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Conversion of glucose into 5-hydroxymethylfurfural on granular zeolite catalysts

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Biomass-derived 5-hydroxymethylfurfural (5-HMF) is a potential raw material for the production of a wide range of valuable chemicals and biofuels. Industrial production of 5-HMF from hexoses on solid catalysts is promising nowadays. Acid zeolites have great potential in application as catalysts for the dehydration of sugars. The purpose of this work was to obtain granular zeolite catalysts with optimal acidity and evaluate their effectiveness depending on the nature of the binder used. A zeolite catalyst without binder and samples with 10 wt % of kaolin/alumina were prepared. Their porous characteristics and acidity were studied by means of nitrogen low temperature adsorption/desorption, ammonia thermo-programmed desorption, and pyridine adsorption with IR control. The activity and selectivity of the catalysts for 5-HMF synthesis from glucose in the dimethyl sulfoxide medium at 160 ◦C were studied. The high efficiency of granular samples in glucose transformation into 5-HMF is confirmed. They are not only not inferior to, but even superior to, powdered samples. The component sources of Brønsted and Lewis acidity of the ammonium form of zeolite, which demonstrates acceptable activity (selectivity for 5-HMF is 34 %) despite the small number of Lewis centers, are considered in detail. The highest efficiency is demonstrated by the sample with aluminum oxide, which not only does not significantly deteriorate the microporous characteristics but also improves the mesoporosity of the catalyst. The selectivity towards 5-HMF on it reaches 44%. However, the developed mesoporosity of the sample with aluminum oxide is not critical to its activity. The main influence on the effectiveness of the catalyst in the synthesis of 5-HMF is played by the presence of acid centers of medium strength.

***Keywords*: zeolite, glucose conversion, 5-hydroxymehtylfurfural, binder.**

Introduction

Biomass carbohydrates are an important inexhaustible natural source of energy. Biomass-derived 5-hydroxymethylfurfural (5-HMF) is a potential raw material for the production of a wide range of valuable chemicals and biofuels [1, 2]. Industrial production of the latter was realized in 2014 by AVA Biochem based only on fructose [3]. Glucose dehydration is not an industrial process now, but a lot of researchers around the world are paying attention to development of this two-stage reaction.

Isomerization of glucose into fructose is followed by dehydration of the latter to 5-HMF. Lewis acid centers are thought to catalyze the first stage, the isomerization of glucose to fructose via the mechanism of 1,2-hydride transfer, while Brønsted acid centers promote the second stage, the dehydration of fructose to 5-HMF [4, 5]. HMF can also degrade into levulinic and formic acids, as well as polymerize into humins. As a result, the acidity nature and acid strength of catalysts are critical factors in the conversion of glucose to 5-HMF. Inorganic acids (H_2SO_4, HCl, H_3PO_4) are the most widely studied catalysts for fructose dehydration, whereas catalysts for glucose transformation are typically a mixture of mineral acids with metal salts as Lewis acids. There is not much information in the scientific literature about the effect of acid strength on 5-HMF yield. Only a few papers remained focused on this question [6, 7]. It was demonstrated, that using of moderate HCl concentrations as well as weak maleic acid lead to better results in comparison with concentrated acid.

The utilization of heterogeneous catalysis in the transformation of hexoses is regarded as a forward-thinking and promising direction that will contribute to the development of technologically feasible processes for obtaining platform substances from sugars. Some solid acids have been tested in the conversion of glucose or fructose. Oxides, phosphates, heteropolyacids, mesoporous acids, and ion exchange resins are being investigated as "green" catalysts for the formation of 5-HMF [1, 6]. Unfortunately, because solid acids do not dissociate in water, it is difficult to compare their acidity to that of liquid mineral acids.

Their acidity is obviously described by using the sorption of basic compounds, especially thermoprogrammed desorption (TPD) technique of basics. The acidity of zeolites is thought to be comparable to that of mineral acids [7], whereas the zeolite lattice structure with pores and channels ranging in size from nanometers to micrometers, as well as the crystalline arrangement of pores in space, transforms zeolites into nanostructured materials with unique properties as molecular sieves. In paper [8] commercial ultrastable zeolite Y (HUSY) modified with mineral acids (10-30% H_3PO_4 and H_2SO_4) shown the best 5-HMF yields on the H_3PO_4-treated sample with medium-strength acidity. These findings are consistent with the conclusions of above-mentioned studies [6, 7].

The importance of using a solid acid catalyst with a certain spectrum of acidity (with a predominance of acid centers of medium strength) to improve the efficiency of zeolite catalysts for the synthesis of 5-HMF was established in our recent work [9]. Weak-strength acid sites as well as strong-strength acid sites seems to be responsible for formation of side products. However, as is well known that powdered zeolite catalysts have a number of disadvantages when used, so the purpose of this work was to obtain granular zeolite catalysts with optimal acidity and evaluate their effectiveness depending on the nature of the binder used.

Experiment

Synthesis of catalyst samples

Two bases for catalysts with kaolin (K-37) and aluminum oxide (K-38) as a binding component in the amount of 10 wt% were obtained by mechanical mixing with synthetic powdered zeolite type X (SiO_2/Al_2O_3=2.3), followed by pressing and grinding with the selection of a fraction of 1-2 mm.

Kaolin of Prosyana deposit (Dnipropetrovs'k region, Ukraine) was used as a binder. It is composed of 97 wt% kaolinite, 3 wt% mica, and traces of quartz. The following are the chemical compositions: 46% SiO_2, 38% Al_2O_3, 1.12% Fe_2O_3, 1.16% TiO_2, 0.52% CaO, 0.28% MgO, 0.6% K_2O, 0.31% Na_2O, 12.0% H_2O. Gamma alumina (DSTU 8136-85) was produced by JS Katalizator (Kamjanske, Ukraine).

The acidic properties to the samples were given by means of consistent ion exchange of native zeolite sodium on calcium, lanthanum, and ammonium cations using aqueous solutions of their nitrates (1 mol/dm^3) at 150 °C for 3 h [10, 11]. Following each exchange filtrates were analyzed for cation content. The inductively coupled plasma optical emission spectrometry (ICP OES, Plasma Quant® PQ 9000 Elite, Analytik Jena GmbH) was used for analysis of filtrates. Table 1 shows cation composition of synthesized catalyst samples. The calcium-lanthanum-ammonium form of synthetic zeolite type X (K-35) and the ammonium form of zeolite type Y (K-36, SiO_2/Al_2O_3=4.7) were used as comparison samples.

Table 1. **Composition of the catalysts**

Sample	Cations, % of total exchange capacity			
	Ca^{2+}	La^{3+}	NH_4^+	Na^+
K-35	28	60	12	<0.5
K-36	-	-	72	28
K-37	30	55	15	<0.5
K-38	28	52	20	<1

Catalytic test

The transformation of glucose solutions in dimethyl sulfoxide (DMSO) was carried out in stainless steel autoclaves (20 cm^3) with polytetrafluoroethylene inserts. Zeolite catalyst samples (0.25 g) with 5 g of 10 wt% glucose solution were heated in autoclaves using an oil bath. The experiments were carried out at 160 °C for 4 hours. Experimental details as well as conditions of gas chromatographic analysis are given in our recent paper [9].

Catalyst characterization

The porous characteristics of the kaolin-based samples were determined using nitrogen adsorption/desorption isotherms measured at low temperatures (-196 °C) with a Nova 1200e (Quantochrome) high-speed surface area and a pore size analyzer.

The Lewis and Brønsted acidity of the samples were investigated by utilizing pyridine sorption with IR-spectroscopic control in the range of 1400–1700 cm^{-1} (Shimadzu IR Affinity-1S FTIR spectrometer).

The ammonia thermoprogrammed desorption (TPD) curves were recorded in a gas chromatograph setup that contained a microreactor [13].

The conditions for catalyst characterization are shown in paper [9].

Results and Discussions

The porous properties of granular zeolite catalysts and powder comparison samples were investigated by low-temperature nitrogen adsorption/desorption.

Figure 1 shows isotherms for zeolite-containing catalysts. A number of isotherms (samples K-35, K-37 and K-36) are classical for microporous objects (type I IUPAC classification) with a small content of larger pores, while the K-38 isotherm corresponds to type IV according to the IUPAC and reflects the presence of different porosities—a combination of microporosity and mesoporosity [12]. The latter is reflected by the presence of a slight hysteresis loop caused by capillary condensation in mesopores of 2–50 nm. Table 2 summarizes the calculated data on the porous characteristics of the samples.

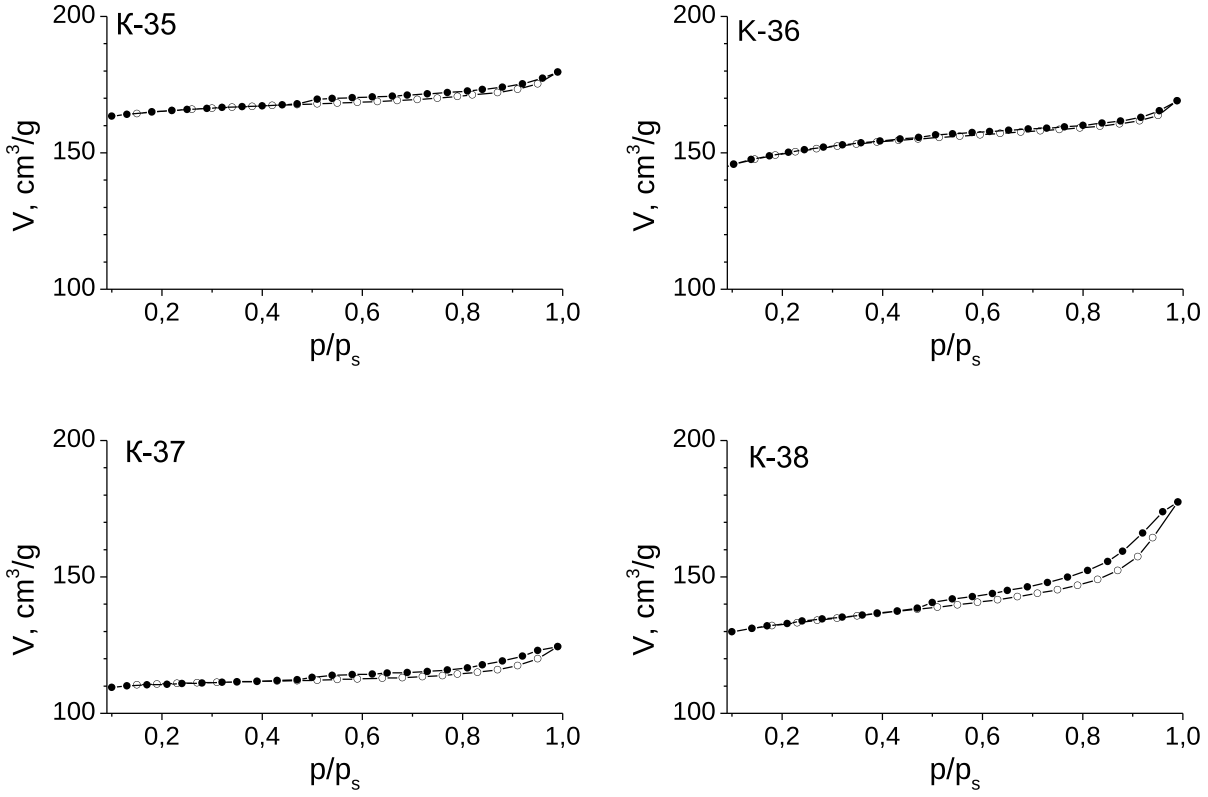

Fig. 1. Nitrogen low temperature adsorption/desorption isotherms for catalysts K-35, K-36, K-37, and K-38

Table 2. **Adsorption properties of the catalysts**

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
K-35	572	7.2	565	0.257	0.240	93.4	2.64	0.90	3.06
K-36	528	12.7	515	0.262	0.233	88.9	1.53	0.99	1.65
K-37	423	9.3	414	0.17	0.19	87	2.8	2.0	0.9
K-38	518	35	482	0.19	0.27	70	2.6	2.0	1.1

As can be seen from the calculations, catalysts based on powdered zeolite without a binder (K-35 and K-36) have the largest BET specific surfaces and micropore surfaces—more than 500 m^2/g. They are characterized by the highest proportions of micropores (89–93%). Samples obtained with the use of a binder are distinguished by higher values of the outer surface. The addition of kaolin has less effect on the outer surface, but significantly reduces the BET surface and microporosity. At the same time, no significant occurrence of mesoporosity is observed. Apparently, small kaolin particles to some extent block access to zeolite cavities. When aluminum oxide is used, on the contrary, microporosity does not suffer much, and mesoporosity becomes noticeable. Its part increases to 30% (K-38) compared to 13% for the K-37 sample. This is also confirmed by the pore size distribution curves presented in Fig. 2, 3. The dominant diameters are 2 and 3 nm in the case of all samples according to BJH and DFT theories, respectively. However, if for

K-35, K-37 and K-36 the volume of pores larger than 2-3 nm is 0.015 cm^3/g, then for K-38 it is 0.05 cm^3/g, i.e. three times more (Fig. 2). Thus, the increase in pore sizes is more significant for the sample with aluminum oxide.

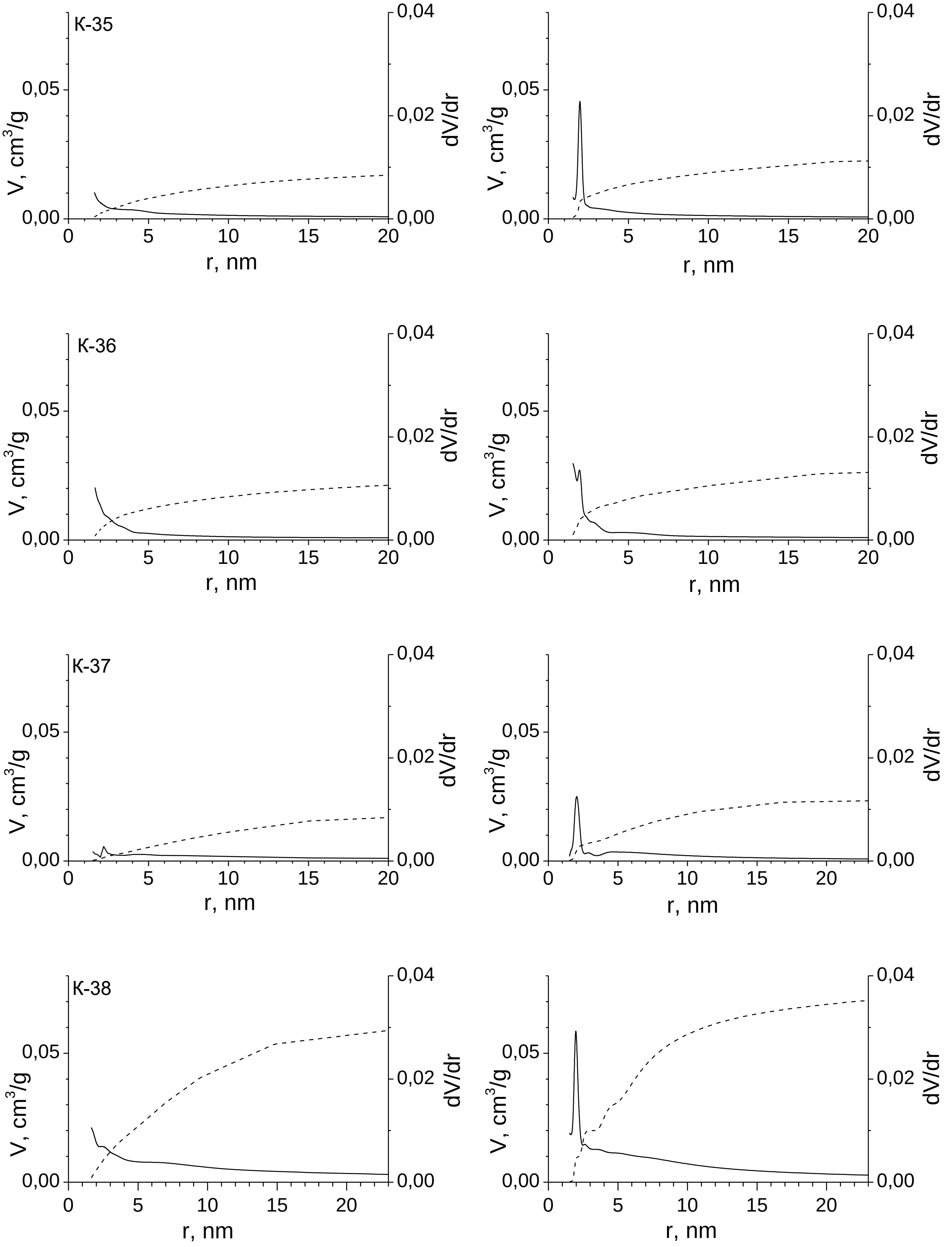

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Fig. 2. Integral and differential pore size distributions calculated from BJH theory using the adsorption (left) and desorption (right) branches of isotherms for catalyst K-35, K-36, K-37, and K-38

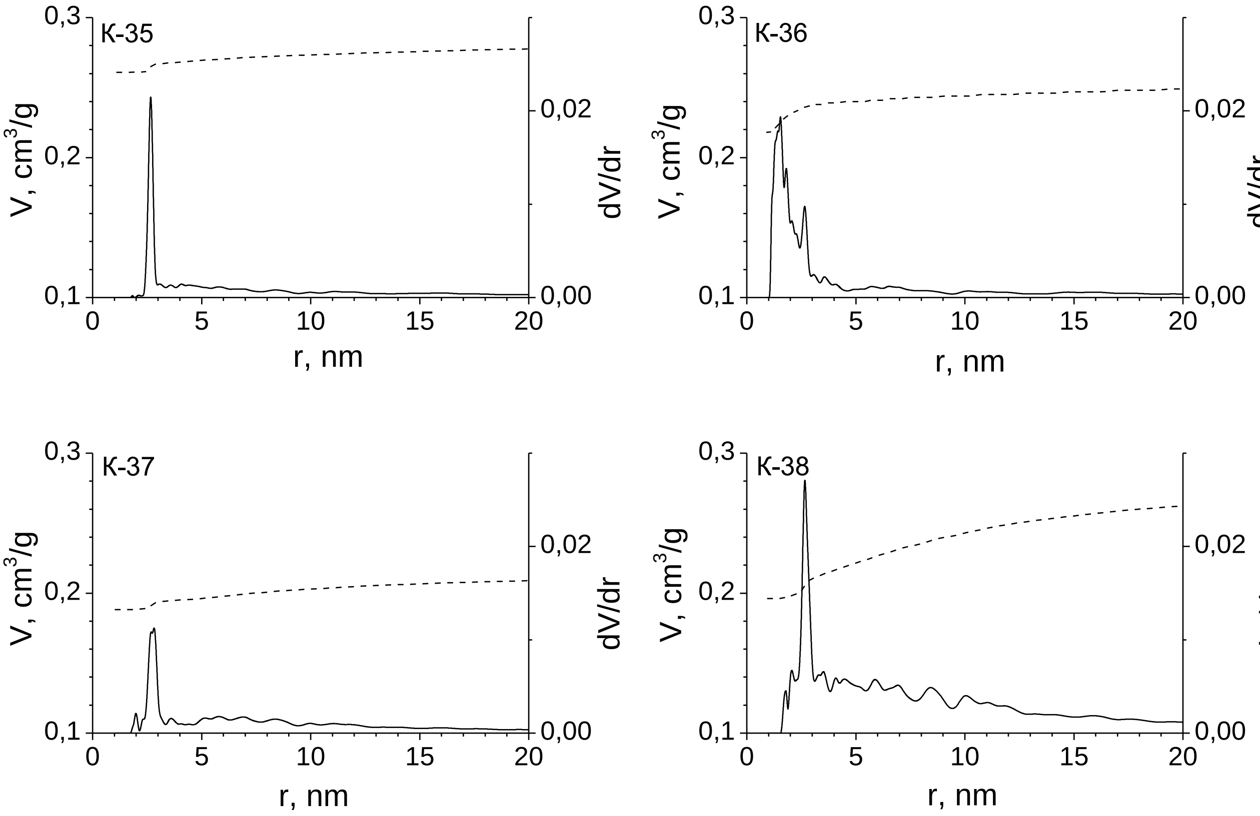

Fig. 3. DFT-calculated integral and differential pore size distributions for samples K-35, K-36, K-37, and K-38

The acidity of the samples was determined by means of thermoprogrammed desorption of ammonia (Table 2). The total number of acid centers in the samples is quite close. Naturally, for the sample with kaolin, which has deteriorated the porous characteristics, the acidity is the lowest because the access to the acid centers in the micropores is impaired. All four samples have a significant number of acid centers of medium strength, but most of them are in the ammonium form (K-36). However, as is known, the acidity according to TPD of ammonia reflects the total number of both Brønsted and Lewis centers.

If in the case of polycationic samples with lanthanum cations having free electronic orbitals, the presence of Lewis acidity is not in doubt, it is not so clear for the ammonium form of zeolite.

Table 2. Number of acid sites in the catalysts

Sample	Number of acid sites, μmol/g			
	200-350 °C	350-450 °C	450-550 °C	Total
K-35	0.45	0.50	0.56	1.51
K-36	0.29	0.81	0.55	1.65
K-37	0.40	0.52	0.50	1.42
K-38	0.35	0.61	0.78	1.74

Fig. 4 shows the spectrum of adsorbed pyridine on a sample of the ammonium form zeolite K-36. The spectrum shows a significant Brønsted acidity (intense band at 1543 cm^{-1}) with an indistinct Lewis acidity (weak band at 1454 cm^{-1}). The band reflecting the combined Brønsted and Lewis acidity (1489 cm^{-1}) is also intense. However, based on the chemical composition of the sample containing exclusively ammonium cations and native sodium, only the latter cations can act as weak Lewis sites together with extra-framework aluminum. Its existence is highly probable in view of the lower BET surface and micropore surface compared to the polycation sample K-35. Although, in general, this sample clearly has mainly Brønsted acidity.

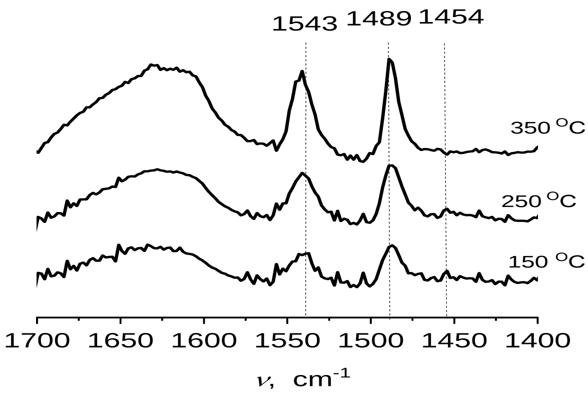

Fig. 4. IR spectra of catalyst K-36 in the region of adsorbed pyridine

Table 3 shows the results of glucose dehydration at 160 °C for 4 hours in the presence of synthesized samples. Analyzing the results, it should be noted that, firstly, glucose conversion was almost complete in all experiments. In our work [9], we showed the existence of a correlation between the activity of samples and the content of ammonium cations in them—the higher the content of ammonium cations, the higher the activity. This tendency is generally confirmed on these samples. The postulated need for acidity of medium strength according to ammonia desorption is also confirmed. It is interesting that this medium acidity is largely contributed by the acidity caused by the presence of ammonium cations (desorption maximum of 375-400 °C). However, one should not forget about the features of the pure ammonium form, which has only a weak Lewis acidity. As it was shown by the sorption of pyridine, Brønsted acidity is present in it, but it should be taken into account that during its determination, the decomposition of the ammonium cation occurred during vacuuming of the sample at 400 °C. This decomposition will not occur in the case of catalysis at 160 °C without prior dehydration of the sample. The ammonium form, which is traditionally used as an intermediate in the production of zeolite hydrogen form with classic hydroxyl bridging Brønsted centers, also has a certain intermediate Brønsted acidity [14]. It is possible to expect protonation of carbohydrates on it by analogy with well-known processes implemented in the water environment:

$$NH_4^+ + H_2O \longrightarrow NH_3 + (H_3O)^+$$

$$NH_4^+ + C_6H_{12}O_6 \longrightarrow NH_3 + (C_6H_{13}O_6)^+$$

That is why the synthesized samples, even without decomposition of the ammonium form to the hydrogen form, still show the appropriate activity, which is the lowest in the case of the pure polycationic sample K-35 with the lowest content of ammonium and medium acid centers, higher for K-37 and the highest for K-38. In the last sample, in addition to acidity, the influence of porous characteristics, in particular mesoporosity, should not be completely rejected. Diffusion complications for the K-38 sample are the least since the improvement of mesopores in it is 30%. K-37 with kaolin as a binder shows worse porous characteristics (total pore volume significantly lower) and, accordingly, the lower selectivity.

Table 3. **Results of glucose conversion on synthesized zeolite catalysts**

Catalyst	Conversion, %	Selectivity for 5-HMF, mol%
K-35	98	33.3
K-36	99.1	34.4
K-37	99	40.9
K-38	99.5	43.9

Conclusions

Thus, the conducted studies showed, firstly, that zeolite catalysts formed by mixing with a binder are not inferior in activity in the conversion of glucose to 5-HMF in the DMSO environment and may even be superior to pure powdered zeolites. Secondly, the use of gamma-aluminum oxide as a binder looks more promising for obtaining granular zeolites. Its use does not deteriorate the microporosity of the sample, while improving its mesoporosity. The optimal strength of Brønsted acidity for the studied transformation is provided by the introduction of an ammonium cation into the composition of zeolite samples, which is reflected in the formation of acid centers of medium strength, which ensure the course of the target reaction of dehydration to 5-HMF.

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Перетворення глюкози до 5-гідроксиметилфурфуролу на гранульованих цеолітних каталізаторах

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Одержаний з біомаси 5-гідроксиметилфурфурол (5-ГМФ) є потенційною сировиною для виробництва широкого спектру цінних хімічних речовин і біопалива. Перспективним напрямком є промислове виробництво 5-ГМФ із гексоз на твердих каталізаторах. Кислотні цеоліти мають великий потенціал у застосуванні як каталізаторів дегідратації цукрів. Метою даної роботи було отримання гранульованих цеолітних каталізаторів з оптимальною кислотністю та оцінка їх ефективності в залежності від природи використовуваного зв'язуючого. Було одержано цеолітний каталізатор без зв'язуючого та зразки з додаванням 10 мас. % каоліну/оксиду алюмінію. Їх пористі характеристики та кислотність вивчали за допомогою низькотемпературної адсорбції/десорбції азоту, термопрограмованої десорбції аміаку та адсорбції піридину з ІЧ-контролем. Досліджено активність та селективність каталізаторів для синтезу 5-ГМФ з глюкози в середовищі диметилсульфоксиду при 160 ◦С. Підтверджено високу ефективність гранульованих зразків у перетворенні глюкози в 5-ГМФ. Вони не тільки не поступаються, а навіть перевершують порошкоподібні зразки. Детально розглянуто джерела кислотності Бренстеда і Льюїса амонійної форми цеоліту, яка демонструє прийнятну активність у перетворенні глюкози (селективність за 5-ГМФ 34%), незважаючи на незначну кількість центрів Льюїса. Найвищу ефективність демонструє зразок із оксидом алюмінію, який не тільки не погіршує мікропористі характеристики, але й вдосконалює мезопористість каталізатора. Селективність за 5-ГМФ на ньому досягає 44 %. Однак розвинена мезопористість зразка із оксидом алюмінію все ж не є визначальною у його активності. Основний вплив на ефективність каталізатора у одержанні 5-ГМФ відіграє наявність кислотних центрів середньої сили.

Ключові слова: цеоліти, конверсія глюкози, 5-гідроксиметилфурфурол, зв'язуюче.