**Impact of Design on the Activity of ZrO$_2$ Catalysts in Cellulose Hydrolysis-Dehydration to Glucose and 5-Hydroxymethylfurfural**

Tatiana B. Medvedeva * , Olga L. Ogorodnikova, Irina S. Yakovleva, Lyubov A. Isupova, Oxana P. Taran, Nikolay V. Gromov * and Valentin N. Parmon

Boreskov Institute of Catalysis SB RAS, Lavrentiev Ave. 5, 630090 Novosibirsk, Russia; ogorod@catalysis.ru (O.L.O.); yakovleva@catalysis.ru (I.S.Y.); isupova@catalysis.ru (L.A.I.); oxanap@catalysis.ru (O.P.T.); parmon@catalysis.ru (V.N.P.)
* Correspondence: tanmedvedeva@catalysis.ru (T.B.M.); gromov@catalysis.ru (N.V.G.)
Tel.: +7-383-32-69-749 (T.B.M.); +7-383-32-69-591 (N.V.G.)

**Abstract:** The one-pot hydrolysis-dehydration of activated microcrystalline cellulose was studied in pure hydrothermal water at 453 K over ZrO$_2$ catalysts produced by thermodegradation, microwave treatment, mechanical activation, and sol–gel methods and spent without any co-catalyst. ZrO$_2$ prepared by microwave treatment was more active compared to ones derived by other methods. ZrO$_2$ prepared by microwave treatment is more active compared to ones derived by other methods. The catalyst calcination temperature also impacted reactivity. The cellulose conversion increased simultaneously with acidity and S$_{BET}$, which in turn were set by the preparation method and calcination temperature. Phase composition did not affect the activity. Yields of glucose and 5-HMF reaching 18 and 15%, respectively, were over the most promising ZrO$_2$ prepared by microwave treatment at 593 K. To our knowledge, this ZrO$_2$ sample provided the highest activity in terms of TOF values (15.1 mmol g$^{-1}$ h$^{-1}$) compared to the pure ZrO$_2$ systems reported elsewhere. High stability of ZrO$_2$ derived by microwave irradiation was shown in five reaction runs.

**Keywords:** cellulose; glucose; 5-Hydroxymethylfurfural; one-pot hydrolysis-dehydration; zirconium oxide

1. Introduction

Cellulose is well known to be the most abundant natural plant polymer. In recent years, it has been proposed for use as a raw material for chemical and material sciences [1–3]. Significant interest in cellulose transformations has been affected by the serious negative influence of traditional fossil resources such as oil and coal on the environment and human health. New catalytic approaches have been developed for the production of various chemicals and biofuels from inedible cellulose [4–14]. 5-Hydroxymethylfurfural (5-HMF) is one of the main platform molecules which can be obtained from cellulose.

5-HMF and its derivatives can become an alternative feedstock which could replace non-renewable sources. Applying 5-HMF in the production of polymers, motor oils, solvents, fuel additives, drugs and chemical reagents seems to be promising [13,15–17]. In 2014, the commercial production of 5-HMF via the acid-catalysed dehydration of fructose was established [18]. Another perspective compound for industry is glucose. Nowadays, it is traditionally produced by enzymatic or acid hydrolysis of starch or sucrose [19–21].

Traditional homogeneous catalysts have some disadvantages in the synthesis of glucose and 5-HMF. Thus, catalyst recycling and separation from reaction mixtures is quite challenging. Mineral acids could have a corrosive effect. The use of heterogeneous catalysts makes it possible to overcome the most serious drawbacks of homogeneous catalytic systems. Moreover, some solid systems, such as oxides of zirconium (IV) or titanium (IV), are quite stable under hydrothermal conditions, which are applied when processing water-insoluble cellulose. The crystal structure of this polysaccharide makes the use of...
harsh conditions inevitable [22,23]. Nowadays, a number of heterogeneous catalysts have been proposed for the depolymerization of cellulose in an aqueous medium such as carbon materials [23–29], noble metals supported on carbon materials [30], polymer resins [31], oxides [31–34], zeolites [33,35], and caesium salts of heteropoly acids [36,37]. However, the development of heterogeneous catalysts for the hydrolysis-dehydration of cellulose into glucose and 5-HMF that are effective and stable under hydrothermal conditions is a very urgent task for the efficient processing of plant raw materials.

Therein, zirconium dioxide appears to be a most promising catalyst due to high stability in hot compressed water. Table 1 presents data on the processing of cellulose and cellulose-containing biomass in the presence of catalysts based on ZrO$_2$. In general, in the presence of the proposed catalytic systems, the yields of glucose and 5-HMF can reach 12.7 and 20.6%, respectively, at temperatures of 453–523 K [38–45]. The use of a co-catalyst such as sulfuric acid can improve the efficiency of the dual catalyst system. [46,47] reported glucose yields up to 62.3–91.0% in the presence of two-component system of ZrO$_2$ + H$_2$SO$_4$. However, the authors did not discuss the formation of 5-HMF. It should be emphasized that the catalysts reported elsewhere were prepared by various methods such as precipitation [40,45], calcination [44], the sol–gel method [40], hydrolysis followed by calcination [43], and precipitation in combination with mechanical activation [46]. Commercial ZrO$_2$ was also used [41,47]. Various precursors of ZrO$_2$ (zirconyl chloride, zirconium dioxide hydroxide, zirconium propoxide) were applied.

| Catalyst       | Substrate         | Reaction Conditions | Glucose Yield/Selectivity, (%) | 5-HMF Yield/Selectivity, (%) | Ref. |
|----------------|-------------------|---------------------|-------------------------------|-----------------------------|------|
| Si/Zr/O        | Softwood          | 423 K, autogenic pressure | -                             | 8.2 $^a$ /-                  | [42] |
| ZnO-ZrO$_2$    | Cotton Cellulose  | 463 K, 1.4 MPa      | 6.01/-                        | 3.76/-                      | [45] |
| ZrO$_2$        | Microcrystalline Cellulose | 453 K, 3 MPa   | -/~2.3                        | -/~20.6                     | [41] |
| m/c-ZrO$_2$    | Glucose Fructose  | 473 K, 2.5 MPa      | ~1.8/-                        | ~4.2/-                      | [44] |
| Zr-P-773$^c$   | Sugarcane bagasse | 523 K, 34.5 MPa     | ~1.2/-                        | ~3.4/-                      | [40] |
| Zr-P-873       |                   |                     | ~0.9/-                        | ~3.3/-                      |      |
| Zr-P-973       |                   |                     | ~0.7/-                        | ~3.2/-                      |      |
| Zr-S-773       |                   |                     | ~1.2/-                        | ~3.4/-                      | [40] |
| Zr-S-873       |                   |                     | ~0.9/-                        | ~3.3/-                      |      |
| Zr-S-973       |                   |                     | ~0.7/-                        | ~3.2/-                      |      |
| ZrO$_2$        | Cellulose         | 433 K [H$_2$SO$_4$] = 0.04 mol·L$^{-1}$ | 65.2 d$^d$ | n/d                          |      |
| ZrO$_2$-1$^e$  |                   |                     | 62.3 d$^d$                    | n/d                         |      |
| ZrO$_2$-2      |                   |                     | 93.6 d$^d$                    | n/d                         |      |
| ZrO$_2$-3      |                   |                     | ~64.9 d$^d$                   | n/d                         | [46] |
| ZrO$_2$-4      |                   |                     | ~80.3 d$^d$                   | n/d                         |      |
| ZrO$_2$-5      |                   |                     | ~91.0 d$^d$                   | n/d                         |      |
| ZrO$_2$        | Cellulose         | 453 K, 1 MPa        | 12.7 /-                       | 13.3 /-                     | [43] |

$^a$ Total yield 5-HMF + Furfural + Levulinic acid; $^b$ means data revealed from figures published; $^c$ Zr-P-773—zirconium dioxide prepared by precipitation and calcined at 773 K; Zr-S-973—zirconium dioxide prepared by sol–gel method and calcined at 973 K; $^d$ Total reducing sugars yield (TRS), %; $^e$ ZrO$_2$-1—amorphous ZrO$_2$, ZrO$_2$-2—amorphous ZrO$_2$ after ball milling, ZrO$_2$-3—ordinary ZrO$_2$ particles, ZrO$_2$-4—ordinary ZrO$_2$ particles after ball milling, ZrO$_2$-5—nano ZrO$_2$.

The aim of this work was to investigate the impact of catalyst design by different techniques (thermodegradation, microwave heating, mechanical activation, and sol–gel method) on the catalytic properties of ZrO$_2$. The influence of acidity, phase composition, and textural properties, which depended on the preparation method on the catalytic
activity of ZrO\textsubscript{2} were studied in the hydrolysis-dehydration of cellulose to glucose and 5-HMF. The efficiency of zirconia catalytic systems was revealed in pure water without any co-catalysts. The best synthesis method was proposed.

2. Materials and Methods

2.1. Materials

Tetraisopropoxide Zr (IV) (Acros Organics, Belgium) (70\% solution in 1-Propanol), zirconyl nitrate monohydrate ZrO(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O (Acros Organics, Geel, Belgium) and ZrCO\textsubscript{3}(OH)\textsubscript{2}·xH\textsubscript{2}O (Acros Organics, Belgium) were used as ZrO\textsubscript{2} precursors. Microcrystalline cellulose spent in the experiments was purchased from Vekton (Saint-Petersburg, Russia) \cite{24–26}. 5-Hydroxymethylfurfural (Sigma-Aldrich, St. Louis, MO, USA), D-cellobiose (Sigma-Aldrich, USA), D-fructose (Sigma-Aldrich), D-mannose (Sigma-Aldrich, USA), D-glucose (Reahim, Moscow, Russia), and levulinic acid (Acros Organics, Belgium) were purchased to be used as standards of HPLC analysis. Milli-Q water (Millipore, Molsheim, France) was applied for preparing all the solutions.

2.2. Catalyst Preparation

Information on ZrO\textsubscript{2} synthesis techniques and parameters can be found in Table 2.

Table 2. Synthesis of ZrO\textsubscript{2} catalysts.

| Synthesis Method a | Catalyst Sample | Precursor of ZrO\textsubscript{2} | Synthesis Conditions |
|--------------------|-----------------|----------------------------------|---------------------|
| TD                 | ZrO\textsubscript{2}-T-723 | ZrO(NO\textsubscript{3})\textsubscript{2} | Thermodegradation at 723 K for 4 h |
|                    | ZrO\textsubscript{2}-T-873 | ZrO(NO\textsubscript{3})\textsubscript{2} | Thermodegradation at 873 K for 4 h |
| MW                 | ZrO\textsubscript{2}-W-1 | ZrO(NO\textsubscript{3})\textsubscript{2} | Total treatment 18 min, microwave irradiation 9 min, 35–60 W (T = 523 K) |
|                    | ZrO\textsubscript{2}-W-3 | ZrO(NO\textsubscript{3})\textsubscript{2} | Total treatment 11 min, microwave irradiation 3 min, 105 W (T = 603 K) |
|                    | ZrO\textsubscript{2}-W-4 | ZrCO\textsubscript{3}(OH)\textsubscript{2} | Total treatment 16 min, microwave irradiation 9 min, 80 W (T = 573 K) followed by 7 min, 150 W (T = 873 K) |
|                    | ZrO\textsubscript{2}-W-5 | ZrO(NO\textsubscript{3})\textsubscript{2} | Total treatment 48 min, microwave irradiation 24 min, 1000 W (T = 873 K) |
|                    | ZrO\textsubscript{2}-W-6 | ZrO(NO\textsubscript{3})\textsubscript{2} | Total treatment 30 min, microwave irradiation 15 min, 1000 W (T = 593 K) |
|                    | ZrO\textsubscript{2}-W-7 | ZrO(NO\textsubscript{3})\textsubscript{2} | Mechanical activation of ZrO\textsubscript{2}-T-873 2 min, followed by MW (total treatment 30 min, microwave irradiation 15 min, 1000 W (T = 593 K) |
| MA + MW            | ZrO\textsubscript{2}-MA-W | ZrO(NO\textsubscript{3})\textsubscript{2} | Mechanical activation of ZrO\textsubscript{2}-T-873 2 min, followed by MW (total treatment 30 min, microwave irradiation 15 min, 1000 W (T = 593 K) |
| MA                 | ZrO\textsubscript{2}-MA-C | ZrCO\textsubscript{3}(OH)\textsubscript{2} | Mechanical activation 2 min followed by calcination at 723 K during 4 h |
|                    | ZrO\textsubscript{2}-MA-N | ZrO(NO\textsubscript{3})\textsubscript{2} | Mechanical activation 2 min followed by calcination at 723 K during 4 h |
| SG                 | ZrO\textsubscript{2}-SG | Tetraisopropoxide Zr(IV) | Sol–gel method followed by calcination at 873 K during 8 h |

\(^a\) TD—thermodegradation, MW—microwave treatment, MA—mechanical activation, SG—sol–gel method.

2.2.1. Thermodegradation (TD)

ZrO\textsubscript{2} samples ZrO\textsubscript{2}-T-723 and ZrO\textsubscript{2}-T-873 were prepared by therodegradation of ZrO(NO\textsubscript{3})\textsubscript{2}·xH\textsubscript{2}O during 4 h at 723 K and 873 K, respectively. The synthesis was carried out in a muffle furnace (Nabertherm, Lilienthal, Germany).

2.2.2. Microwave Treatment (MW)

To prepare zirconia materials by microwave treatment, 1.5 g of ZrO(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O or ZrCO\textsubscript{3}(OH)\textsubscript{2}·xH\textsubscript{2}O precursor were placed into a quartz cell and exposed to a microwave
irradiation in a microwave oven PYRO (Milestone, Sorisole (BG), Italy). Treatment time and oven power were varied to prepare different ZrO$_2$ samples [48] (Table 2).

2.2.3. Mechanical Activation (MA)

To prepare ZrO$_2$-MA-N and ZrO$_2$-MA-C samples, ZrO(NO$_3$)$_2$·$x$H$_2$O or ZrCO$_3$(OH)$_2$·$x$H$_2$O were exposed to mechanical activation in a planetary mill APF-5 according to the technique described by [49]. Conditions of mechanical activation were the following: 2 min, precursor/ball ratio = 1/10 (g/g), precursor mill feeding 15 g, acceleration 40 g (Table 2). The calcination of activated samples was carried out at 723 K for 4 h.

2.2.4. Microwave Heating Combined with Mechanical Pre-Activation (MW + MA)

ZrO$_2$-MA-W sample was prepared by microwave treatment (total treatment 30 min, microwave irradiation 15 min, 1000 W (T = 593 K)) of ZrO(NO$_3$)$_2$·$x$H$_2$O preliminarily activated in a planetary-type mill according to the technique described in Section 2.2.3.

2.2.5. Sol–Gel Method (SG)

To prepare the ZrO$_2$-SG sample, zirconium hydroxide was precipitated from a solution of zirconium (IV) tetraisopropoxide in anhydrous isopropyl alcohol by dropwise addition of ethanol (96%) under Ar atmosphere. The precipitate was kept for 7 days under the liquor, then separated by decantation and calcined at 873 K for 8 h.

2.3. Catalyst Characterization

The texture properties of the catalysts were revealed by low-temperature nitrogen adsorption at 77 K (ASAP-2400, Micromeritics, GA, USA). The X-ray of the catalysts were carried out using a Bruker D8 Advanced diffractometer (Bruker, Germany) with Cu-K$_\alpha$ ($\lambda$ = 1.5418 Å) radiation. The POLYCRYSTAL program package was used to determine the unit lattice constants by the least squares method [50]. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) applied for chemical analysis was carried out using a PERKIN-ELMER OPTIMA 4300 instrument. Catalyst characterization techniques are described in detail in our previous papers [24–26].

To evaluate the acidic properties of the catalysts, the pH values of the mixtures of catalyst with water were determined. To evaluate this parameter, a 100 mg of ZrO$_2$ sample were added to Milli-Q water (10 mL) purged with argon for 10 min; then the glass cell was closed. The pH values were measured with an Anion 4100 pH-meter (Anion, Novosibirsk, Russia) under vigorous stirring and constant argon blowing until a constant pH value was reached.

2.4. Mechanical Activation and Characterization of Cellulose

Cellulose was treated in a planetary mill Pulverizette 5 (Fristch, Germany) to activate the substrate. Optical microscope Zeiss-Axiostar plus (Zeiss-Axiostar, Germany) and XRD diffractometer Bruker D8 Advanced (Bruker, Germany) were used to evaluate a particle size and crystallinity degree of the polysaccharide, respectively. The average length of activated cellulose particles was 13 ± 6 µm, crystallinity index was 35–55%. Cellulose activation and characterization techniques are presented in our previous works [24,36,51].

2.5. Catalytic Tests

Testing the stability of ZrO$_2$ catalysts was carried out under hydrothermal conditions in a high-pressure autoclave purchased from Autoclave Engineers, USA. The treatment conditions were 453 K, 1 MPa of argon and vigorous stirring of 1000 rpm. A weighed portion of the catalyst equal to 10 g·L$^{-1}$ was added to 45 mL of Milli-Q water placed into the reactor. The reactor was purged with argon, heated to 453 K, and held for 5 h. The Zr content in the reaction medium after hydrothermal treatment was measured by an ICP-AES spectrometer Optima 4300 DV (PerkinElmer Inc., Shelton, CT, USA).
Catalytic tests were carried out in a high-pressure autoclave (Autoclave Engineers, Erie, PA, USA). Cellulose transformation conditions were 453 K, 1 MPa of Ar, 1000 rpm. To control the composition of the reaction mixtures by HPLC, a ~1 mL portion of the reaction solution was collected in 0, 1, 2, 3, 5 and 7 h. The volume of the reaction mixture samples did not influence on the cellulose processing. The experimental mixtures were investigated by HPLC Shimadzu Prominence LC-20 (Shimadzu, Kyoto, Japan). HPLC apparatus was equipped by RI detector, Rezex RPM-Monosaccharide Pb²⁺ and Rezex ROA-Organic Acids columns (Phenomenex, Torrance, CA, USA), 300 × 5.0 mm) thermostated at 343 and 313 K, respectively. Total organic carbon balance (TOC) was controlled using Multi N/C 2100S TOC equipment (Analytik Jena, Jena, Germany). More detailed information about cellulose hydrolysis-dehydration experimental techniques, as well as analytic methods of reaction mixtures by HPLC and TOC can be found in our previous papers [23,24,36,52].

Product yields were revealed by the formula [26]:

\[ Y = \frac{C_{pr} V}{N_c \left( \frac{m_{Cell}}{M_{gly}} \right)} \cdot 100\% \]  

(1)

where \( Y \)—a product yield, mol%, \( C_{pr} \)—a product concentration, mol·L⁻¹, \( V \)—the reaction mixture volume, L, \( N_c \)—ratio of carbon in a product and glucose unit (1—for glucose, fructose, 5-HMF, etc.), \( M_{gly} \)—molar weight of glucose unit in cellulose, 162 g mol⁻¹, \( m_{Cell} \)—cellulose weighted, g.

3. Results and Discussion

3.1. Catalyst Characterization

The samples of ZrO₂ catalysts were prepared from different precursors by thermodegradation (TD), microwave treatment (MW), mechanical activation (MA), microwave treatment combined with mechanical activation (MA + MW), and the sol–gel method (SG). A description of the catalyst synthesis methods can be found in Section 2.2 and Table 2.

Two samples were prepared by thermal decomposition at 723 K (ZrO₂-T-723) and 873 K (ZrO₂-T-873). Zirconium dioxide samples prepared by microwave treatment differ in microwave irradiation power and processing temperature from <523 K to 873 K (samples ZrO₂-W-x where x = 1–7). When synthesizing ZrO₂-W-4 sample, the ZrO₂ precursor was ZrCO₃(OH)₂·xH₂O, for other five samples zirconyl nitrate monohydrate was used. Samples ZrO₂-MA-C and ZrO₂-MA-N both prepared by mechanical activation differ in the precursors of zirconium oxide: ZrCO₃(OH)₂·xH₂O and ZrO(NO₃)₂·H₂O, respectively.

The textural parameters of the catalysts were determined by low temperature nitrogen adsorption (Table 3). In general, the prepared catalysts were characterized by the absence of micropores and an insignificant volume of mesopores (except for ZrO₂-T-723, ZrO₂-W-7, ZrO₂-MA-W, and ZrO₂-MA-N). The specific surface area varied in a wide range of 6–134 m²·g⁻¹. Specific surface area and total pore volume decreased linearly with increasing temperature of calcination (Table 3, lines 1 and 2). Samples ZrO₂-T-873, ZrO₂-W-5, ZrO₂-W-6, ZrO₂-MA-W, and ZrO₂-SG, which were subjected to thermal or microwave treatment at 873 K, have a low specific surface area of 6–14 m²·g⁻¹.

The phase composition of the catalysts was studied by XRD. Dependence on the catalyst preparation method is observed (Table 3). Thus, zirconium oxides ZrO₂-MA-C and ZrO₂-MA-N prepared by mechanical activation contain a tetragonal phase, the phase composition does not depend on the zirconium oxide precursor (Table 3, lines 10 and 11). ZrO₂-MA-W prepared by mechanical activation, followed by microwave treatment has a monoclinic structure (Table 3, line 9). Sample ZrO₂-T-723 (Table 3, line 1) prepared by thermal decomposition contains equal proportions of monoclinic and tetragonal ZrO₂ phases. It should be noted that the monoclinic structure is more thermally stable than the tetragonal one. Samples prepared by microwave treatment turned out to be X-ray amorphous (Table 3, lines 3–8). Complement studies were carried out on the ZrO₂-W-7 sample, which was additionally calcined for 1 h at 723 K and 853 K. During this heat treatment, recrystallization
accompanied by an increase in the crystallite size occurs. The X-ray diffraction pattern of the additionally calcined sample shows lines of tetragonal and monoclinic zirconium oxide (Supplementary Information, SI, Figure S1). The content of the monoclinic phase is 38% and 56%, and the tetragonal phase is 62% and 44% when ZrO$_2$-W-7 sample calcined at 723 K and 853 K, respectively. We assume that pristine ZrO$_2$-W-7 sample prepared by microwave treatment at 593 K could contain small monoclinic structures.

Table 3. Textural properties, phase composition of ZrO$_2$ catalysts.

| No. | Catalyst Sample | Synthesis Method $^a$ | Texture Properties | Phase Composition $^b$ | pH$_{ZrO2}$ |
|-----|-----------------|-----------------------|--------------------|------------------------|------------|
|     |                 |                       | $S_{BET}$ (m$^2$ g$^{-1}$) | $V_0$ (cm$^3$ g$^{-1}$) | Main | Admixture |            |
| 1   | ZrO$_2$-T-723   | TD                    | 88                 | 0.24                   | 50% M | - | 7.7 |
| 2   | ZrO$_2$-T-873   | TD                    | 14                 | 0.11                   | n.d. | n.d. | 6.0 |
| 3   | ZrO$_2$-W-1     | W                     | n.d.               | n.d.                   | A | M | 6.5 |
| 4   | ZrO$_2$-W-3     | W                     | 12                 | 0.06                   | A | - | 1.0 |
| 5   | ZrO$_2$-W-4     | W                     | 85                 | 0.18                   | A | - | 2.1 |
| 6   | ZrO$_2$-W-5     | W                     | 13                 | 0.04                   | A | - | 7.4 |
| 7   | ZrO$_2$-W-6     | W                     | 13                 | 0.08                   | A | - | 6.0 |
| 8   | ZrO$_2$-W-7     | W                     | 134                | 0.37                   | A | - | 2.2 |
| 9   | ZrO$_2$-MA-W    | MA + MW              | 10                 | 0.39                   | M | - | 5.8 |
| 10  | ZrO$_2$-MA-C    | MA                    | 22                 | 0.06                   | T | M | 7.2 |
| 11  | ZrO$_2$-MA-N    | MA                    | 116                | 0.24                   | T | M | 7.5 |
| 12  | ZrO$_2$-SG      | SG                    | 6                  | 0.02                   | n.d. | n.d. | 8.7 |

$^a$ TD—thermodegradation, W—microwave treatment, MA—mechanical activation, SG—sol–gel method; $^b$ Phase composition: T—tetragonal, A—X-ray amorphous, M—monoclinic.

The acidic properties of zirconium oxide catalysts were estimated by measuring the pH of the mixtures of ZrO$_2$ with water ($\text{pH}_{\text{ZrO}_2}$) (Table 3). Previously, a correlation between total amount of acidic groups on the surface of solid catalysts and the pH at point of zero charge, as well as the pH of aqueous catalyst slurry was demonstrated [53]. The catalysts prepared by thermodegradation (Table 3, lines 1, 2) and mechanical activation (Table 3, lines 10, 11) showed moderate acidity values; $\text{pH}_{\text{ZrO}_2}$ was in the range of 6.0–7.7. $\text{pH}_{\text{ZrO}_2}$ varied in a wider range for the samples prepared by microwave treatment. ZrO$_2$-W-1 sample made using short processing time and lower microwave irradiation power had a pH value of 6.5 (Table 3, line 3). On the other hand, the increase in preparation time and micro-oven power (Table 3, lines 4, 5, 8) turned out to increasing catalyst acidity ($\text{pH}_{\text{ZrO}_2}$ 1.0–2.2). However, if the calcination temperature reaches 873 K (samples ZrO$_2$-W-5, ZrO$_2$-W-6, ZrO$_2$-MA-W, Table 3, lines 6, 7, 9), $\text{pH}_{\text{ZrO}_2}$ gains significantly up to 5.8–7.4. The sample ZrO$_2$-SG prepared by the sol–gel method had a weakly alkaline $\text{pH}_{\text{ZrO}_2}$ value of 8.7 (Table 3, line 12).

3.2. Cellulose Hydrolysis-Dehydration in the Presence of ZrO$_2$ Catalysts

The process of depolymerization of cellulose in an aqueous medium requires the use of rather harsh conditions, namely high temperatures and pressures. Therefore, solid catalysts are required to be highly stable in the hydrothermal reaction medium. To determine the stability of the prepared catalysts, they were subjected to hydrothermal tests at 453 K for 5 h. The amount of dissolved Zr revealed by ICP turned out to be insignificant. The values of zirconium dissolved after hydrothermal treatment were in the range of $\leq 1.3 \times 10^{-4} - 1.3 \times 10^{-3}$%. However, 1.3% of Zr dissolved in the case of processing ZrO$_2$-W-1 and ZrO$_2$-W-3 samples. These tests confirm high stability of the ZrO$_2$ catalysts.

Hydrothermal hydrolysis-dehydration of cellulose polysaccharide in the presence of ZrO$_2$ catalysts was carried out at 453 K under inert argon atmosphere. The results are shown in Table 4. Activity of ZrO$_2$ samples was studied in pure water without any co-catalysts. Glucose and 5-HMF were the major reaction products. Mannose and fructose
formation during isomerization of glucose was confirmed by HPLC. Formic and levulinic acids derived during the decomposition of 5-HMF, as well as furfural produced by the side transformation of fructose were also observed by HPLC analysis (Scheme 1). The total yield of all identified by-products did not exceed 5%. The only exception was the 14.6% yield of levulinic acid achieved in the presence of ZrO2-W-7 in 7 h of reaction. The formation of humins was also observed under hydrothermal reaction conditions.

Table 4. Glucose and 5-HMF yields and cellulose conversion achieved during cellulose hydrolysis-dehydration in the presence of ZrO2 catalysts.

| Entry No. | Catalyst Sample | Xb | TOFc | Glucose Yield, % | 5-HMF Yield, % |
|-----------|-----------------|----|------|------------------|----------------|
| 1         | ZrO2-T-723      | 37.4 | 0.12 | 0.0 0.5 0.6 1.3 1.4 1.4 | 0.0 0.3 1.0 2.4 3.0 3.8 |
| 2         | ZrO2-T-873      | 16.0 | 0.02 | 0.3 0.1 0.3 0.4 0.5 0.5 | 0.0 0.2 0.7 1.0 1.9 2.8 |
| 3         | ZrO2-W-1        | 37.8 | 0.09 | 0.0 0.5 0.2 1.4 1.9 0.0 | 0.0 0.5 n/d 2.6 3.9 0.9 |
| 4         | ZrO2-W-3        | 45.0 | 1.79 | 14.3 3.0 1.0 0.4 0.1 0.1 | 0.7 4.5 3.4 2.5 1.4 1.1 |
| 5         | ZrO2-W-4        | 50.1 | 0.62 | 0.8 1.1 8.8 7.9 4.5 2.8 | 2.2 4.0 6.2 7.0 7.5 7.4 |
| 6         | ZrO2-W-5        | 24.3 | 0.06 | 0.0 0.0 0.1 0.2 0.4 0.1 | 0.7 0.0 0.2 0.3 0.6 1.6 3.3 |
| 7         | ZrO2-W-6        | 16.1 | 0.02 | 0.0 0.1 0.2 0.4 0.6 0.7 | 0.0 0.2 0.5 0.7 1.6 2.4 |
| 8         | ZrO2-W-7        | 62.4 | 0.70 | 0.5 0.0 0.0 0.5 0.7 0.0 | 0.0 0.0 0.0 0.2 0.4 0.8 1.8 |
| 9         | ZrO2-MA-W       | 22.6 | 0.03 | 0.0 0.0 0.1 0.2 0.4 0.1 | 0.7 0.0 0.2 0.6 1.0 2.2 3.5 |
| 10        | ZrO2-MA-C       | 24.2 | 0.02 | 0.0 0.0 0.5 0.7 0.8 0.9 | 0.0 0.0 0.2 0.4 0.8 1.8 |
| 11        | ZrO2-MA-N       | 27.3 | 0.01 | 0.0 0.0 0.1 0.1 0.4 0.8 | 0.1 0.2 0.4 1.0 1.8 2.8 |
| 12        | ZrO2-SG         | 30.3 | 0.21 | 0.0 0.0 0.9 2.6 4.6 7.0 | 7.9 0.0 0.5 1.4 2.9 5.7 8.2 |

a Reaction conditions: initial concentrations of cellulose and catalyst 10 g·L−1, reaction volume 45 mL, 453 K, PAr 1 MPa, 1000 rpm, reaction time 7 h; b Cellulose conversion revealed by TOC at 7 h of the reaction; c mmol (5-HMF + Glu)·g−1·h−1.

Scheme 1. The hydrolysis-dehydration reaction of cellulose to glucose and 5-HMF.

It is interesting to compare cellulose conversion values with both pHZrO2 and specific surface values and phase composition of ZrO2 samples (Figure 1).

Note that pHZrO2 and SBET depend on preparation techniques. Thus, samples ZrO2-T-873, ZrO2-W-5, ZrO2-W-6, ZrO2-MA-W, ZrO2-MA-C and ZrO2-SG which has low SBET values of 6–14 m2·g−1 and high pHZrO2 in the range of 5.8–8.7 demonstrated moderate activity in cellulose depolymerization (16.0–30.3%) (Figure 1, Table 1 lines 2, 6, 7, 10 and 12). The increase in specific surface area of ZrO2 up to 88–116 m2·g−1 without significant changing of pHZrO2 (7.5–7.7) did not improve actives of zirconia (samples ZrO2-MA-N and ZrO2-T-723, Figure 1, Table 1 lines 1 and 11). On the other hand, ZrO2-W-3, which has low SBET value of 12 m2·g−1 and high pHZrO2 equal to 1.0 let one to reach 45.0% of cellulose conversion (Figure 1, Table 1 line 4). The highest activities have been demonstrated by ZrO2-W-4 and ZrO2-W-7 samples prepared by microwave treatment, which
has both significant specific surface areas and pH\(_{\text{ZrO}_2}\) values of 2.1–2.2. 50.1 and 62.4% cellulose conversions have been achieved in the presence of ZrO\(_2\)-W-4 and ZrO\(_2\)-W-7, respectively (Figure 1, Table 1 lines 5, 7, and Table 4 lines 5, 8). Interestingly, both ZrO\(_2\)-W-4 and ZrO\(_2\)-W-7 were more active compared to ZrO\(_2\)-W-3, characterized by higher acidity but lower \(S_{\text{BET}}\) value. Thus, activity of ZrO\(_2\) significantly increases with increasing catalyst acidity and density of acid sites, which depends on a specific surface area. The highest cellulose depolymerization value equal to 62.4% have been demonstrated for ZrO\(_2\)-W-7. Interestingly, the increasing temperature of microwave treatment causes decreasing activities of ZrO\(_2\)-W series due to diminishing both acidity and \(S_{\text{BET}}\) value. It should be emphasized, that catalysts prepared by different techniques and having similar parameters of pH\(_{\text{ZrO}_2}\) and \(S_{\text{BET}}\) show compatible values of the polysaccharide conversion, for example ZrO\(_2\)-T-873 and ZrO\(_2\)-W-6 as well as ZrO\(_2\)-MA-C and ZrO\(_2\)-W-5 (Figure 1).

The phase composition of ZrO\(_2\) could also influence the catalytic properties of zirconia [40]. However, in our study, the phase composition of ZrO\(_2\), which had similar pH\(_{\text{ZrO}_2}\) and \(S_{\text{BET}}\) parameters, did not affect cellulose conversion significantly. For example, depolymerization degrees of the polysaccharide were 24.2–24.3% for ZrO\(_2\)-MA-C with tetragonal phase and X-ray amorphous ZrO\(_2\)-W-5 catalysts. Precursors of ZrO\(_2\) could also affect the textural and acid properties of the catalysts. Thus, ZrO\(_2\)-MA-C and ZrO\(_2\)-MA-N were prepared from ZrCO\(_3\)(OH)\(_2\)·xH\(_2\)O and ZrO(NO\(_3\))\(_2\)·H\(_2\)O, respectively, under equal conditions of mechanical activation. Specific surface area and pore volume of ZrO\(_2\)-MA-N (116 m\(^2\)·g\(^{-1}\), 0.24 cm\(^3\)·g\(^{-1}\)) were 4–5 times higher compared to ones of ZrO\(_2\)-MA-C (22 m\(^2\)·g\(^{-1}\), 0.06 cm\(^3\)·g\(^{-1}\)). However, both ZrO\(_2\)-MA-C and ZrO\(_2\)-MA-N demonstrated moderate activity in terms of cellulose conversion due to similar acidity 7.2–7.5 (Table 3, lines 10,11,12, Table 4, lines 10,11).

Watanabe et al. [44] and Charoenlimkun et al. [40] previously reported that catalytic activity depended on both acid and base properties of catalysts. Acid centres are responsible...
for hydrolysis, while base sites catalyse isomerization of glucose to fructose, facilitating 5-HMF formation [40]. According to our results shown on Figure 2, the initial reaction rates (R) of glucose and 5-HMF formation depended on pH\textsubscript{ZrO2}. The decrease in pH\textsubscript{ZrO2} gains both initial rates of glucose and 5-HMF formation. However, ZrO\textsubscript{2}-SG samples with pH\textsubscript{ZrO2} value of 8.7 demonstrated notable activity to glucose dehydration to 5-HMF. This may indicate that both acid and base sites of ZrO\textsubscript{2} are involved to reaction.

Summarizing the above section, the proposed catalyst ZrO\textsubscript{2}-W-7 was prepared by microwave treatment under low temperature. Thus, such a synthesis approach can be assumed to be the most promising. This catalyst preparation technique provides high acidity and specific surface areas which supply high catalytic efficiency.

3.3. Perspectives of ZrO\textsubscript{2} Catalysts

As mentioned above, the yields of glucose and 5-HMF can reach 12.7 and 20.6%, respectively, over ZrO\textsubscript{2} catalysts [38–45]. The main results published previously are captured in Table 1. Gliozzi et al. [42] showed 8.2% total yield of 5-HMF and furfural from softwood in the presence of silica-zirconia catalyst at 423 K. Biomass conversion was 34%. Yang et al. [45] transformed cotton cellulose over mixed ZnO–ZrO\textsubscript{2} under hydrothermal conditions. 5-HMF yield reached 3.76% at 1.4 MPa autogenic pressure, 463 K and cellulose conversion 52.18%. Gavilà et al. [41] reported transformation of microcrystalline cellulose to 5-HMF at 453 K, pressure 3 MPa. The selectivity of the target product was ~20.6%. Watanabe et al. [44] investigated transformation of glucose and fructose in the presence of oxide catalysts at 473 K. 5-HMF yields were ~5.4% and ~15% from glucose and fructose, respectively, over zirconium oxide. Chareonlimkun et al. [40] used TiO\textsubscript{2}, ZrO\textsubscript{2} and mixed TiO\textsubscript{2}–ZrO\textsubscript{2} catalysts prepared by co-precipitation, sol–gel and physical mixing methods when processing different biomass resources (sugarcane, bagasse, rice husk and corn cob). ZrO\textsubscript{2} catalyst derived via precipitation demonstrated higher activity; 4.2 and 1.8% yields of 5-HMF and glucose were reached at 523 K and 34.5 MPa. Qiao et al. [46,47] investigated transformation of microcrystalline cellulose over NbO\textsubscript{x}/ZrO\textsubscript{2} and pure ZrO\textsubscript{2} catalysts was reported by [34]. Experiments were carried out at 453 K under 1 MPa pressure of Ar. Maximum yields of 5-HMF and glucose were 12.7 and 13.3%, respectively, in the presence of ZrO\textsubscript{2}.

According to the data obtained in this work, the most promising catalyst is ZrO\textsubscript{2}-W-7 prepared by microwave treatment of zirconyl oxyxinitrate for 3 min. High activity of the
catalyst is confirmed by significant cellulose conversion degree equal to 62.4% and notable yields of glucose and 5-HMF (Table 3, line 8). Influence of ZrO\textsubscript{2}-W-7 catalyst loading was also investigated. Catalyst: cellulose ratio equal to 1:20 was found to be the optimum one (Table 5 and Figure 3).

Table 5. One-pot depolymerization of cellulose to glucose and 5-HMF in the presence of ZrO\textsubscript{2}-W-7 at [Cat]/[Cell] ratios 1:1 and 1:20 g·g\textsuperscript{−1}\textsuperscript{a}.

| Catalyst Sample | [Cat]/[Cell] | pH\textsubscript{ZrO\textsubscript{2}} | X\textsuperscript{c} (%) | \(R_r\) \((\text{mol}·\text{L}^{-1}·\text{s}^{-1}·10^7)\) | Maximum Yields of the Products (%) |
|----------------|--------------|----------------------------------|-----------------|-----------------|----------------------------------|
| ZrO\textsubscript{2}-W-7 | 1:1          | 2.2                              | 62.4            | 12.4            | \(Y_{\text{Glu}}\) | \(\tau\), h | \(Y_{5\text{-HMF}}\) | \(\tau\), h |
|               | 1:20\textsuperscript{b} | 3.4                              | 53.1            | 18.6            | 18.0              | 7       | 15.0              | 7       |

\textsuperscript{a} Reaction conditions: initial concentrations of cellulose and catalyst 10 g·L\textsuperscript{−1}, reaction volume 45 mL, 453 K, P\textsubscript{Ar} 1 MPa, 1000 rpm, reaction time 7 h; \textsuperscript{b} [Cat]/[Cell] = 1:20 g·g\textsuperscript{−1}. Catalyst loading 0.5 g·L\textsuperscript{−1}; \textsuperscript{c} Cellulose conversion revealed by TOC at 7 h of the reaction.

Figure 3. Glucose and 5-HMF yields reached during cellulose hydrolysis-dehydration in the presence of ZrO\textsubscript{2}-W-7 catalyst. Reaction conditions: initial concentration of cellulose 10 g·L\textsuperscript{−1}, initial catalyst loading 10 (0.5) g·L\textsuperscript{−1}, reaction volume 45 mL, 453 K, P\textsubscript{Ar} 1 MPa, 1000 rpm, reaction time 7 h.

Catalyst: cellulose = 1:1 caused a decrease in yields of glucose and 5-HMF due to significant transformation of the target products into side products in the presence of an excess of active sites in the reaction medium; 18 and 15% yield of glucose and 5-HMF were achieved under the optimum ratio of cellulose:ZrO\textsubscript{2}-W-7 = 20:1 (Table 5).

To compare the efficiency of ZrO\textsubscript{2} catalysts, TOF values were calculated according to the following equation [26]:

\[
\text{TOF} = \frac{C_{\text{Glu}+5\text{-HMF}}}{m_{\text{cat}} \cdot t}
\]

where TOF is the turnover frequency, mmol·g\textsuperscript{−1}·h\textsuperscript{−1}, \(C_{\text{Glu}+5\text{-HMF}}\) is amount of glucose and 5-HMF formed, mmol, \(m_{\text{cat}}\) is the catalyst amount, g, and \(t\) is the reaction time, h.

The most promising ZrO\textsubscript{2} catalyst studied in this work (TOF value 15.1 mmol·g\textsuperscript{−1}·h\textsuperscript{−1}) was significantly more active than the systems reported elsewhere (Table 6).
Table 6. TOF of ZrO2 catalysts in cellulose hydrolysis-dehydration.

| Reaction Conditions | TOF (mmol·g⁻¹·h⁻¹) | Ref. |
|---------------------|----------------------|------|
| T, P                | Cell:H₂O:Cat a       |      |
| 463 K, 1.4 MPa      | 1:100:1              | 0.10 | [45] |
| 453 K, 3 MPa        | 4:250:1              | 3.5 × 10⁻⁵ | [41] |
| 453 K, 1 MPa        | 1:100:1              | 0.83 | [43] |
| 453 K, 1 MPa        | 20:2000:1            | 15.1 | This work |

a Cell:H₂O:cat—ratio of cellulose (g)—water (mL)—catalyst (g).

To reveal the stability of zirconia catalytic systems, ZrO₂-W-7 was tested in five runs of cellulose hydrolysis-dehydration reaction. After each cycle, the catalyst spent was separated by centrifugation, washed several times with Milli-Q water, dried at 333 K, and reused in a new cycle. Figure 4 shows the results of catalyst reuse experiments. In five cycles, the yields of glucose and 5-HMF decreased by 5%.

Figure 4. Glucose and 5-HMF yields reached during 5 runs of cellulose depolymerization over ZrO₂-W-7 catalyst. Reaction conditions: [Cell] = 10 g·L⁻¹, [Cell]:[Cat] = 1:20, 453 K, P Ar 1 MPa, 1000 rpt, reaction time 7 h.

4. Conclusions

The transformation of cellulose was studied in hydrothermal pure water at 453 K to efficiently derive glucose and 5-HMF. The ZrO₂ catalysts prepared by microwave treatment gained higher efficiency than ones derived by thermolysis, mechanical activation and sol–gel methods. The catalyst calcination temperature also had a significant impact on reactivity with regard to acidity and S_BET. The most promising ZrO₂ prepared by microwave irradiation at 593 K demonstrated high stability in five reaction runs and the highest activity (TOF 15.1 mmol·g⁻¹·h⁻¹) compared to the systems reported elsewhere; 18 and 15% yields of glucose and 5-HMF were reached without any co-catalyst under optimized cellulose/catalyst ratio = 20/1 (g/g).

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11111359/s1. Figure S1: XRD-patterns of ZrO₂-W-7 sample.

Author Contributions: Conceptualization, L.A.I., O.P.T. and N.V.G.; Methodology, L.A.I. and I.S.Y.; Validation, L.A.I. and N.V.G.; Investigation, O.L.O., T.B.M. and I.S.Y.; Writing—Original Draft Preparation, O.L.O.; Writing—Review and Editing, N.V.G.; Visualization, O.L.O. and N.V.G.; Supervision, V.N.P.; Project Administration, N.V.G. and O.P.T.; Funding Acquisition, O.P.T. All authors have read and agreed to the published version of the manuscript.
Funding: This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the framework of State research program of the Boreskov Institute of Catalysis (project AAAA-A21-121011390007-7).

Conflicts of Interest: The authors declare that they have no conflict of interest.

References
1. Corma, A.; Iborra, S.; Veltay, A. Chemical Routes for the Transformation of Biomass into Chemicals. Chem. Rev. 2007, 107, 2411–2500. [CrossRef]
2. Agarwal, B.; Ahluwalia, V.; Pandey, A.; Sangwan, R.S.; Elumalai, S. Sustainable Production of Chemicals and Energy Fuel Precursors from Lignocellulosic Fractions. In Biofuels, Green Energy and Technology; Springer: Singapore, 2017, pp. 7–33. [CrossRef]
3. Gromov, N.V.; Taran, O.P.; Parmon, V.N. CHAPTER 3 Catalysts for Depolymerization of Biomass. In Sustainable Catalysis for Biorefineries; The Royal Society of Chemistry: Croydon, UK, 2018; pp. 65–97. [CrossRef]
4. Chernyshev, V.M.; Kravchenko, O.A.; Ananikov, V.P. Conversion of plant biomass to furan derivatives and sustainable access to the new generation of polymers, functional materials and fuels. Russ. Chem. Rev. 2017, 86, 357–387. [CrossRef]
5. Alonso, D.M.; Bond, J.Q.; Dumesic, J.A. Catalytic conversion of biomass to biofuels. Green Chem. 2010, 12, 1493–1513. [CrossRef]
6. Delidovich, I.; Leonhard, K.; Palkovits, R. Cellulose and hemicellulose valorisation: An integrated challenge of catalysis and reaction engineering. Energy Environ. Sci. 2014, 7, 2803–2830. [CrossRef]
7. Chernyshhev, VM.; Kravchenko, O.A.; Ananikov, V.P. Conversion of plant biomass to furan derivatives and sustainable access to the new generation of polymers, functional materials and fuels. Russ. Chem. Rev. 2017, 86, 357–387. [CrossRef]
8. Razonovskii, S.D.; Podmaster’ev, V.V.; Zelenetskii, A.N. Mechanochemical methods of activating processes of biomass pretreatment. Top. Catal. 2011, 54, 1–14. [CrossRef]
9. van Putten, R.-J.; van der Waal, J.C.; de Jong, E.; Rasrendra, C.B.; Heeres, H.J.; de Vries, J.G. Hydroxymethylfurfural, A Versatile Green Process: A promising biochemical and biofuel feedstock. Biofuels, Green Energy and Technology 2012, 3, 6–8. [CrossRef]
10. Lewkowski, J. Synthesis, Chemistry and Applications of 5-Hydroxymethyl-furfural And Its Derivatives. ARKIVOC 2001, 2001, 17–54. [CrossRef]
11. Hii, S.L.; Tan, J.S.; Ling, T.C.; Ariff, A.B. Pullulanase: Role in Starch Hydrolysis and Potential Industrial Applications. Enzym. Res. 2012, 2012, 2012, 921362. [CrossRef]
12. He, Y.; Hoff, T.C.; Emdadi, L.; Wu, Y.; Bouraima, J.; Liu, D. Catalytic consequences of micropore topology, mesoporosity, and acidity on the hydrolysis of sucrose over zeolite catalysts. Catal. Sci. Technol. 2014, 4, 3064–3073. [CrossRef]
13. Scholz, M.J.; Riley, M.R.; Cuello, J.L. Acid hydrolysis and fermentation of microalgal starches to ethanol by the yeast Saccharomyces cerevisiae. Biomass Bioenergy 2013, 48, 59–65. [CrossRef]
14. Razumovskii, S.D.; Podmaster’ev, V.V.; Zelenetskii, A.N. Mechanochemical methods of activating processes of biomass pretreatment. Top. Catal. 2011, 54, 1–14. [CrossRef]
15. Aymonier, C.; Gromov, N.V.; Taran, O.P.; Parmon, V.N. Hydrolysis–dehydration of cellulose to glucose and 5-hydroxymethylfurfural over Sibunit solid acid carbon catalysts under semi-fluid conditions. Wood Sci. Technol. 2021, 55, 607–624. [CrossRef]
16. Aymonier, C.; Gromov, N.V.; Taran, O.P.; Parmon, V.N. Hydrolysis–dehydration of cellulose to glucose and 5-Hydroxymethylfurfural Over Solid Acid Carbon Catalysts. Top. Catal. 2018, 61, 1912–1927. [CrossRef]
26. Gromov, N.V.; Taran, O.P.; Aymonier, C.; Parmon, V.N. Kinetic modeling of the multistep hydrolysis-dehydration of cellulose to platform molecules over a solid carbon acid catalyst in pure water. React. Kinet. Mech. Catal. 2020, 130, 669–684. [CrossRef]

27. Pang, J.; Wang, A.; Zheng, M.; Zhang, T. Hydrolysis of cellulose into glucose over carbons sulfonated at elevated temperatures. Chem. Commun. 2010, 46, 6935–6937. [CrossRef] [PubMed]

28. Cao, L.; Iris, K.M.; Chen, S.S.; Tsang, D.C.; Wang, L.; Xiong, X.; Poon, C.S. Production of 5-hydroxymethylfurfural from starch-rich food waste catalyzed by sulfonated biochar. Bioresources. Technol. 2018, 252, 76–82. [CrossRef]

29. Lam, E.; Luong, J.H.T. Carbon Materials as Catalyst Supports and Catalysts in the Transformation of Biomass to Fuels and Chemicals. ACS Catal. 2014, 4, 3393–3410. [CrossRef]

30. Kobayashi, H.; Komanoya, T.; Hara, K.; Fukuoka, A. Water-Tolerant Mesoporous-Carbon-Supported Ruthenium Catalysts for the Hydrolysis of Cellulose to Glucose. ChemSusChem 2010, 3, 440–443. [CrossRef]

31. Onda, A.; Ochi, T.; Yanagisawa, K. Selective hydrolysis of cellulose into glucose over solid acid catalysts. Green Chem. 2008, 10, 1033–1037. [CrossRef]

32. Wang, H.; Zhang, C.; He, H.; Wang, L. Glucose production from hydrolysis of cellulose over a novel silica catalyst under hydrothermal conditions. J. Environ. Sci. 2012, 24, 473–478. [CrossRef]

33. Dhepe, P.L.; Fukuoka, A. Cellulose Conversion under Heterogeneous Catalysis. ChemSusChem 2008, 1, 969–975. [CrossRef] [PubMed]

34. Dhepe, P.L.; Ohashi, M.; Inagaki, S.; Ichikawa, M.; Fukuoka, A. Hydrolysis of sugars catalyzed by water-tolerant sulfonated mesoporous silicas. Catal. Lett. 2005, 102, 163–169. [CrossRef]

35. Nandiwa, K.Y.; Galande, N.D.; Thakur, P.; Sawant, S.D.; Zambre, V.P.; Bokade, V.V. One-Pot Synthesis of 5-Hydroxymethylfurfural over Highly Active Bimodal Micro/Mesoporous H-ZSM-5 Catalyst. ACS Sustain. Chem. Eng. 2014, 2, 1928–1932. [CrossRef]

36. Gromov, N.V.; Medvedeva, T.B.; Taran, O.P.; Timofeeva, M.N.; Parmon, V.N. Hydrolysis of Cellulose in the Presence of Catalysts Based on Cesium Salts of Heteropoly Acids. Catal. Ind. 2021, 13, 73–80. [CrossRef]

37. Tian, J.; Fang, C.; Cheng, M.; Wang, X. Hydrolysis of Cellulose over CsH3–xPW12O40 (X = 1–3) Heteropoly Acid Catalysts. J. Struct. Chem. 2019, 60, 11359–11365. [CrossRef]

38. Pattnaik, F.; Nanda, S.; Kumar, V.; Naik, S.; Dalai, A.K. Subcritical water hydrolysis of Phragmites for sugar extraction and utilization of ZrO2 to inhibit recrystallization of cellulose. Carbohydr. Polym. 2020, 295, 150–156. [CrossRef] [PubMed]

39. Antonetti, C.; Melloni, M.; Licursi, D.; Fulignati, S.; Ribechini, E.; Rivas, S.; Parajó, J.C.; Cavani, F.; Raspoli Galletti, A.M. Microwave-assisted dehydration of fructose and inulin to HMF catalyzed by niobium and zirconium phosphate catalysts. Appl. Catal. B Environ. 2017, 206, 364–377. [CrossRef]

40. Chareonlimkun, A.; Champreda, V.; Shotipruk, A.; Laosiripojana, N. Catalytic conversion of sugarcane bagasse, rice husk and corn cob in the presence of TiO2, ZrO2 and mixed-oxide TiO2–ZrO2 under hot compressed water (HCW) condition. Bioresour. Technol. 2010, 101, 4179–4186. [CrossRef]

41. Gavilá, L.; Güell, E.J.; Maru, B.T.; Medina, F.; Constanti, M. Combining catalytical and biological processes to transform cellulose into high value-added products. Phys. Sci. Rev. 2017, 2, 26. [CrossRef]

42. Gliozzi, G.; Innorta, A.; Mancini, A.; Bortolo, R.; Perego, C.; Ricci, M.; Cavani, F. Zr/TiO2 Catalyst for the Direct acid Chemo-hydrolysis of non-pretreated microcrystalline cellulose and softwood sawdust. Appl. Catal. B Environ. 2014, 141, 24–33. [CrossRef]

43. Gromov, N.V.; Taran, O.P.; Semeykina, V.S.; Danilova, I.G.; Pestunov, A.V.; Parkhomchuk, E.V.; Parmon, V.N. Solid Acidic NbOx/ZrO2 Catalysts for Transformation of Cellulose to Glucose and 5-Hydroxymethylfurfural in Pure Hot Water. Catal. Lett. 2017, 147, 1485–1495. [CrossRef]

44. Watanabe, M.; Aizawa, Y.; Iida, T.; Nishimura, R.; Inomata, H. Catalytic glucosylation and fructose conversions with TiO2 and ZrO2 in water at 473K: Relationship between reactivity and acid–base property determined by TDSP measurement. Appl. Catal. A Gen. 2005, 295, 150–156. [CrossRef]

45. Yang, F.; Li, G.; Gao, P.; Lv, X.-N.; Sun, X.; Liu, Z.-H.; Fan, H. Mild Hydrothermal Degradation of Cotton Cellulose by using a Mixed-Metal-Oxide ZnO–ZrO2 Catalyst. Energy Technol. 2013, 1, 581–586. [CrossRef]

46. Qiao, Y.; Feng, L.; Li, Z.; Zhang, Z.; Chen, J.; Na, H.; Zhu, J.; Chen, L. Effect of Adsorption of ZrO2 in Catalysts on the Efficiency of Hydrolysis of Cellulose to Sugar in Aqueous System under Microwave Radiation. Chin. J. Chem. 2020, 38, 399–405. [CrossRef]

47. Qiao, Y.; Zhai, C.; Liu, F.; Chen, L.; Na, H.; Chen, J.; Zhu, J. Highly efficient microwave driven assisted hydrolysis of cellulose to sugar with the utilization of ZrO2 to inhibit recrystallization of cellulose. Carbohydr. Polym. 2020, 228, 115358. [CrossRef] [PubMed]

48. Bolotov, V.A.; Chernousov, Y.D.; Udalov, E.I.; Tanashev, Y.Y.; Parmon, V.N. Features of high-temperature chemical reactions under the action of a microwave field. Vestnik NGU. Ser. Fiz. 2009, 4, 78–83. [CrossRef]

49. Avvakumov, E.G. Mechanical Methods of Activation of Chemical Processes; Nauka: Novosibirsk, Russia, 1986.

50. Tsibulya, S.V.; Cherapeanova, S.V.; Soloviyova, L.P. Polycrystal software package for IBM/PC. J. Struct. Chem. 1996, 37, 332–334. [CrossRef]

51. Yatsenko, D.A.; Medvedeva, T.B. Estimating Crystallity Index of Microcrystalline Cellulose Using Diffraction Methods. J. Struct. Chem. 2019, 60, 1430–1436. [CrossRef]
52. Gromov, N.V.; Medvedeva, T.B.; Rodikova, Y.A.; Timofeeva, M.N.; Panchenko, V.N.; Taran, O.P.; Kozhevnikov, I.V.; Parmon, V.N. One-pot synthesis of sorbitol via hydrolysis-hydrogenation of cellulose in the presence of Ru-containing composites. *Bioresour. Technol.* 2021, 319, 124122. [CrossRef] [PubMed]

53. Taran, O.P.; Polyanskaya, E.M.; Ogorodnikova, O.L.; Descorme, C.; Besson, M.; Parmon, V.N. Sibunit-based catalytic materials for the deep oxidation of organic ecotoxicants in aqueous solution: I. Surface properties of the oxidized sibunit samples. *Catal. Ind.* 2010, 2, 381–386. [CrossRef]