація, 5-гідроксиметилфурфурол.