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## Influence of the Nature of Acid Solid Catalysts on their Activity in the Hydrolysis of Sucrose and Cellulose

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*Activity of solid acid catalysts (based on SBA-15 and carbon Sibunit) in hydrolysis of sucrose at 80 °C and of microcrystalline cellulose (MCC) at 150 °C was compared. The maximal activity in sucrose hydrolysis (rate constant  $9,2 \cdot 10^{-4} \text{ s}^{-1}$ ) was observed for SBA-15 containing anchored  $\text{SO}_3\text{H}$ -groups. All studied catalysts increase the conversion of MCC in the following order (for hydrolysis time 12 h): without catalyst (4,2 % wt.) < Sibunit (16-19 % wt.) < acid Nafion® (21,5 % wt.) < SBA-15 (80,1 % wt.). Products of MCC hydrolysis contain along with glucose the oligosaccharides and impurities of mannose and xylose.*

*Keywords: solid acid catalysts, hydrolysis, sucrose, cellulose, glucose, fructose.*

### Introduction

The attention to the use of renewable lignocellulosic biomass, primarily cellulose, as its main component to obtain valuable chemicals was increased in recent years. Glucose is among the most popular products and may be obtain by acid hydrolysis of cellulose [1, 2]. Traditional catalysts for the acidic cellulose hydrolysis are mineral acids mainly  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$ . The main limitations of the homogeneous catalytic processes with inorganic acids are their toxicity and corrosive activity, and also

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the difficulty of separating the catalyst and reaction products [3]. To overcome these limitations it is necessary to use solid acid catalysts [4-16].

The possibilities of application in cellulose hydrolysis different acid catalysts such as zeolites with Bronsted acid sites [4], sulfated activated carbons (AC-SO<sub>3</sub>H) [5], mesoporous materials modified with sulfonic acids [6, 7] were studied. It was established that the sulfated solid catalysts give higher yields of glucose than zeolites in H-form [8].

Mesoporous silicate materials are very attractive for the synthesis of new catalysts due to high surface area (up to 1000 m<sup>2</sup>/g) and large pore volume [9, 10]. In addition, mesoporous silicate materials SBA family have thicker walls and a highly ordered hexagonal 2D porous structure [11, 12], as compared with other typical mesoporous silicate materials such as the family of M41S [13]. SBA materials also sufficiently are stable for introduction of the other components [14]. The combination of these beneficial textural properties of ordered silicate mesoporous materials with high acidity embedded modifiers improves the properties of the synthesized catalysts in hydrolysis of the plant biomass under hydrothermal conditions.

Porous carbon materials may be produced from any carbonaceous raw material by high temperature pyrolysis with physical or chemical activation. Depending on the preparation conditions the carbon materials differ in specific surface area from 10-300 m<sup>2</sup>/g (for graphite) to 100-2500 m<sup>2</sup>/g (for the activated carbon and carbon blacks), and pore size distribution from micropores (<2 nm) and mesopores (>2-50 nm) up to the macropores (>50 nm)). Catalysts based on carbon carrier are more stable as compared with oxides, and they have a lower cost, as compared with catalysts containing noble metals. Analysis of the literature indicates a growing number of studies aimed at developing the efficient carbon catalytic systems for cellulose hydrolysis [5, 15, 16].

In the present study the activity of solid acid catalysts based on SBA-15 and a mesoporous graphite-like carbon material Sibunit-4 in hydrolysis of sucrose and microcrystalline cellulose (MCC) was compared.

## Experimental

### *Reagents and Materials*

The sucrose “pure for analysis” grade (GOST 5833-75) and microcrystalline cellulose Vivapur® Type 101 were used in experiments. As standards for the analysis of monosaccharides solutions the crystalline fructose (TU 9111-02-51760333-2002), crystalline glucose (GOST 975-88), D-xylose 142080.1208 (Panreac), D-mannose 373195,1208 (Panreac), D – sorbitol (Panreac) were applied. All solutions were prepared using distilled water (GOST 6709-72).

As comparison catalyst in the hydrolysis of sucrose and cellulose an ion-exchange resin membrane Nafion® N551PW (Aldrich) reinforced polytetrafluoroethylene (PTFE) fiber with thickness of 0.005 inches was used.

### *Preparation of the catalysts*

Modification of mesoporous graphite-like carbon material was carried out by oxidation of Sibunit-4 with 20 % vol. O<sub>2</sub> in N<sub>2</sub> in the presence of water vapor at 450 °C for 4 h; with 0.54 M sodium hypochlorite solution for 20 min at 25 °C; and with 6.5 M nitric acid solution at 110 °C [17]. Samples

prepared by Sibunit oxidation with sodium hypochlorite and nitric acid solution were washed with water repeatedly until pH 5 and dried for 24 h at 160 °C.

Modification of SBA-15 (mesoporous SiO<sub>2</sub>) was carried out by introduction of SH-groups into its structure by of method co-condensation with the 3-mercaptopropyltrimethoxysilan [18]. The used surface active substances were removed by boiling of the samples in ethanol for 24 h at a solid-liquid ratio 1:100. The resulting product was filtered and air dried. The oxidation of SH-groups in modified SBA-15 to SO<sub>3</sub>H-groups was performed by treatment at 1 g sample with 50 ml of 30 % H<sub>2</sub>O<sub>2</sub> with stirring for 48 h at room temperature.

#### *Characterization of catalyst texture*

Textural properties of the catalysts were measured using nitrogen adsorption at T 98K isotherms on ASAP-2420 (Micromeritics, USA) in the range of relative pressures ( $p/p_0$ ) 0,06-0,99 in increments of 0,015. Surface areas were calculated by the BET (Brunauer-Emmett-Teller) method [19] within the range  $p/p_0$  0,06-0,25, the pore volumes were determined by using «Single point BET» [20], and the pore size distribution was obtained using equation isotherm BJH (Barrett Joyner-Halenda) method [21].

X-ray fluorescence spectroscopy (XRF) was performed using a spectrometer «Axios Advanced» (PANalytical, Netherlands). Spectra were recorded throughout the wavelengths range of the periodic table of elements starting from oxygen. Then using the program IQ+semi-quantitative analysis the elements were analyzed. This method determined the content of elements such as silica, sulfur, chlorine and sorbed metals (palladium, mercury). Sensitivity of the method is 0.01 %, accuracy 5 % rel. According to the dates XRF the amount of grafted sulfur in acid modified SBA-15 was about 1.6 mmol/g.

#### *Procedures of sucrose hydrolysis*

Sucrose hydrolysis was performed at 80 °C in a glass reactor of 250 ml volume with constant stirring of the reaction mixture. To prevent the interaction of hydrolysis products of sucrose with oxygen air the reactor was purged with nitrogen. In all experiments the initial concentration of sucrose in distilled water was 111 g/l and weight ratio of solid catalyst to the weight of sucrose was 1:4. Sampling of the reaction mixture was performed with a given time intervals.

Hydrolysates of sucrose were analyzed by HPLC method with use of a liquid microcolumn chromatograph «MILIKHRON A-02» with scanning UV-detector. The stainless steel column (2,0×75 mm) packed with silica gel with a grain size about 5,0 microns (Prontosil-120-5-NH<sub>2</sub>) was used for analysis. The temperature of column was 35,0±0,3 °C. Mobile phase was acetonitrile-deionized water in a ratio of 82:18, the flow rate – 100 mL/min. The volume of analysed substance was 2 ml. Registration time of chromatogram was 12 min. The processing of obtained data was performed with use of MultiKhrom-SPEKTR program for Windows (Ampersand Ltd.). Chromatographic peaks of monosaccharides were identified according to retention time in regard to the channel 190 nm.

#### **Procedures of cellulose hydrolysis**

Microcrystalline cellulose Vivapur® Type 101 previously treated in a ball mill «KM-1» within 24 h was used in hydrolysis experiments. The hydrolysis of MCC was carried out at temperature of 150 °C

in a rotating steel autoclave with inner fluoroplastic test tube 35 ml. After reaction, the hydrolysate was separated from the reaction mixture by filtration on Buchner funnel with filter paper under vacuum. Conversion of cellulose was determined by the gravimetric method with an accuracy of  $\pm 2-3\%$ . The samples of hydrolyzate were analyzed by gas chromatograph of "VARIAN-450 GC" with flame ionization detector. The capillary column VF-624ms (length – 30 m, inside diameter – 0,32 mm) was used. The used chromatography conditions: the carrier gas – helium; injector temperature – 250 °C; reference temperature of columns thermostat – 50 °C (5 min.), temperature lifting to 180 °C was carried out with a speed of 10 °C/min., then kept at 180 °C within 37 min. Temperature of the detector was 280 °C. Duration of chromatographic analysis of monosaccharides was 55 min. For oligosaccharides analysis the thermostat temperature lifted to 250 °C (10 °C/min.) and then kept within 30 min.

The hydrolysate sample was exposed to a derivatization with formation of trimethylsilyl (TMS) ethers according to the procedure, described in [22].

The obtained chromatograms include peaks of all tautomer forms of monosaccharides containing in the hydrolysate sample. Identification of peaks was carried out, using retention times values for each tautomeric forms of monosaccharides. The ratio of the sum of the areas of monosaccharide characteristic peaks to the area of peak of the internal standard ( $S_i/S_{st}$ ) was calculated. Using these ratios, and the calibration curves, the amount of each monosaccharide in the hydrolysate sample was calculated.

## Results and Discussion

### *Texture characteristics of acid-modified catalysts*

A regular decrease of the specific surface area and pore size was observed as a result of acid modification of the catalysts Sibunit-4 and SBA-15 (Table 1). Obviously the part of mesopores is destroyed after Sibunit oxidation treatments and in the case of SBA-15 the mesopores were blocked by trimethoxysilan molecules.

The information about of number and nature of functional groups on the surface of modified Sibunit was obtained by the method of acid-base titration with solutions NaOH, Na<sub>2</sub>CO<sub>3</sub> or NaHCO<sub>3</sub>, and C<sub>2</sub>H<sub>5</sub>ONa in absolute ethanol. It was found that the total concentration of the specific acidic groups (carboxyl, lactone, phenol, carbonyl) on the surface of the carbon material decreases in the following order: Sibunit modified HNO<sub>3</sub> (0,77 mmol/g) > Sibunit modified NaOCl (0,42 mmol/g) > Sibunit modified O<sub>2</sub> in N<sub>2</sub> in the presence of water vapor (0,36 mmol/g) > Sibunit initial (0,10 mmol/g).

Table 1. Textural properties of the modified catalysts samples

Initial and modified materials	S <sub>BET</sub> , m <sup>2</sup> /g	V <sub>pores</sub> , sm <sup>3</sup> /g	<d> <sub>pores</sub> , nm
Initial Sibunit-4	379	0,63	6,6
Sibunit-4 treated by O <sub>2</sub> and water vapor mixture at 450 °C	348	0,44	5,1
Sibunit-4 treated by NaOCl at 25 °C	268	0,37	5,5
Sibunit-4 treated by HNO <sub>3</sub> at 110 °C	250	0,41	6,6
Initial SBA-15	550	0,82	5,9
SBA-15 modified by SO <sub>3</sub> H-groups	370	0,20	2,0

*Catalytic hydrolysis of sucrose*

The initial Sibunit-4 has no catalytic activity in the hydrolysis reaction of sucrose in an aqueous medium at temperature of 80 °C. Sibunit treated by O<sub>2</sub> in water vapor at 450 °C was low inactive at similar reaction conditions.

Higher catalytic activity in the hydrolysis of sucrose showed Sibunit samples modified NaOCl and HNO<sub>3</sub> (Fig. 1). Sibunit treated by HNO<sub>3</sub> gives after 200 minutes of sucrose hydrolysis the concentration of glucose 36,7 g/l and fructose 37,4 g/l. These values are about 64 % of the theoretically possible yields of monosaccharides from sucrose.

Industrial ion-exchange polymeric material Nafion® N551PW showed sufficiently high catalytic activity in the hydrolysis of sucrose. After 120 minutes of hydrolysis approximately 75 % of the theoretically possible yields glucose and fructose were obtained. After 200 minutes of hydrolysis almost all sucrose (111 g/l) was converted into an equivalent amount of glucose 57,8 g/l and fructose 55,7 g/l (Fig. 1).

According to the obtained results, the SBA-15 catalyst modified by sulfonic acid groups showed the maximum catalytic activity in sucrose hydrolysis. Already after 40 minutes of the hydrolysis the concentration of glucose and fructose in the solution were 56,9 g/l and 55,7 g/l respectively (Fig. 1). The rate constants (k) of sucrose hydrolysis at 80 °C over a different solid acidic catalysts were compared. For Sibunit samples modified by NaOCl and HNO<sub>3</sub> the rate constants were  $1,0 \cdot 10^{-5} \text{ s}^{-1}$  and  $3,0 \cdot 10^{-5} \text{ s}^{-1}$  respectively. The rate constant of sucrose hydrolysis in the presence of commercial polymer Nafion® N551PW is higher by an order and equal to  $1,2 \cdot 10^{-4} \text{ s}^{-1}$ . The maximum rate constant of sucrose hydrolysis at these conditions ( $9,2 \cdot 10^{-4} \text{ s}^{-1}$ ) was observed in the presence of SBA-15 modified by SO<sub>3</sub>H groups.

It is known from the literature [23] that the styrene divinylbenzene copolymers Amberlite IR-120H (20 %) and Amberlite IR-200 (8 %) are the most active catalysts in the hydrolysis reaction of sucrose. The rate constants of sucrose hydrolysis in the temperature range 50-80 °C for these catalysts are  $7,0-56,3 \cdot 10^{-4} \text{ s}^{-1}$  and  $5,3-105,8 \cdot 10^{-4} \text{ s}^{-1}$  respectively. The catalyst V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (16 % wt.) is less active in the hydrolysis of sucrose at similar conditions (rate constant  $12,28 \cdot 10^{-6} \text{ s}^{-1}$  at 80 °C) [24]. According to [25], the rate constant of sucrose hydrolysis at 80 °C over solid catalyst SiO<sub>2</sub> modified by 12-phosphotungstic acid is  $6,15 \cdot 10^{-6} \text{ s}^{-1}$ . Thus, the rate constants of the sucrose hydrolysis over Sibunit samples modified by

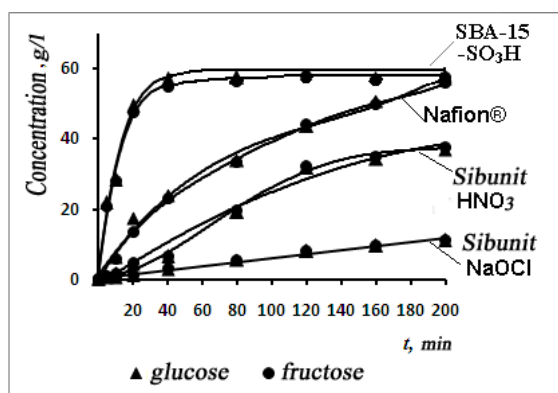


Fig. 1 Kinetics of glucose and fructose formation in the hydrolysis of sucrose at 80 °C (5,54 g sucrose, 1,4 g catalyst; 50 ml H<sub>2</sub>O)

NaOCl and HNO<sub>3</sub> are comparable to catalysts V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and 12-phosphotungstic acid/SiO<sub>2</sub>. But the activity of SO<sub>3</sub>H- modified SBA-15 is much higher.

Previously we found [26], that the hydrolysis of sucrose with the dissolved catalyst 5 % H<sub>2</sub>SO<sub>4</sub> can be carried out at lower temperature (50-60 °C) and the rate constants for these conditions are 9,69·10<sup>-4</sup>s<sup>-1</sup> and 14,4·10<sup>-4</sup>s<sup>-1</sup>. However the advantages of solid acid catalysts are environmental safety, lack of corrosiveness, the absence of the additional stages of the reaction solutions neutralization and glucose and fructose isolation.

### *Catalytic hydrolysis of cellulose*

The catalytic properties of different solid acid catalysts was compared in hydrolysis microcrystalline cellulose Vivapur® Type 101 at 150 °C. Data on MCC conversion and glucose yield in the presence of the acid-modified samples of Sibunit, SBA-15 and Nafion® N551PW are shown in Figure 2.

Obviously that in the case of an insoluble cellulose, unlike soluble sucrose, the hydrolysis in the presence of solid catalysts occurs much slower because of the insufficient contact of a solid substrate with the catalyst surface.

The maximum conversion of cellulose (80,1 % wt.) and a highest yield of glucose (36,1 % wt.) were achieved within 12 h of hydrolysis in the presence of modified SBA-15. The high catalytic activity of modified SBA-15 in hydrolysis of sucrose and cellulose stipulates by the presence of -SO<sub>3</sub>H groups in modified SBA-15 and larger specific surface area as compared to of samples modified Sibunit. Carboxyl, lactone, phenolic and carbonyl acid groups on the surface of Sibunit samples provides only moderate conversion of cellulose (16-19 % wt.) and the rather low yield of glucose (5-8,2 wt. %) in MCC hydrolysis at 150 °C. Like that the conversion of cellulose under the same conditions of hydrolysis in the presence of Nafion® N551PW for 12 h was only 21.5 wt. % and the yield of glucose was 6.2 wt. %.

Fig. 3 shows the activity and stability of the samples Sibunit modified by NaOCl and HNO<sub>3</sub> and Nafion® membrane in the hydrolysis of cellulose Vivapur® Type 101 at a temperature of 150 °C in three consecutive cycles. The first cycle was performed with a fresh linkage catalyst, and the second and the third cycles were performed with a catalyst separated from the hydrolyzate and insoluble residue of

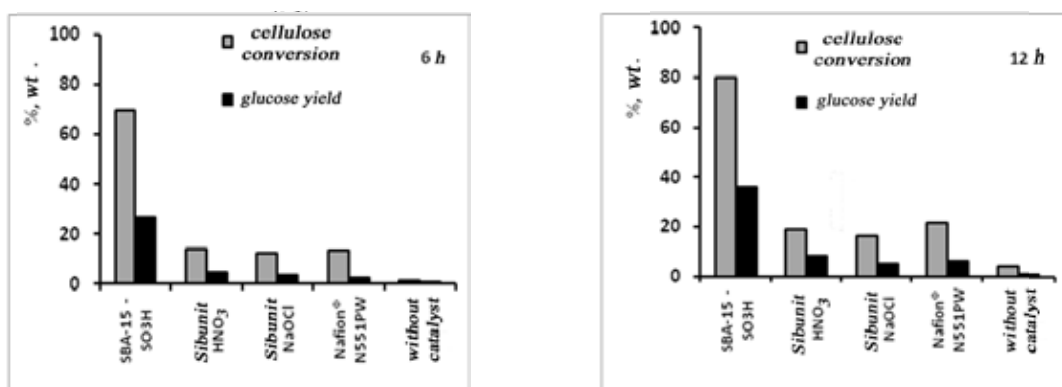


Fig. 2. Influence of solid acid catalysts on the conversion of cellulose Vivapur® Type 101 and glucose yield at 150 °C at duration of 6 and 12 h (0,45 g cellulose; 0,45 g of catalyst; H<sub>2</sub>O 11 ml)

cellulose. Each time the catalyst was washed with hot distilled water after previous experiment. Total time for testing of each catalyst was 18 h.

No reduction of catalytic activity of the modified Sibunit samples in the hydrolysis of MCC was observed after 3 cycles. This agrees well with the results obtained in [5] and [15] in which the performance of carbon catalysts was not reduced after repeated use in the hydrolysis of cellulose at temperatures of 100-150 °C for time 6-24 h. The decrease of glucose yield from 2.6 to 1.4 wt %, in the presence of Nafion® was observed to the third cycle.

The most active among examined catalysts was the modified SBA-15 but its undergoes to some structural changes after the cellulose hydrolysis at 150 °C for 12 h. Namely the specific surface area of the catalyst decreases and the content of sulfur reduces (Table 2).

It should be noted that without catalyst the conversion of the cellulose is approximately 4 % wt. for 12 h. This agrees well with literature data on the non-catalytic conversion of cellulose. At 160 °C and a duration of 12 h the conversion of cellulose did not exceed 4,5 % wt. [27].

Analysis of cellulose hydrolysates by gas chromatography method showed the presence of glucose as a main product (Fig. 4). But also minor amounts of mannose and xylose were detected. Mannose may be produced by catalytic epimerization of glucose. Xylose can be a product of hydrolysis of hemicelluloses impurities present in MCC. Furthermore, the some peaks presumably related to soluble oligosaccharides were detected (Fig. 4).

### Conclusion

The activities of solid acid catalysts SBA-15, Sibunit and industrial acid polymer Nafion® in hydrolysis of sucrose at 80 °C and hydrolysis of microcrystalline cellulose at 150 °C were compared.

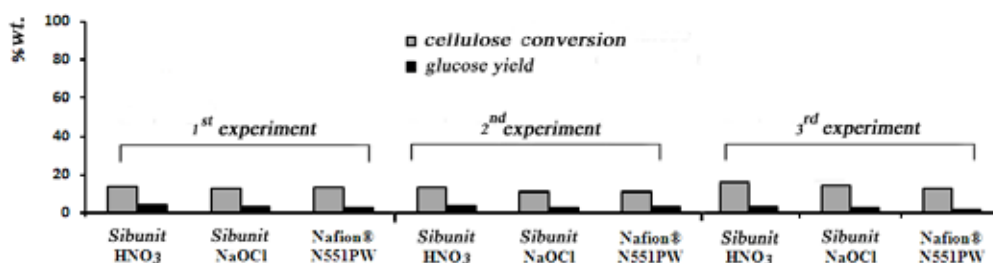


Fig. 3. Activity of catalysts in hydrolysis of cellulose Vivapur® Type 101 at a temperature of 150 °C in three consecutive cycles at the duration of each experiment 6 h (0.45 g cellulose, 0.45 g of catalyst, 11 ml of H<sub>2</sub>O)

Table 2. Some characteristics of modified SBA-15 catalyst before and after hydrolysis of cellulose

Initial and modified SBA-15	$S_{\text{BET}}$ , m <sup>2</sup> /g	$V_{\text{nop}}$ , cm <sup>3</sup> /g	$\langle d \rangle_{\text{nop}}$ , nm	Content S, mmol/g
Initial SBA-15	550	0,82	5,9	-
Modified SBA-15 before hydrolysis reaction	370	0,20	2,0	1,6
Modified SBA-15 after hydrolysis reaction	255	0,19	2,9	0,6

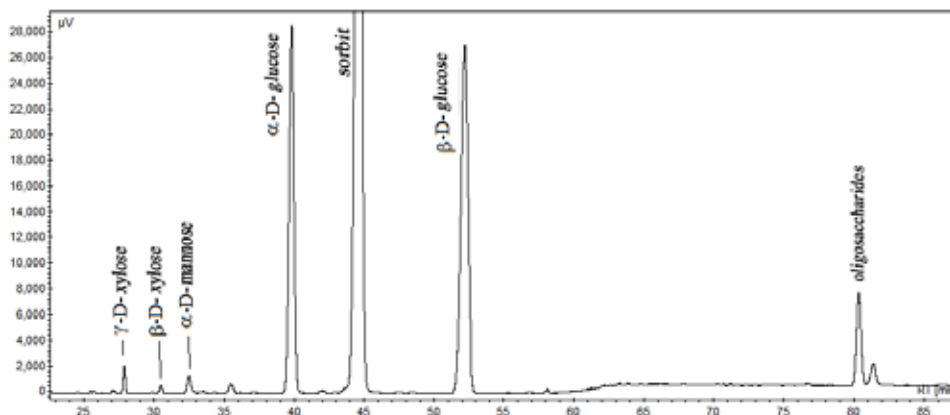


Fig. 4. The typical chromatogram of cellulose hydrolyzate

It was established that the samples of Sibunit modified by NaOCl and HNO<sub>3</sub> have the lower activity in hydrolysis of sucrose at 80 °C (rate constants 1,0·10<sup>-5</sup>s<sup>-1</sup> and 3,0·10<sup>-5</sup>s<sup>-1</sup> respectively) as compared to Nafion® (rate constant 1,2·10<sup>-4</sup>s<sup>-1</sup>). The maximal activity in sucrose hydrolysis under these conditions (rate constant 9,2·10<sup>-4</sup> s<sup>-1</sup>) has SBA-15 modified by SO<sub>3</sub>H-groups.

The catalyst SBA-15 containing SO<sub>3</sub>H- groups also showed higher activity in the hydrolysis of MCC at 150 °C as compared to samples of Sibunit treated by HNO<sub>3</sub> and NaOCl to create carboxyl groups. The degree of MCC conversion at 150 °C and time of hydrolysis 12 h decreases in a following order: SBA-15 (80,1 % wt.) > Nafion (21,5 % wt.) > Sibunit (16-19 % wt.) > without catalyst (4,2 % wt.). It was established that the products of MCC hydrolysis include, along with glucose, the oligosaccharides and impurities of mannose and xylose.

The stability of the samples of modified Sibunit in reaction of cellulose hydrolysis was confirmed experimentally by triple using the same catalyst sample without the loss of catalytic activity.

The reduction of specific surface area and sulfur content after the using of modified SBA-15 catalyst in cellulose hydrolysis at 150 °C was detected.

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**Исследование влияния природы  
твердых кислотных катализаторов  
на их активность  
в гидролизе сахарозы и целлюлозы**

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*Сопоставлена активность твердых кислотных катализаторов на основе SBA-15 и Сибунита в гидролизе сахарозы при 80 °С и микрокристаллической целлюлозы (МКЦ) при 150 °С. Максимальная активность в реакции гидролиза сахарозы наблюдалась у SBA-15 (константа скорости  $9,2 \cdot 10^{-4} \text{с}^{-1}$ ), содержащего закрепленные  $\text{SO}_3\text{H}$ -группы. Для всех изученных катализаторов конверсия МКЦ за время гидролиза 12 ч увеличивается в следующем порядке: без катализатора (4,2 % мас.) < Сибунит (16-19 % мас.) < Nafion® (21,5 % мас.) < SBA-15 (80,1 % мас.). Установлено, что продукты гидролиза МКЦ содержат наряду с глюкозой олигосахариды и примеси маннозы и ксилозы.*

*Ключевые слова: твердые кислотные катализаторы, гидролиз, сахароза, целлюлоза, глюкоза, фруктоза.*

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