

The Use of WO₃-ZSM-5 Zeolites in the Dehydration of Monosaccharides

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In this work, a procedure was developed for the synthesis of WO₃-containing catalysts based on zeolites of the ZSM-5 type. Zeolites with different Si/Al ratios and different numbers of acid sites were used: ZSM-5-CVM, ZSM-5-CVN and ZSM-5-Acros. The synthesized catalysts were characterized and tested in the reaction of the conversion of fructose and glucose to 5-hydroxymethylfurfural (5-HMF) and levulinic acid (LA). It was shown that the introduction of tungsten (VI) oxide into the composition of ZSM-5 leads to a noticeable increase in the number of active acid sites on the catalyst surface, which plays an important role in the reaction. In particular, the total concentration of weak and strong Brønsted acid centres for ZSM-5-Acros was 0.057 mmol/g; after the modification of zeolite WO₃, the concentration of acid sites increased to 0.575 mmol/g. As a result, the activity of the catalysts in the reaction of dehydration of monosaccharides and rehydration of 5-HMF increased sharply. The results of the study show the promise of using zeolites of the ZSM-5 type, modified with tungsten oxide (VI), in the conversion of biomass to platform chemicals.

1. Introduction

5-HMF is one of the most important multifunctional chemicals derived from biomass, which can be used to produce new generation plastics (Santiago et al., 2020) and biofuels (Huber et al., 2006). From 5-HMF, a large number of derivatives that are important for chemical synthesis can be obtained, such as LA, furan-2,5-dicarboxylic acid, 2,5-diformylfuran, 2,5-bis (hydroxymethyl) furan, 2, 5-bis- (aminomethyl) furan, 2,5-dimethylfuran, 2,5-dimethyltetrahydrofuran, 2,5-bis (methoxymethyl) furan, 5-ethoxy-methylfurfural, etc. However, despite the wide prospects for the practical application of 5-HMF in the chemical and fuel industries, synthesis methods for its large-capacity production have not yet been developed (Kohli et al., 2019). 5-HMF and LA can be obtained from mono- and polysaccharides contained in plant biomass (Figure 1) using acid catalysts (Rout et al., 2016).

Studies show that dimethyl sulfoxide (DMSO) is the optimal solvent for carrying out the dehydration reaction of hexoses to 5-HMF (Esposito and Antonietti, 2015). However, its high boiling point creates a problem in the separation of reaction products. Water is free from such a disadvantage, cheap and non-toxic, but the yield of 5-HMF in an aqueous medium usually does not exceed 50 % due to its hydrolysis (Wang et al., 2014). In this regard, the use of biphasic media is promising. In this case, the resulting 5-HMF is continuously extracted into the organic layer without undergoing degradation (Saha, 2014). Mineral acids can be used as acid dehydration catalysts, which, however, is associated with problems of equipment corrosion, the need to clean the product and utilize acids; soluble salts of Zn, Nb, Fe and other metals; as well as heterogeneous acid-type catalysts, in particular, cation exchangers, oxides and sparingly soluble salts of transition metals, zeolites (Chernyshev et al., 2017).

The US Department of Energy in 2004 included levulinic acid in the list of the most promising multifunctional reagents obtained from biomass. Due to the presence of two highly active functional groups (carbonyl and carboxyl), LA easily enters the reactions of oxidation, reduction, esterification, substitution, condensation, which makes it a very valuable "platform compound" (Lopes et al., 2020). Like 5-HMF, LA is the precursor of a

large number of industrially important chemicals and is widely used in the production of lubricants, chiral reagents, resins, biologically active substances, adsorbents, electronics, and batteries (Kohli et al., 2019).

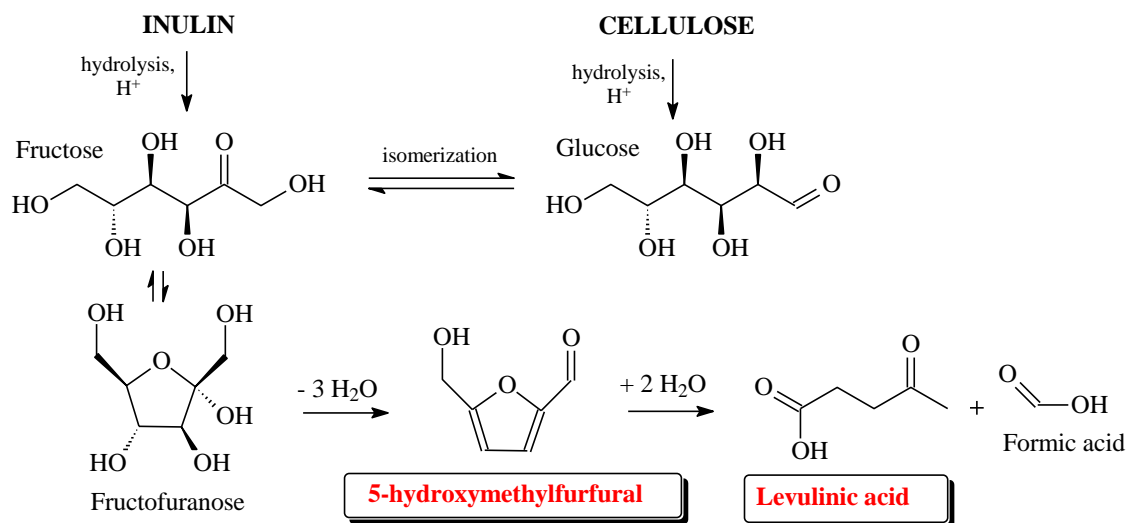


Figure 1: Scheme of the synthesis of 5-HMF and LA from plant polysaccharides

Levulinic acid is the product of 5-HMF rehydration, and Brønsted acids play an important role in this reaction (Lopes et al., 2017). High yields of 5-HMF and LA (56 % and 74 %) were obtained using sulfuric acid as a catalyst (Yang et al., 2013). With the introduction of increasingly stringent environmental standards, the use of inorganic acids is becoming less attractive, and solid acids with Brønsted and/or Lewis acid centers can become a real alternative to them. Lewis acid sites promote glucose isomerization into fructose, while a combination of Brønsted and Lewis sites promotes the dehydration reaction of fructose to 5-HMF and its rehydration to LA. The use of Lewis and Brønsted acids ($AlCl_3$ and HCl) in the microreactor made it possible, in combination with the simultaneous extraction of 5-HMF with the organic phase of methyl isobutyl ketone, to obtain a high yield of the product - up to 66.2 % (Guo et al., 2020). A similar approach using a Lewis acid and a microreactor made it possible to obtain an even higher yield of 5-HMF – 85 mol% (Muranaka et al., 2020). In this regard, zeolites with both types of acid sites are of particular interest (Signoretto et al., 2019). Zeolites have a combination of valuable properties: no problems with equipment corrosion, easy heat treatment regeneration, stability in hydrothermal conditions, non-toxicity, long service life, etc. The acidic zeolite BEA (H-BEA-18) was studied in the reactions of dehydration of fructose and glucose to 5-HMF and rehydration of the latter to LA (Kruger et al., 2013). It is shown that glucose isomerization into fructose is catalyzed by octahedral aluminium atoms, which act as Lewis acid sites. Bimodal zeolite HZ-5 (Bimodal-HZ-5), obtained by the modification of zeolite H-ZSM-5, was studied in the process of one-reactor conversion of microcrystalline cellulose to 5-HMF (Nandiwale et al., 2014). The modified sample, due to the larger surface area, pore volume and acidity, compared with the initial H-ZSM-5, allowed us to obtain a 5-HMF yield of 46 % at a 67 % conversion of cellulose. Good results were obtained using zeolites in the synthesis of LA. An almost 70 % yield of LA was obtained in the course of glucose conversion using a ZSM-5 type zeolite catalyst (Zhuang et al., 2013). In (Zeng et al., 2010) LA was obtained from glucose using an MFI type ZRP zeolite. The authors showed the key nature of the relationship between acidity and the structure of the pores of the catalyst with the yield of LA (maximum, 35.8 %). The aim of this work is to study the possibility of using WO_3 -containing catalysts based on ZSM-5 zeolites for the conversion of C6 monosaccharides to 5-hydroxymethyl furfural and levulinic acid.

2. Experimental

In the course of the study, the methods for the synthesis of catalysts and the conditions for the reaction of dehydration of monosaccharides were optimized. Below are the final versions of the synthesis procedures and experiments.

2.1 Materials

Zeolites ZSM-5-CVM and ZSM-5-CVN were purchased from Nizhny Novgorod sorbents (Russia), zeolite ZSM-5-Acros was purchased from Acros organics (Switzerland). Phosphotungstic acid was purchased from

Sigma-Aldrich (Japan). Fructose and glucose were purchased from ChimMedService (Russia). All other reagents were of analytical grade.

2.2 The catalyst synthesis

The initial sample of zeolite ZSM-5 weighing 10 g was calcined for 2 hours in air at 550 °C and cooled in a desiccator. After cooling, the sample is suspended in 100 ml of a 0.1 mol/L solution of NH_4NO_3 , left overnight, separated and washed with distilled water. The washed sample is dried at 105 °C and calcined at 550 °C. 1.6 g of phosphotungstic acid is dissolved in a minimum amount of water. To the resulting solution add 10 g of the prepared zeolite, mix thoroughly for 30 minutes and dry at 90 °C. The dried sample is calcined in air at 600 °C for 5 hours, cooled in a desiccator, washed with distilled water and dried at 100 °C.

2.3 Characterization

Nitrogen adsorption measurements were carried out at liquid nitrogen temperature on a surface analyzer Beckman Coulter SA 3100 (Coulter Corporation, USA). Samples were degassed at 90 °C in vacuum. The XPS spectra were obtained using an ES 2403 M-T spectrometer (Russia). For photoelectron excitation, characteristic $\text{MgK}\alpha$ radiation ($h\nu = 1,253.6$ eV) was used. The power of the radiation source is 200 watts. To determine the amount and strength of the Brønsted acid centers located on the surface of the synthesized catalysts, a thermally programmed desorption of ammonia was carried out on a Chemisorb 4580 gas chemisorption analyzer (Micrometrics, USA). For analysis, 0.4 g of the catalyst was placed in a quartz cuvette and flushed with helium at a rate of 50 mL/min and heated to a temperature of 550 °C at a speed of 50 °C/min, after which it was kept at this temperature for one hour, after which the sample was cooled to 100 °C. After cooling to a temperature of 100 °C, the sample was purged with a mixture of ammonia in helium with an ammonia content of 15 vol. % for one hour, after which the sample was blown with helium also for an hour. Then, the sample was warmed up to 550 °C at a rate of 50 °C/min for the whole time the profile of ammonia desorption was recorded. The amount of desorbed ammonia was determined using a katharometer and a pre-calculated calibration line. The amount of ammonia was converted to the number of surface acid sites.

2.4 Monosaccharides conversion

The reaction was carried out in a high-pressure reactor with a volume of 50 cm³ and a working pressure range from 1 to 300 bar equipped with a PARR 4843 controller (Parr Instrument, USA), a heater (operating temperature range from room temperature to 300 °C), a propeller stirrer (mixing speed range from 0 to 700 rpm), a thermocouple and a manometer. In a typical experiment monosaccharide and water were loaded into the reactor, a gas line, a thermocouple and a reactor cover with a propeller stirrer were connected. After checking for leaks, the internal volume of the reactor was purged with nitrogen. Upon reaching the operating temperature, the number of revolutions of the mixer was increased to 600 rpm. The timing of the experiment began from the moment the operating temperature was reached. 5-HMF was determined by micellar electrokinetic chromatography under the following conditions: buffer 5 mmol/L sodium tetraborate + 120 mmol/L sodium dodecyl sulfate, voltage 20 kV, detector wavelength 284 nm, analysis temperature 20 °C. LA was determined by capillary zone electrophoresis under the following conditions: buffer 10 mmol/L sodium tetraborate (pH 9.18), voltage 20 kV, detector wavelength 266 nm, analysis temperature 20 °C.

3. Results and discussion

Table 1 presents the results of studies of initial samples of zeolites and synthesized catalysts by low-temperature nitrogen adsorption.

Table 1: Porosity data for the initial zeolites and the catalysts based on them

Sample	Surface area ^a , m ² /g		Si/Al ^b
	micropores	mesopores	
ZSM-5-CVM	288	48	92
ZSM-5-CVN	248	71	72
ZSM-5-Acros	269	105	5
WO ₃ /ZSM-5-CVM	246	39	-
WO ₃ /ZSM-5-CVN	275	38	-
WO ₃ /ZSM-5-Acros	276	52	-

^a - surface area calculated from nitrogen adsorption curves in accordance with the t-graph model;
^b - Si/Al molar ratio determined by XPS.

As can be seen from the data obtained, the introduction of tungsten oxide into the zeolites practically did not affect the microporous nature of the zeolite structure, although the proportion of mesopores, which is especially noticeable with ZSM-5-CVN and, to a greater extent, ZSM-5-Acros, decreased. It can be assumed that the formation of tungsten oxide particles occurs in the mouths of mesopores on the surface of the zeolite. The presence of WO_3 on the support surface is confirmed by the results of XPS (Figure. 2a).

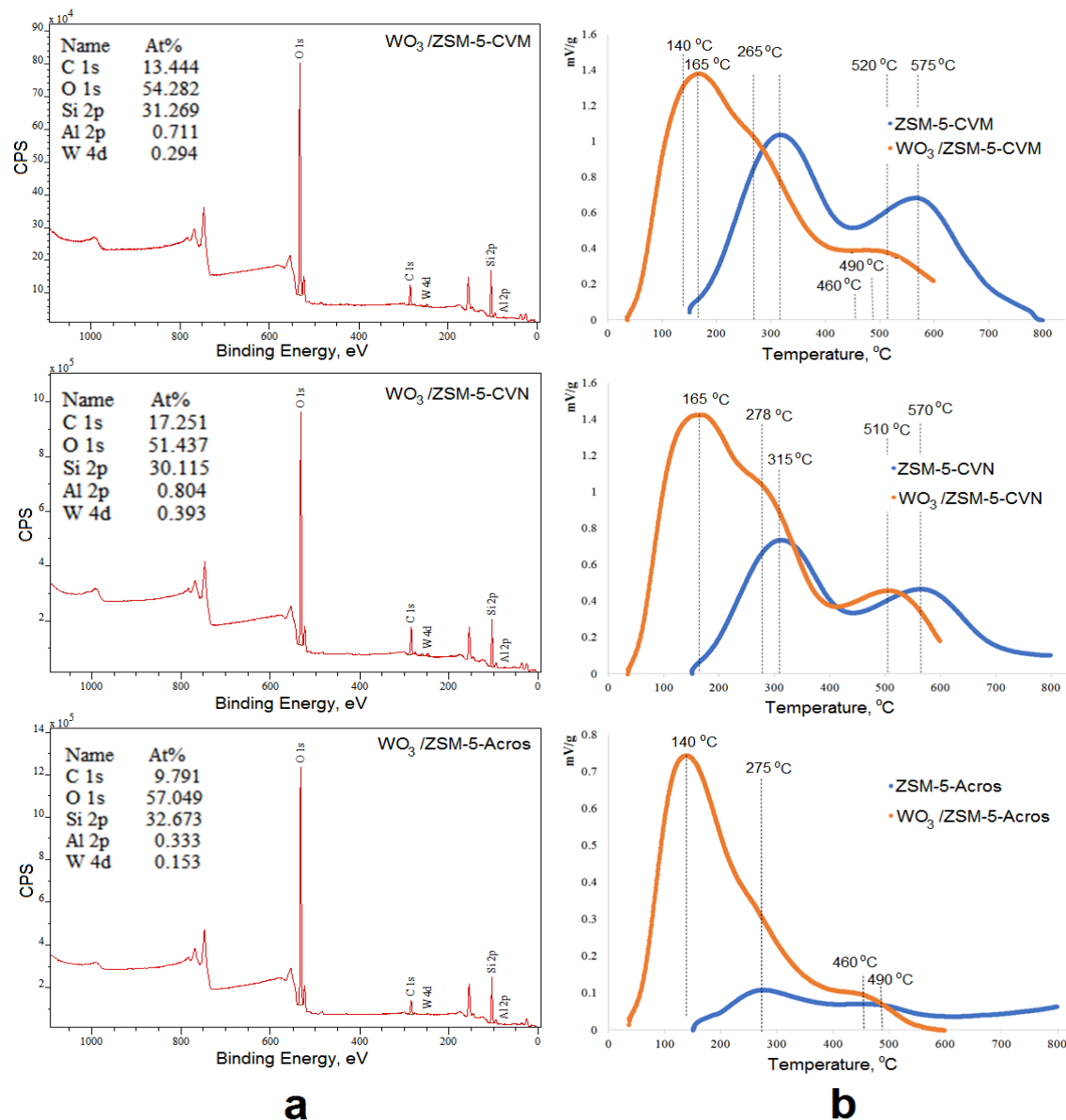


Figure 2: (a) Models of survey spectra for catalysts and (b) thermal desorption curves of ammonia from the surface of modified and unmodified zeolite

In Figure 2b shows the results of chemisorption of ammonia. It was shown that the introduction of WO_3 into the composition of zeolite ZSM-5-CVM leads to a significant change in the pattern of desorption compared with the initial sample. In the initial sample, standard peaks are observed, corresponding to the desorption of ammonia from the surface of weak (320 °C) and strong (575 °C) Brønsted centers. In $\text{WO}_3/\text{ZSM-5-CVM}$, a reflex appears with a maximum of 165 °C, which corresponds to the appearance of a new type of weak acid centers on the zeolite surface. A shift of the peak maxima at strong and weak Brønsted centers to the low-temperature region by 50-60 °C is also observed, which also indicates their modification. The same is observed for other catalyst samples.

The most pronounced is the increase in the number of acid sites for the WO₃/ZSM-5-Acros catalyst. Modification of the zeolite has led to a significant change in the pattern of desorption compared with the original sample. In the initial sample, standard peaks corresponding to ammonia desorption from the surface of weak (275 °C) and strong (490 °C) Brønsted centers are observed. A modified sample appears with a maximum of 140 °C, which corresponds to the appearance of a new type of weak acid centers on the zeolite surface. Table 2 provides quantitative data characterizing the acidity of the initial samples of zeolites and catalysts based on them.

Table 2: The number of active acid sites (C) in the initial zeolites and WO₃-containing catalysts based on them

Sample	t, °C	C, mmol/g	Sample	t, °C	C, mmol/g
ZSM-5-CVM	-	-	WO ₃ /ZSM-5-CVM	165	1.124
	320	0.722		265	0.158
	575	0.516		520	0.077
ZSM-5-CVN	-	-	WO ₃ /ZSM-5-CVN	165	1.143
	315	0.747		278	0.215
	570	0.376		510	0.121
ZSM-5-Acros	-	-	WO ₃ /ZSM-5-Acros	165	0.517
	315	0.041		278	0.021
	570	0.016		510	0.037

The synthesized catalysts were tested in the reaction of the conversion of fructose and glucose to 5-hydroxymethyl furfural and levulinic acid in an aqueous medium at temperatures in the range of 150 - 180 °C under an inert atmosphere of nitrogen. Table 3 presents the test results of the synthesized catalysts. As can be seen from the data presented in table 3, the maximum yield of 5-hydroxymethylfurfural is observed when using initial zeolites as catalysts. The relationship between the acidity of the catalyst and the yield of 5-HMF is quite obvious. The higher the acidity, the greater the yield of 5-HMF (20.9 % when using ZSM-5-CVM, while ZSM-5-Acros yielded half as much).

Table 3: Conversion of substrate (X), yield of 5-hydroxymethyl furfural ($\eta_{5\text{-HMF}}$) and levulinic acid (η_{LA})

Catalyst	Fructose			Glucose		
	X, %	$\eta_{5\text{-HMF}}$, %	η_{LA} , %	X, %	$\eta_{5\text{-HMF}}$, %	η_{LA} , %
ZSM-5-CVM	100	20.9	36.5	76.0	12.3	18.0
ZSM-5-CVN	100	19.4	32.3	76.5	14.6	17.3
ZSM-5-Acros	87.0	11.2	23.5	42.3	9.4	14.0
WO ₃ /ZSM-5-CVM	100	5.7	54.7	88.5	17.7	34.0
WO ₃ /ZSM-5-CVN	100	6.3	52.5	91.3	18.2	36.3
WO ₃ /ZSM-5-Acros	100	13.5	33.2	68.6	12.1	18.5

Substrate 0.5 g; catalyst 0.3 g; H₂O 30 mL; 170 °C; 2.5 h; N₂

However, after the introduction of tungsten oxide into the zeolites and an increase in the number of acid sites on the catalyst surface, the yield of 5-HMF is significantly reduced. At the same time, the yield of levulinic acid significantly increases. This fact is probably due to an increase in the rate of 5-HMF rehydration with the formation of levulinic and formic acids. In addition, the formation of solutions with a black-brown color, characteristic of humins, is observed. The formation of black plaque on the surface of the catalyst is also observed, which leads to its inactivation after 1-2 uses. The problem of increasing the efficiency of the synthesized catalysts and their stability can be solved in the future by optimizing the quantitative ratio of substrate/catalyst, in which the formation of by-products, such as humins, will be minimized.

4. Conclusions

5-hydroxymethylfurfural and levulinic acid are some of the most important multifunctional chemicals derived from biomass. In this study, WO₃-containing catalysts based on zeolites of the ZSM-5 type were proposed for the conversion reaction of monosaccharides (fructose and glucose) into 5-HMF and levulinic acid. It was shown that the introduction of tungsten oxide into the zeolites significantly increases the number of Brønsted acid sites on their surface. Due to the ability of acid sites to accelerate the fructose dehydration reaction, glucose isomerization to fructose, and 5-HMF rehydration to form levulinic acid, the reaction activity of the modified zeolites has increased significantly. The maximum yield of levulinic acid from fructose and glucose

was 54.7 and 36.3 %, at 170 °C for 2.5 hours. At the same time, the intense dark color of the solutions indicates the formation of significant amounts of humins, the deposition of which on the catalyst surface leads to their inactivation. The developed WO₃/ZSM-5 catalytic systems still need further optimization. But already from the preliminary results obtained, it can be concluded that such catalysts may find application in the conversion of carbohydrate biomass into chemicals and biofuels in the future. The results obtained are valid only for monosaccharides. To obtain significant economic benefits and practical significance, it is necessary to use nonfood polysaccharides such as cellulose, inulin, and others as substrates. In turn, this requires the development of one-pot technologies, when the process of dehydration of monosaccharides will be preceded by the reaction of hydrolysis of the initial polysaccharide. The proposed catalysts, due to the presence of additional acid sites WO₃, can facilitate the hydrolysis reaction.

Acknowledgements

This work was supported by the Russian Science Foundation, project no. 19-19-00490; and by the Russian Foundation for Basic Research, project nos., 19-08-00414, 20-08-00079, 18-29-06004.

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