

*Obtaining such substances-platforms as, in particular, 5-hydroxymethylfurfural is one of the areas most actively investigated at present. They can act as raw materials for the further production of a new generation of biopolymers, fuels, pharmaceuticals, dietary supplements, and other chemicals. This paper reports the catalysts, synthesized by using methods of ion exchange and impregnation, based on the large-pore zeolites X, Y, and M, which contain the cations of rubidium, lanthanum, calcium, and ammonium. It was found that the zeolites' specific surface was 400–500 m<sup>2</sup>/g; the selected synthesis conditions did not cause noticeable destruction of the microporous structure. In the presence of the synthesized catalysts, glucose dehydration in the aqueous medium and in dimethyl sulfoxide was carried out at 150–160 °C. The higher efficiency of polycationic forms of zeolites in a non-aqueous medium has been established. In the latter case, a 40 % yield of 5-hydroxymethylfurfural was achieved at an almost complete glucose conversion. Deactivated catalyst samples were investigated using the methods of infrared spectroscopy and differential thermal analysis/thermogravimetry. It was found that the catalyst accumulates fewer oligomerization process by-products when the reaction is implemented in dimethyl sulfoxide. The loss of mass by the samples deactivated in an aqueous medium is 30–33 %, while in dimethyl sulfoxide – up to 24 %. The obtained results are important for practical application as the only volatile conversion product is 5-hydroxymethylfurfural with a yield of up to 40 %. That is acceptable for the possible implementation of a one-stage process of obtaining 5-hydroxymethylfurfural in the future*

**Keywords:** large-pore zeolites, polycationic forms, glucose dehydration, 5-hydroxymethylfurfural, yield, glucose conversion

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## OBTAINING GLUCOSE-BASED 5-HYDROXYMETHYLFURFURAL ON LARGE-PORE ZEOLITES

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### 1. Introduction

Widely available and almost inexhaustible, in contrast to fossil resources, biomass carbohydrates are a natural source of energy. However, the bulk of carbohydrates in plant raw materials are in the form of cellulose, which, despite being the most common non-food component of biomass, is little used in the chemical industry due to poor solubility and low reactivity. This natural biopolymer can be hydrolyzed to simple carbohydrates, and the latter can be dehydrated to furan derivatives, in particular, 5-hydroxymethylfurfural (5-HMF) [1–3]. The latter, in turn, can serve as a raw

material for further synthesis with the production of a new generation of biopolymer materials, fuels, pharmaceuticals, pesticides, food additives, and a series of other important chemicals [3–5].

It is known that up to 40 % of all solid catalysts in the chemical industry and 80 % of petrochemical industry catalysts are obtained on the basis of zeolites with increased thermal and chemical stability [6, 7]. The ordering of the crystalline structure of zeolites in combination with the extremely narrow distribution of micropores in size is decisive in the dimensional and chemical-selective action of zeolites. They have many opportunities to change the nature of active

centers, and, therefore, large-pore zeolites can be promising catalysts for the conversion of carbohydrates [7, 8].

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## 2. Literature review and problem statement

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It is known that the process of obtaining 5-HMF from glucose takes place in two stages. First, glucose is isomerized to fructose, after which the latter undergoes dehydration. It is possible to implement these processes step by step on different catalysts, while their combination is a more difficult task. It is believed [2] that Lewis acid centers in the first stage catalyze the isomerization of glucose to fructose according to the mechanism of 1,2-hydride transfer, while Brønsted acid centers contribute, in turn, to the dehydration of fructose to HMF. If the stage of isomerization is too slow, then HMF decomposes to levulinic and formic acids or polymerizes to humins.

In the isomerization of glucose in aqueous solutions, mineral acids, the soluble salts of zinc, niobium, lanthanum, as well as solid-phase catalysts of the acid type, for example, ion-exchange resins, oxides, aluminosilicates, insoluble salts [9–11], are used as catalysts. At present, solid catalysts are significantly inferior to enzymes in terms of selectivity in the isomerization of glucose to fructose, so finding new effective solid-phase catalysts remains a relevant task. As catalysts for the isomerization of glucose to fructose, a series of samples have been studied recently [12]. In particular, paper [9] investigated the conversion of glucose on the commercially available H-USY zeolite in methanol and water, implementing the process in two stages. In the first stage, glucose reacts with methanol to form methyl fructoside, while in the second stage, after adding water, fructoside hydrolyzes to fructose. In this way, it is possible to convert glucose at 120 °C, but the two stages make this method quite inconvenient.

In work [12], it was possible to implement the one-stage isomerization of 10–40 % aqueous glucose solutions on mixed MgO–ZrO<sub>2</sub> oxide under the stationary and flow-through modes at temperatures 80–120 °C and under atmospheric pressure. It was established that MgO–ZrO<sub>2</sub> allows for a fructose yield of up to 35 %, with a maximum selectivity for fructose of 96 % achieved at 80 °C, and the maximum glucose conversion, 49 %, at 120 °C. The possibility of processing concentrated (40 %) glucose solutions under a flow-through mode at 90 °C is also shown. However, the issues related to the direct conversion of glucose into HMF remained unresolved.

In [13], chromium oxide was applied onto the zeolite HZSM-5. As a result, the catalyst had both Brønsted and Lewis acidity and ensured the conversion of 2 % aqueous glucose solution to levulinic acid, the yield of which was 64 % at 180 °C within 3 hours. However, the yield of 5-HMF, in this case, was a trace.

Since the direct conversion of glucose to 5-HMF in an aqueous medium is not an easy task, organic solvents are often used [2, 4]. The role of the latter is not only to ensure the access of reagents to active catalyst centers but also to suppress side processes and prevent the catalyst deactivation [14, 15]. Those include methanol, ethanol, dimethyl sulfoxide (DMSO), *N,N*-dimethylacetamide (DMA), gamma-valerolactone, acetone, etc. [10, 11, 16]. The disadvantage of the studies so far is the limitation of the concentrations of glucose used in the range of 0.5–5 % by weight.

Zeolites, being objects with a strictly defined crystal structure and a developed porous system, have not yet been widely used in the conversion of carbohydrates. The kinetic diameter of molecules of simple carbohydrates, in particular, glucose is 0.8 nm, and 5-HMF – 0.62 nm, furfural – 0.55 nm [17], which is quite acceptable for the use of large-pore zeolites such as faujasite and mordenite [7, 8]. It should be noted that the polycationic forms of zeolites, modified by rare earth elements containing both the Brønsted and Lewis acid centers, are known to be the most effective solid catalysts for the alkylation of isobutane with butene [18, 19].

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## 3. The aim and objectives of the study

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The aim of this work was to obtain 5-hydroxymethylfurfural by the catalytic dehydration of glucose in the medium of water and dimethyl sulfoxide in the presence of large-pore zeolites (*X*, *Y*, and *M*), synthesized by methods of ion exchange and impregnation. That could make it possible to devise technology for the one-stage process of hydroxymethylfurfural synthesis in the presence of solid-phase catalysts.

To accomplish the aim, the following tasks have been set:

- to determine the features of the porous characteristics of large-pore zeolite catalysts;
- to convert glucose on the obtained catalysts in the medium of DMSO and water, to determine the yield of 5-HMF and the glucose conversion;
- to investigate the deactivation of zeolite catalysts.

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## 4. Materials, sample synthesis procedure, and research methods

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### 4.1. The synthesis of zeolite catalysts

Samples of catalysts were obtained from sodium forms of industrial powdered zeolites of type *X*, *Y*, and *M*, manufactured by JS “Sorbent” (Nizhny Novgorod, Russia, TU 38.102168-85), the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio was 2.3; 4.7 and 9, respectively.

To obtain the hydrogen form, the zeolite *M* was modified by ion exchange. A sample was poured with ammonium nitrate solution (3 mol/l) and aged in a water bath for 80 °C for 3 hours, it was then filtered and washed with distilled water. The exchange procedure was repeated four times. The resulting NH<sub>4</sub> form was calcined in a muffle furnace in the air atmosphere at 550 °C for 2 hours after each exchange [20]. Thus, the hydrogen form HM was obtained, onto which the lanthanum was applied. To this end, the sample was pre-dried (100 °C, 3 h) and impregnated with a solution of lanthanum nitrate hexahydrate at the rate of 5 % by weight of the lanthanum content. The sample was vacuumed at 20 °C for 6 hours, after which it was roasted at 780 °C for 3 hours. As a result, a sample of HM-La was made.

Two polycationic samples were synthesized based on the faujasite-type zeolite. In their synthesis, the following sequence of exchanges was used: first calcium was introduced (four exchanges), followed by lanthanum (two exchanges), and, in the end, ammonium (one exchange) [21].

To exchange Na<sup>+</sup>, in the NaX/NaY zeolites on Ca<sup>2+</sup>, we used a solution of Ca(NO<sub>3</sub>)<sub>2</sub> (1.0–1.5 mol/l), with a solid-to-liquid phase ratio (S:L) of 1:2; reaction time, 1–2 hours, temperature, 85–90 °C. Then we introduced lanthanum using lanthanum nitrate hexahydrate (1 mol/l). Exchanges

were carried out at the same temperatures and ratios S:L; their duration was 1.5–2 hours. The last was the exchange for ammonium for 1–1.5 hours using ammonium nitrate solution (1 or 3 mol/l). As a result, the samples KA-35 and KA-36 were obtained. Their chemical composition is represented by the following formulae:  $17\text{NH}_460\text{La}23\text{CaNaX}$  and  $20\text{NH}_452\text{La}28\text{CaNaY}$ .

A lanthanum form of the zeolite LaNaY was also synthesized. To this end, the starting NaY was dehydrated for 1 hour at 400 °C, after which three consecutive exchanges for lanthanum were carried out at 80–85 °C for 3 hours using a solution of nitrate with a concentration of 1 mol/l. After each exchange, intermediate ultra-stabilization was carried out in a muffle furnace at 550 °C in the presence of air for 2 hours.

Based on the X-type zeolite, a sample of RbX was also obtained. To this end, NaX was subjected to a two-time exchange for rubidium cations with 1 mol/l aqueous solution of rubidium nitrate under hydrothermal conditions (150 °C, 2 h, S:L=1:5) in a rotating stainless-steel autoclave.

#### 4. 2. Procedure for the catalytic conversion of glucose

The conversion of glucose solutions (10–20 % by weight) was carried out in soldered test tubes or in a reflux apparatus with water condenser.

A catalyst (0.325–1.125 g) was added to an aqueous glucose solution or glucose solution in DMSO (10–20 % by weight, 5–15 ml) and placed in a glass ampoule or flask. The ampoules were sealed. The reaction was carried out at 150–160 °C for 1–4 hours. The reaction temperature was chosen based on the analysis of the literary data. The ampoules were placed in a special holder in a furnace with electric heating. At the end of the reaction, the ampoules were cooled to room temperature, depressurized, the liquid layer was filtered under a vacuum on the Buchner funnel through a paper filter. The obtained products were collected and analyzed. For the reaction in a reflux set-up, heating and mixing were provided with a magnetic stirrer.

#### 4. 3. Methods for the physicochemical study of catalysts

The isotherms of low-temperature adsorption/desorption ( $t=-196$  °C) of nitrogen on catalysts were acquired from the Quantachrome Autosorb NOVA 1200e® (USA) automatic sorbometer after the dehydration of samples in a muffle furnace (380 °C, 2 h), followed by vacuum *in situ* (250 °C, 1 hour). Parameters of the porous structure were calculated using the software NOVAVin™ (USA).

Based on the obtained isotherms, the multipoint method by Brunauer-Emmett-Teller (BET) was used to calculate the specific surface area  $S^{\text{BET}}$ ;  $t$ -method – the area of the outer surface  $S^t$ , and the volume of micropores  $V_{\text{micro}}^t$ ; the surface of micropores  $S_{\text{micro}}$  was calculated as the difference  $S^{\text{BET}}-S^t$ . The total volume of pores  $V_{\Sigma}$  was determined by the volume of adsorbed nitrogen at  $p/p_s > 0.991$ . The average pore size  $R$  was calculated using the  $R=2V_{\Sigma}/S^{\text{BET}}$  formula, the  $R^{\text{DFT}}$  pore size is based on the density functional theory, and the  $R^{\text{BJH}}$  pore size is based on the Barrett-Joiner-Halenda theory.

The Fourier transform IR spectroscopy technique by using the Shimadzu IRAffinity-1Sn spectrometer (Japan), was applied to investigate deactivated catalyst samples.

Thermogravimetric studies were carried out at the Linseis STA 1400 (Germany) derivatograph. Deactivated samples weighing 25 mg were previously crushed to a powdery state. Heating was carried out in the air presence from 20 °C to 1,000 °C at a heating rate of 10 °C/min.

Before our physicochemical research, the catalysts deactivated in the aqueous medium were dried at room temperature for 48 hours; those deactivated in DMSO were vacuumed for 6 hours at 30 °C.

#### 4. 4. Establishing the yield of HMF and the degree of glucose conversion

Reaction products were analyzed using the gas chromatography method (Agilent GC 7890A chromatograph, made in the USA), flame-ionization detector, split/splitless inlet, the capillary column J&W HP-5 (USA), (5%-phenyl)-methylsiloxane, 30 m, inner diameter 0.32 mm, film thickness 0.25 μm.

The concentration of 5-HMF was calculated using the method of calibration curves. To determine the concentration of glucose in liquid products of catalytic transformation, the gas-chromatographic analysis was carried out with preliminary derivatization of hydroxyl groups by trimethyl silanization with *N*-methyl-*N*-(trimethylsilyl)-trifluoroacetamide.

#### 5. Results of studying the porous characteristics of catalysts

The texture properties of the starting and synthesized samples determined by the low-temperature nitrogen adsorption/desorption are given in Table 1.

Table 1

Samples' adsorption properties

Sample	$S^{\text{BET}}$ , m <sup>2</sup> /g	$S^t$ , m <sup>2</sup> /g	$S_{\text{micro}}^t$ , m <sup>2</sup> /g	$V_{\Sigma}$ , cm <sup>3</sup> /g	$V_{\text{micro}}^t$ , cm <sup>3</sup> /g	$V_{\text{micro}}/V_{\Sigma}$ , %	$R^{\text{DFT}}$ , nm	$R$ , nm	$R^{\text{BJH}}$ , nm
NaX	615	7.9	608	0.277	0.267	96.4	1.01	0.90	1.51
KA-35	572	7.2	565	0.257	0.240	93.4	2.64	0.90	3.06
RbX	446	11	435	0.211	0.189	89.6	2.64	0.95	1.80
NaY	576	4.1	572	0.256	0.241	94.1	1.09	0.89	1.66
KA-36	528	12.7	515	0.262	0.233	88.9	1.53	0.99	1.65
LaNaY	422	16.4	405	0.217	0.171	78.8	2.64	1.03	2.20
HM-La	14	3.9	10.1	0.021	0.005	23.8	1.29	3.00	1.51

Naturally, in the process of modifying zeolites by hydrothermal ion exchange, there is a decrease in the specific surface of samples according to BET, as well as the surface of micropores, there is also a drop in the volume of pores. Judging by a change in the surface of micropores for samples obtained without a significant thermal load (hydrothermal synthesis up to 100 °C), the destruction of the zeolite phase for them is up to 10 %. The application of high temperatures contributes to the destruction of up to 30 % of the zeolite phase. Samples do not have significant mesoporosity. The HM-La sample obtained by the impregnation method is characterized by a very low specific surface, which may be associated with the formation of lanthanum oxide agglomerates on the surface.

## 6. Results of studying glucose dehydration in the presence of the synthesized zeolite catalysts

Table 2 gives the results of catalytic studies involving zeolite samples in converting 10 % by weight of glucose solution in water and DMSO at 160 °C for 4 hours. The HM-La sample demonstrated insignificant HMF yields – only 2.1 % by weight at 94 % glucose conversion. This result was even worse than a glucose conversion without a catalyst, which resulted in a 4.7 % HMF yield, however, at a 48 % conversion value.

Table 2

Glucose conversion in DMSO (160 °C; glucose solution mass, 5 g; 4 h)

Catalyst	Conditions		HMF yield, % mol	Glucose conversion, %
	Catalyst mass, g	Glucose solution concentration, % by weight		
Water				
Glucose/H <sub>2</sub> O	–	10	4.7	48.0
HM-La	0.75	10	2.1	94.0
KA36-	0.75	10	12.0	95.8
DMSO				
Glucose/DMSO	–	10	13.7	96.5
RbX	0.75	10	6.7	99.8
LaNaY	0.75	10	5.1	96.9
KA-35	0.75	10	34.6	94.3
KA-35	1.5	10	36.7	95.0

In the case of the use of glucose solution in DMSO on the basic catalyst RbX, a rather insignificant yield of HMF was also obtained – 6.7 %. And this is despite the fact that the scientific literature [2] mentions the possibility of proceeding the stage of glucose isomerization to fructose on the basic sites. However, at the same time, the conversion of glucose is almost complete, that is, humins are formed since no light products and fructose were recorded. Insignificant yields also characterize the conversion into LaNaY, while on the polycationic sample KA-35 (based on the X zeolite) the yield of 5-HMF is about 35 %. It is likely that HM-La, RbX, and LaNaY are selective in the side process of humin formation running in parallel; 5-HMF does not act as an intermediate product in this case.

Using the polycationic sample KA-36, a change in the yield of 5-HMF was studied depending on the time of the reaction during the conversion of 10 % by weight of aqueous glucose solution; KA-35 – when converting 20 % glucose solution in DMSO (Fig. 1).

Interestingly, the products of the reaction in the aqueous medium demonstrate, on the 4<sup>th</sup> hour, in addition to 5-HMF, levulinic acid, the yield of which is about 3 %. At the same time, during the reaction in the DMSO, regardless of the catalyst and the resulting yield of HMF, levulinic acid was not detected in the conversion products. The maximum yield of 5-HMF in DMSO reached 42 %, which is significantly larger than that in water, despite the higher concentration of glucose solution. In both cases, a maximum is registered in about 2–3 hours.

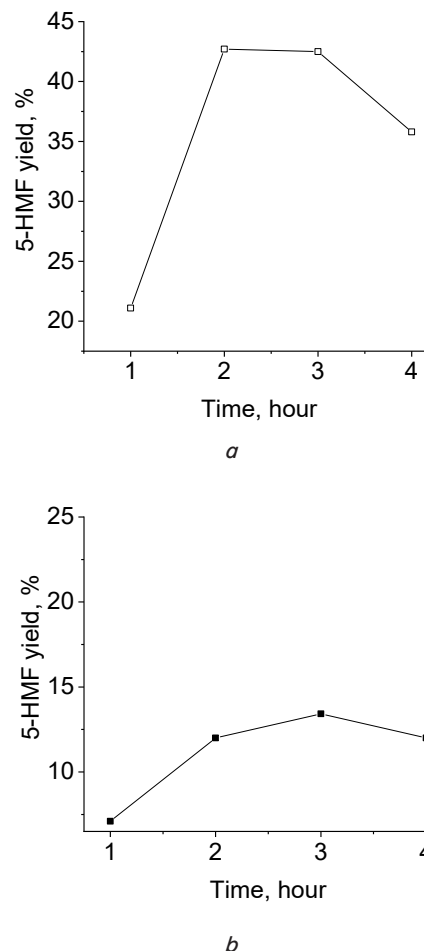


Fig. 1. Time-dependent 5-HMF yield: *a* – on the catalyst KA-35; *b* – on the catalyst KA-36

## 7. Results of studying deactivated catalysts

Fig. 2 shows the results of thermogravimetric studies of the deactivated KA-36 catalyst samples.

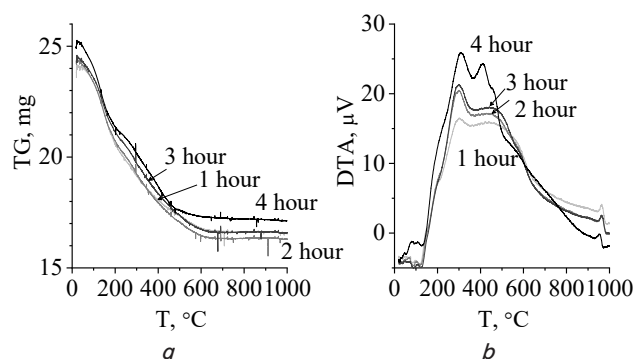


Fig. 2. Studying the deactivated KA-36 samples (1–4 hours): *a* – differential thermal analysis curves; *b* – samples thermogravimetry

In general, the pattern of samples thermogravimetry is similar to the curves acquired from the deactivated faujasite nickel-containing sample 5NiHY [22]. Half of the mass loss occurs as a result of dehydration of samples up to 200 °C,



which is displayed by the endoeffect on the differential-thermal analysis curve (DTA). The second half is lost when organic deposits are oxidized (exoeffects at 300 and 450 °C on the DTA curve). Interestingly, the total weight loss is 30–33 % and does not tend to increase with an increase in reaction time. At about 950 °C, there is a phase transition without changing the mass of the sample.

Thermogravimetric studies of samples deactivated in the DMSO medium have some peculiarities (Fig. 3, 4). Thus, catalysts are characterized by less weight loss (22–24 %) compared to samples deactivated in the aqueous medium. Of these, about 8 % accounts for the desorption products, which, in this case, consist of water as a reaction product and DMSO (endothermic effects at 120 °C and 250 °C). Up to 15 % account for the oxidation products, occurring in the temperature range of 250–350 °C (exoeffect). Most likely, in this case, the oxidation of residual DMSO, and not humins, is observed. Their insignificant combustion could be indicated by an exoeffect at 420–430 °C. The formation of humins as by-products occurs quite intensively, since the 5-HMF yield is 40 %, and the conversion of glucose is almost complete, but they accumulate mainly in the liquid phase. Thus, when diluting the reaction products with water, oligomer structures are deposited while 5-HMF remains dissolved.

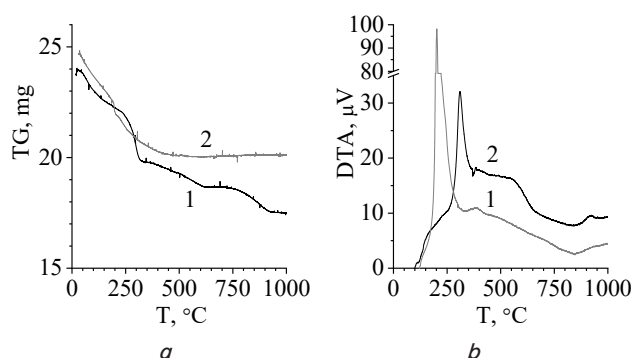


Fig. 3. Studying the samples of RbX (1) and KA-35 (2), deactivated in the conversion of glucose in the DMSO medium: *a* – differential thermal analysis curves; *b* – samples thermogravimetry

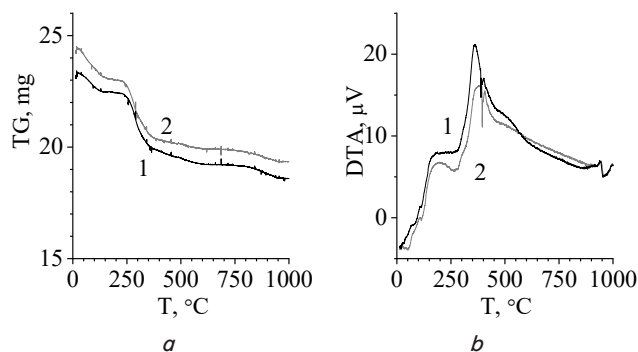


Fig. 4. Studying the deactivated zeolite LaNaY (1) and fresh LaNaY treated with DMSO (2): *a* – differential thermal analysis curves; *b* – samples thermogravimetry

In the thermogravimetric study of the deactivated LaNaY catalyst and the fresh LaNaY sample treated with DMSO (Fig. 4), a very similar pattern was observed. Initially, there is DMSO desorption (up to 250 °C, endoeffect),

followed by the burning of DMSO (250–380 °C, exoeffect) and dehydroxylation of the zeolitic surface (400–600 °C and >800 °C). The drop in the mass of samples in the temperature range of 400–600 °C is likely caused by the dehydroxylation of the zeolitic surface. On LaNaY and KA-35 samples, slight dehydroxylation is also emerged after 800 °C before the phase transition at 950 °C, although it is not registered on the RbX sample.

Fig. 5 shows the IR spectra of deactivated catalyst samples. In the region of 400–1,200  $\text{cm}^{-1}$  there are intense bands that occur as a result of fluctuations in the bonds of Si-O-Si(Al) of the zeolite lattice [25, 26]. In the spectra absorption bands at 2,900 and 2,990  $\text{cm}^{-1}$ , reflecting the valence fluctuations of C-H-bonds [27], are present only at the noise level. The bands at 1,400 and 1,600  $\text{cm}^{-1}$  may reflect the deformation oscillations of the C-H-bonds of the aldehyde group and the valence fluctuations of C=O. However, most likely, these two bands, in addition to the wide band in the region of 3,300  $\text{cm}^{-1}$ , reflect the presence of water in the sample: a band at 1,400  $\text{cm}^{-1}$  – valence fluctuations of  $\nu(\text{OH-group})$ , and 1,600  $\text{cm}^{-1}$  –  $\nu(\text{H}_2\text{O})$  [28]. This assumption is confirmed by the spectrum of a fresh sample of KA-35, in which these two bands are also represented.

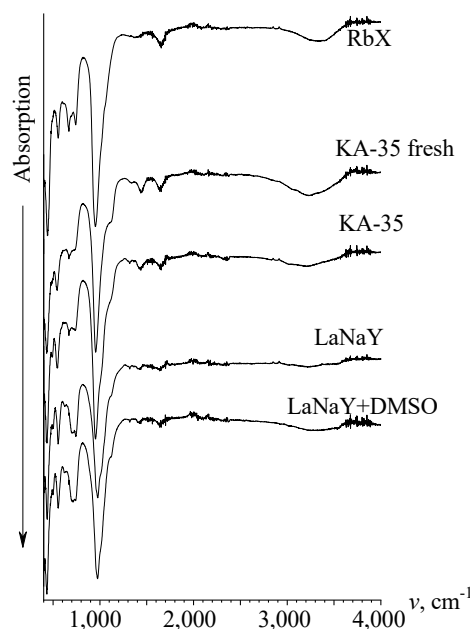


Fig. 5. The IR spectra of catalysts deactivated in the environment of DMSO (RbX, KA-35, LaNaY), as well as fresh catalyst KA-35 and LaNaY, treated with DMSO

In general, it seems that there are so few humins on the samples that the IR spectra change little compared to the fresh sample. The bands characteristic of DMSO largely overlap with the oscillations of the zeolite lattice in the region of 600–1,000  $\text{cm}^{-1}$ .

## 8. Discussion of results of proceeding of oligomerization side processes

Thus, analyzing the above results, of special attention is the almost quantitative glucose conversions, even with minor yields of 5-HMF (Table 2). To explain this fact, let us turn to the research reported in works [29, 30]. Their

authors studied the peculiarities in the formation of humins from glucose [29], fructose and HMF [30] in the presence of hydrochloric and sulfuric acids as catalysts. Based on the data from IR spectroscopic studies, it was concluded that humins were formed both as a result of the opening of the cycle and the nucleophilic attack of the carbonyl group of 5-HMF by  $\alpha$  and  $\beta$  positions of the furan ring. Moreover, when adding DMSO as a co-solvent, the latter path is practically excluded. Humin molecules occur in the form of small particles (about 100 nm) unlike large particles up to 3–4  $\mu\text{m}$  observed in water. However, the cited work does not provide quantitative data on the formed humins.

In addition, analyzing the spectra, the authors draw conclusions about the structure of humins obtained from different raw materials. Thus, when using 5-HMF, in the spectra there is a band at  $1,680\text{ cm}^{-1}$ , which reflects the oscillations of the C=O bonds of the aldehyde group. Therefore, it is in this case that HMF fragments are most represented in humins, and, in the formation of humins directly from glucose/fructose, there may be completely different compounds, in particular, 2,5-dioxo-6-hydroxyhexanal [30]. This pathway of humin formation directly from glucose can explain the obtained quantitative glucose conversions on the RbX and LaNaY samples, which, at the same time, showed a slight yield of 5-HMF (Table 2).

It should also be noted that the thermogravimetry data indicate that in the case of a reaction in the aqueous environment, there is a tendency to accumulate humins on the catalyst in the form of coke/coke precursors. In the case of using DMSO as a solvent, humins remain mainly in the liquid phase and render dark brown coloration to catalysis products. In water, catalysis products have a light brown or caramel color, and, over time (after 1–2 days or more), brown sediment is observed.

The accumulation of humins mainly in the liquid phase is probably one of the factors contributing to the more effective conversion of glucose to 5-HMF in the case of using DMSO as a solvent. When implementing the process in an aqueous environment, humins, accumulating largely in a porous structure or on the outer surface of a zeolite catalyst, can reduce its activity.

Our study has certain limitations, in particular, one organic solvent was used. As for the caveats regarding the

application of the reported results, the process of catalytic dehydration of glucose solution was investigated in the range of concentrations of 10–20 % by weight and only at  $160\text{ }^{\circ}\text{C}$ . It is advisable to optimize the parameters of the process, as well as to further search for solvents, which would increase the selectivity of the target process of 5-HMF formation.

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## 9. Conclusions

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1. The porous characteristics of the synthesized catalysts by the method of low-temperature adsorption/desorption of nitrogen were investigated. We established a reduction in the surface of samples according to BET, as well as in the surface of zeolite micropores, by 10–30 %. This is due to their partial destruction in the process of ion exchange. The introduction of lanthanum by impregnation adversely affects the specific surface and volume of pores, which may be associated with the formation of lanthanum oxide agglomerates on the surface.

2. Polycationic forms of faujasite zeolite, catalyzing glucose dehydration both in the aqueous solution and in the DMSO, proved the most effective in the one-stage conversion of glucose to 5-HMF among the samples studied. Higher efficiency of the process in the DMSO medium has been established. The yields of 5-HMF in water amounted to 14 %, while in DMSO – up to 40 %. Glucose conversion in all cases was greater than 90 %.

3. The samples of zeolite catalysts deactivated in the aqueous environment demonstrate a greater accumulation of by-products – humins. In DMSO, they are formed, firstly, less, since the selectivity for HMF is higher, and, secondly, they are concentrated mainly in the liquid phase. The formation of humins on the zeolite catalysts, non-selective for 5-HMF, occurs directly from glucose.

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