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Hydrolysis–dehydration of cellulose to glucose and 5-hydroxymethylfurfural over Sibunit solid acid carbon catalysts under semi-flow conditions

Cyril Aymonier¹ · Nikolay V. Gromov^{2,3} · Oxana P. Taran^{2,4} · Valentin N. Parmon²

Abstract

Glucose is a widely used chemical, food and feedstock. 5-Hydroxymethylfurfural (5-HMF) is one of the platform molecules, which could be applied in chemical and fuel industries. This work presents the possibility of glucose and 5-HMF production from inedible cellulose, which is the main component of renewable plant (wood) biomass via one-pot hydrolysis–dehydration over solid acid catalysts based on Sibunit carbon material. The catalysts prepared via oxidation with wet air mixture, HNO₃, sulfonation by fuming H₂SO₄ at 80–200 °C or combination of the techniques demonstrated high activity under hydrothermal semi-flow conditions. Dependences of both glucose and 5-HMF formation on catalyst acidity and the nature and amount of surface acid groups are revealed. The total surface acidity but not the chemical nature of the groups is responsible for effective cellulose hydrolysis to glucose. On the other hand, sulfo groups demonstrate noticeable activity in 5-HMF formation from glucose. Glucose and 5-HMF can be derived from the polysaccharide with yields up to 75 and 10%, respectively.

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Introduction

Cellulose is the main component of renewable wood biomass and a promising environmentally friendly alternative to fossil resources for the production of fuel components and valuable chemicals (Besson et al. 2014; Bhaumik and Dhepe 2016; Murzin and Salmi 2012; Van de Vyver et al. 2011; van Putten et al. 2013). Glucose, which can be derived by the hydrolysis of cellulose, is a valuable chemical, food and feedstock. 5-Hydroxymethylfurfural (5-HMF), which is one of *platform molecules*, can also be derived from the polysaccharide via hydrolysis–dehydration. Chemical industry (polymer materials, solvents, resins, biofuel additives) is a potential field for 5-HMF application (Mukherjee et al. 2015). The development of catalytic one-pot technologies seems to be a promising way for the synthesis of glucose and 5-HMF directly from cellulose in aqueous medium (Bhaumik and Dhepe 2016; Gallezot 2012; Mukherjee et al. 2015; Murzin and Salmi 2012; Van de Vyver et al. 2011; van Putten et al. 2013). One-pot technique eliminates stages of semi-product isolation and purification. Non-aqueous media are highly prohibited for the cellulose depolymerization because of environmental problems and the high cost of organic solvents and ionic liquids. The crystal structure makes inedible cellulose chemically stable and water insoluble (Gromov et al. 2016; Perez and Mazeau 2005) and, therefore, the advanced cellulose processing to glucose and 5-HMF is rather difficult (Bobleter 2005; Yu et al. 2008). Harsh conditions (high temperatures) are unavoidable for cellulose to be depolymerized efficiently.

Cellulose depolymerization in sub-, near- and supercritical water is suitable for different products to be derived (Fig. 1). However, after passing through the critical point, the rates of cellulose depolymerization and glucose destruction increase significantly (Sasaki et al. 1998). Hence, time for the formation of target products, which are soluble in water, becomes critically short. The processing could be finished in few seconds. Longer reaction times result in the formation of deep decomposition products: coke and gases. Subcritical conditions (150–350 °C) seem to be more perspective for the liquefaction of biomass; the low-temperature limit is suitable for manufacturing valuable compounds (Fig. 1) (Loppinet-Serani and Aymonier 2014).

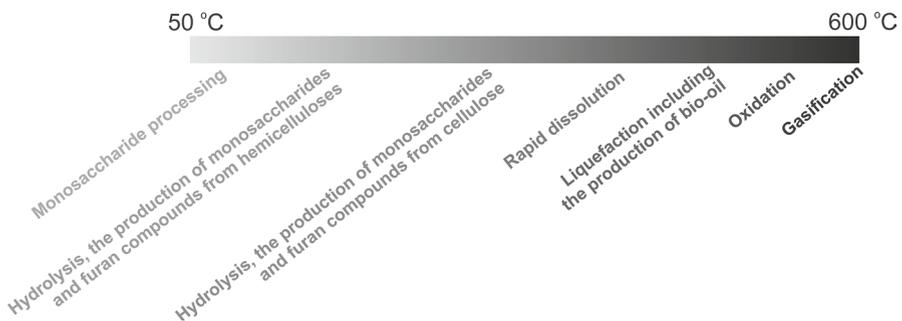


Fig. 1 Optimal temperature ranges for processing cellulose

Cellulose hydrolysis can take place in pure water without any catalyst at temperatures higher than 150 °C (Bobleter 2005; Yu et al. 2008). So far, most of the studies on cellulose depolymerization have been carried out in batch reactor, whereas flow systems have been rarely used. Sasaki et al. (1998) investigated the hydrolysis of microcrystalline cellulose in a flow reactor at 290–400 °C and under a pressure of 25 MPa. They confirmed the formation of soluble oligosaccharides and some other products (erythrose, dihydroxyacetone, fructose, glucose, glyceraldehyde, piruvaldgid). The total yield reached 75% (Sasaki et al. 1998). Rogalinski et al. (2008a, b) studied the conversion of cellulose in both batch and flow reactors under relatively mild subcritical conditions; the experiment temperatures were in the range of 210–310 °C. The liquefaction of the substrate reached 25% and the yields of glucose and the monosaccharide degradation products were 5 and 10%, respectively (Rogalinski et al. 2008a). Zhao et al. (2009, 2011) suggested to combine super- and subcritical conditions to increase the total yield of glucose. The authors proposed a processing method, which consisted of two steps. In the first step, supercritical conditions were applied to the cellulose dissolution and the second step operated under subcritical conditions was used for the hydrolysis of soluble oligosaccharides. They achieved a 40% yield of glucose and glyceraldehyde; erythrose, dihydroxyacetone and 5-HMF were also recorded. The maximum total yield of the side products was equal to 28.3%. Apparently, this is the best result achieved in sub- and supercritical water in terms of glucose and 5-HMF production (Zhao et al. 2009, 2011).

The combination of hydrothermal and catalytic approaches makes possible the improvement in substrate conversion, yields and selectivity of major product, as well as decreasing the energetic consumption due to milder conditions (Loppinet-Serani and Aymonier 2014). Cellulose depolymerization can be carried out in the presence of soluble or solid catalysts and the latter seem to be more prospective. Among the solid catalysts being stable in subcritical aqueous medium (TiO₂, ZrO₂, CeO₂, Al₂O₃, C) and interesting for cellulose transformation to glucose and 5-HMF, carbons are of particular interest due to their high mechanical and chemical stability (Amarasekara 2013; Bhatnagar et al. 2013; Burgess et al. 2015; Chareonlimkun et al. 2010a, b; Jiang et al. 2014; Kim and Ihm 2011; Lai et al. 2011; Levec and Pintar 2007; Liu et al. 2010; Nakajima and Hara 2012; Nakajima et al. 2008; Nandiwale et al. 2014; Shrotri et al. 2017; Takagaki et al. 2011, 2008; Taran et al. 2013, 2011b; Wang et al. 2012; Watanabe et al. 2005; Yang et al. 2011a, b). However, pure non-modified carbons characterized by insufficient surface acidity show insignificant catalytic activity in polysaccharide depolymerization reactions (Foo and Sievers 2015; Fukuhara et al. 2011; Pang et al. 2010). Therefore, carbons undergo additional modifications for strong acidic groups which may be catalytically active to be fixed or generated on their surfaces (Bhatnagar et al. 2013; Burgess et al. 2015; Liu et al. 2010; Nakajima and Hara 2012; Nakajima et al. 2008; Shrotri et al. 2017; Taran et al. 2013, 2011b). The treatment of carbon materials with concentrated or fuming sulfuric acid is the most well-practiced method for supporting acid groups (Cao et al. 2018a; Dora et al. 2012; Foo and Sievers 2015; Guo et al. 2012b; Kitano et al. 2009; Li et al. 2013, 2018; Liu et al. 2014; Nakajima and Hara 2012; Onda et al. 2008, 2009; Pang et al. 2010; Shen et al. 2014; Suganuma et al. 2008, 2010; Xiong et al. 2018). Moreover, treatments with solutions of H₃PO₄ (Cao et al. 2018b;

Gromov et al. 2018), HNO_3 (Gromov et al. 2018; Pang et al. 2010; Van Pelt et al. 2014), H_2O_2 (Foo and Sievers 2015; Van Pelt et al. 2014), oxidation by air (Shrotri et al. 2017; Van Pelt et al. 2014), wet air (Gromov et al. 2018; Taran et al. 2011a) and NaOCl (Taran et al. 2011a) are also possible.

This work reports the activity of Sibunit carbon material modified by different agents (H_2SO_4 , HNO_3 or wet air) in the transformation of cellulose to the target molecules glucose and 5-HMF under semi-flow conditions as well as the main factors, which influence the catalytic activity.

Materials and methods

Chemicals and materials

The following inorganic and organic chemicals were used in this work without any preliminary purification: H_2SO_4 (96%, extra pure, Acros Organics), NaOH (high purity, Ekros), HNO_3 (high purity, 18–4, Reakhim, Russia), acetic acid (Acros Organics), formic acid (98%, Panreac), D-glucose (99%, Fisher Chemical), D-fructose (>99%, Sigma-Aldrich), D-mannose (>99%, Sigma-Aldrich), D-cellobiose (>99%, Alfa Aesar), 5-hydroxymethylfurfural (>98%, Sigma-Aldrich), levulinic acid (98%, Acros Organics) and furfural (>99%, Sigma-Aldrich). Milli-Q water (Millipore, France) was used for preparing all the solutions.

Mechanically activated microcrystalline cellulose ($13 \pm 6 \mu\text{m}$, crystallinity ca. 37%, Vekton, Russia) was used in all the experiments. Cellulose activation and characterization techniques were the same as discussed previously (Gromov et al. 2016, 2017, 2018; Pestunov et al. 2015).

Synthesis and characterization of catalysts

Commercial mesoporous graphite-like carbon material Sibunit (fraction of 56–94 μm , Omsk, Russia) washed with boiling deionized water was used to prepare all the catalysts. The catalysts were prepared as detailed previously (Gromov et al. 2018). Three series of catalysts were prepared. The first one was prepared via treatment of Sibunit by fuming H_2SO_4 for 10 h at 80, 150 and 200 °C (the sulfonated samples Sib-S80, Sib-S150 and Sib-S200, respectively). The second series was made by treating initial carbon with 23 or 32 v/v.% HNO_3 solution at 90 °C or wet gas mixture (20 v/v.% of O_2 in N_2) at 450 °C (Gromov et al. 2018; Taran et al. 2011a) (oxidized catalysts Sib-N23, Sib-N32 and Sib-WA, respectively). To prepare the third group of oxidized–sulfonated catalysts, Sib-N23, Sib-N32 and Sib-WA were treated by fuming H_2SO_4 at 200 °C additionally for 10 h (samples Sib-WA-S200, Sib-N23-S200, Sib-N32-S200). Previously, this temperature of sulfuric acid treatment provided the best performance of carbon catalysts (Gromov et al. 2018). Prior to any catalytic experiments to remove weakly fixed acidic groups, all the catalysts were treated under hydrothermal conditions for 3 h, washed with boiling water and dried in argon. The preparation techniques are described in brief in Table 1.

Table 1 Techniques used for the modification of Sibunit carbon surface

Catalyst	Preparation technique
Sib	Mesoporous carbon material Sibunit used for the preparation of all the catalysts
Sib-S80	Sulfonation by fuming H ₂ SO ₄ at 80 °C
Sib-S150	Sulfonation by fuming H ₂ SO ₄ at 150 °C
Sib-S200	Sulfonation by fuming H ₂ SO ₄ at 200 °C
Sib-WA	Oxidation by wet air mixture at 450 °C
Sib-N32	Oxidation by 32 v/v.% HNO ₃ solution at 90 °C
Sib-N23	Oxidation by 23 v/v.% HNO ₃ solution at 90 °C
Sib-WA-S200	Subsequent oxidation by wet air mixture at 450 °C and sulfonation by fuming H ₂ SO ₄ at 200 °C
Sib-N32-S200	Subsequent oxidation by 32 v/v.% HNO ₃ solution at 90 °C and sulfonation by fuming H ₂ SO ₄ at 200 °C
Sib-N23-S200	Subsequent oxidation by 23 v/v.% HNO ₃ solution at 90 °C and sulfonation by fuming H ₂ SO ₄ at 200 °C

The detailed description of the physicochemical techniques is given in Supporting Information (SI). Texture characteristics of catalysts and non-treated Sibunit were investigated using low-temperature nitrogen absorption at $-196\text{ }^{\circ}\text{C}$ on ASAP-2400 device (“Micromeritics,” USA). Concentrations of strong acidic groups (phenolic, lactonic, carboxylic and sulfo groups) on the surface of carbon catalysts were determined using acid–base titration with NaOH (Boehm 1966; Gromov et al. 2018; Toles et al. 1997). XPS analysis was carried out with photoelectron spectrometer SPECS (Germany) with MgK α radiation ($h\nu = 1253.6\text{ eV}$, 150 W).

Cellulose hydrolysis–dehydration under semi-flow conditions

Catalytic hydrolysis-dehydration of cellulose was carried out in a flow reactor operated under semi-flow conditions (Fig. 2). The stainless steel tube reactor (length 200.00 mm, internal diameter 2.7 mm) was fed by mechanical mixture of cellulose (250 mg) and the catalyst (200 mg). Deionized water was pumped with a rate of 0.5 mL min^{-1} through the reactor thermostated at the reaction temperature. At the outlet, the reaction mixture was cooled and collected into individual flask during each process hour (0–1 h, 1–2 h, etc.) for HPLC analysis. The reactor was operated in a stop-flow mode. The flow and the stop of water flow were alternated with each other. The flow of water through the reactor was stopped for 0, 10, 20 or 40 min during each hour of the reaction. The total volume of water spent in an experiment was 120, 80, 40 and 20 mL when the water flow was stopped for 0, 10, 20 or 40 min, respectively. Total experimental time was 4 h.

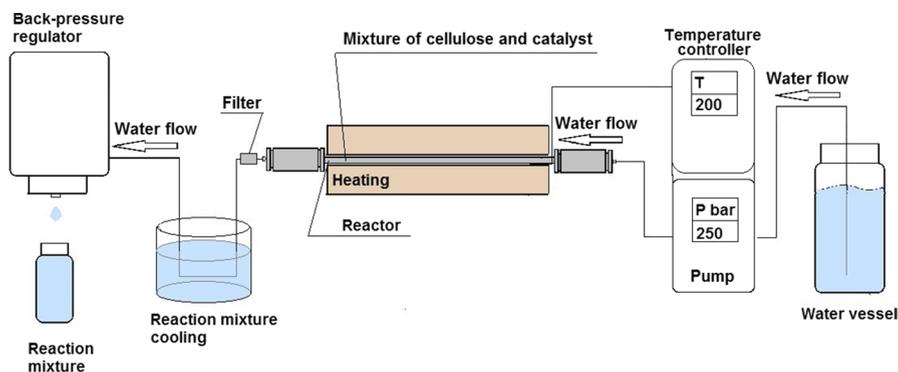


Fig. 2 Scheme of the flow reactor

Analytical techniques

Dionex Ultimate 3000 (Thermo Scientific) apparatus equipped with Rezex ROA-Organic Acids columns (Phenomenex, 300 mm * 5.0 mm) thermostated at 40 °C and RI detector was used for HPLC analysis of the reaction samples. 1.25 mM H₂SO₄ solution was flowed through the column, and the eluent rate was equal to 0.6 mL min⁻¹. The analysis of each sample was repeated three times. The analysis error was 2%. Each analysis of the reaction mixtures was carried out three times. The standard deviation of the results was less than 2%.

The product yields in the reaction mixtures collected into individual flasks during each hour of the process were calculated as follows (1):

$$Y = \frac{C_{\text{product}} V}{N \left(m_{\text{Cellulose}} / M_{\text{Glucan}} \right)} \cdot 100 \quad (1)$$

where Y —the product yield, C_{product} —the product concentration (mol L⁻¹), V —the volume of a sample collected during 1 h (L), N —a stoichiometric coefficient between a glucan unit and a product (for glucose $N=1$, for formic acid $N=6$, etc.), $m_{\text{Cellulose}}$ —the cellulose mass (g) and M_{Glucan} —the molar mass of glucan in cellulose (162 g mol⁻¹).

The total product yields were evaluated as the sum of the yields calculated via the previous formula for each hour of the reaction (2):

$$Y_{\Sigma} = \sum_{i=1}^4 Y_i \quad (2)$$

Results and discussion

Catalyst characterization

As mentioned previously, carbon materials appear to be promising catalysts for hydrolytic transformations of cellulose (Bhaumik and Dhepe 2016; Guo et al. 2012a; Likholobov 2001). At the same time, additional modification of carbon surface is needed for the surface acidity to be increased. This stage is unavoidable when designing effective catalysts of cellulose depolymerization. The carbon material Sibunit used to prepare catalysts (Table 2) had a high specific surface area equal to $379 \text{ m}^2 \text{ g}^{-1}$ and an amount of acidic surface groups (phenolic, lactonic, carboxylic) of only 0.11 mmol m^{-2} (Gromov et al. 2018).

The low-temperature adsorption studies revealed a partial destruction of the carbon structure during all the treatment procedures used (Table 2, Gromov et al. 2018). The harsher the chemical treatment of carbon was, the lower the specific surface area was observed, i.e., additional treatment of oxidized catalysts by sulfuric acid caused a more significant decrease in the specific surface area than the oxidation itself. The wet air oxidation was structure-friendlier than the oxidation with nitric acid. Only treatment by H_2SO_4 at $200 \text{ }^\circ\text{C}$ led to an increase in the surface area (S_{BET}) and mesopore volume (V_{mesopore}). This may result from an “opening” of closed voids formed during synthesis of Sibunit via soot burning from globules of pyrolytic carbon (Likholobov 2001).

Qualitative and quantitative analyses of the surface groups were carried out by titration with NaOH and XPS according to techniques described in Sect. Synthesis and characterization of catalysts and previous work (Gromov et al. 2018). When treating carbon by oxidizing agent, phenolic, lactonic, carboxylic and sulfo (in the case of treatment by sulfuric acid) groups were formed (Table 2, Gromov et al. 2018). In general, the amount of acid groups on the surface determined by titration with NaOH of catalysts increased by a factor of 3–16 compared to the initial Sibunit sample. Carbons treated by sulfuric acid contained $0.41\text{--}1.00 \text{ } \mu\text{mol m}^{-2}$ of acid surface groups. The acid group concentration per surface area of the sample Sib-S200, equal to $1.00 \text{ } \mu\text{mol m}^{-2}$, was comparable to the one reported previously ($1.1 \text{ } \mu\text{mol m}^{-2}$) (Onda et al. 2008, 2009; Pang et al. 2010). The contents of the acid groups varied from 0.80 to $1.12 \text{ } \mu\text{mol m}^{-2}$ after the oxidation and increased up to $1.43\text{--}1.76 \text{ } \mu\text{mol m}^{-2}$ after the treatment by H_2SO_4 .

According to XPS analysis (Table 2, SI, Gromov et al. 2018), the surfaces of the developed acid catalysts had basically acidic oxidized species. In samples Sib-S80, Sib-S150, Sib-S200, Sib-WA-S200, Sib-N32-S200 and Sib-N23-S200, two states of sulfur were identified: the sulfides (S^{2-}) and the sulfo groups ($-\text{SO}_3^-$) (Table 2, Fig. S1, SI) (Janaun and Ellis 2011; Takagaki et al. 2006). In pure Sibunit and oxidized samples, Sib-WA, Sib-N32 and Sib-N23, only sulfide state was identified. Seemingly, sulfides were in the untreated Sibunit carbon. Oxidation by wet air or nitric acid did not cause the formation of sulfo groups from sulfides, but $-\text{SO}_3^-$ was fixed by treatment with sulfuric acid. The treatment by H_2SO_4 at

Table 2 Textural characteristics of Sibunit catalysts determined by low-temperature N_2 adsorption, the content of acid groups on the surface of the catalysts measured by titration with NaOH and atom concentrations of different element states of the sample surface according to XPS (Gromov et al. 2018)

#	Catalyst	Textural characteristics			Atom concentrations of different element states revealed by XPS							
		S_{BET} , ($m^2 g^{-1}$)	$V_{mesopore}$, ($cm^3 g^{-1}$)	$C_{acid\ groups}$, ($\mu mol\ m^{-2}$)	C	S	O	N	(C-N)	NO_2^-/NO_3^-	Na	
1	Sib	379	0.21	0.11	92,928	33	0	3511	0	0	0	0
2	Sib-S80	345	0.20	0.41	81,517	19	45	3414	0	0	0	0
3	Sib-S150	364	0.22	0.88	82,259	27	82	4528	0	0	0	0
4	Sib-S200	400	0.24	1.00	78,981	27	51	5502	0	0	0	728
5	Sib-WA	348	0.33	0.80	85,856	42	0	4396	0	0	0	0
6	Sib-N32	320	0.27	1.12	80,857	21	0	4566	192	111	0	0
7	Sib-N23	306	0.22	1.08	n.d	-	-	-	-	-	-	-
8	Sib-WA-S200	343	0.30	1.43	89,989	26	31	6257	0	0	0	0
9	Sib-N32-S200	290	0.27	1.76	77,757	24	19	5272	112	0	0	0
10	Sib-N23-S200	299	0.23	1.64	n.d	-	-	-	-	-	-	-

80 °C fixed only sulfo groups on the surface. On the other hand, higher temperature (150 and 200 °C) of the treatment by sulfuric acid caused an additional formation of surface acid species (hydroxyl, carboxylic, lactic, carbonylic) along with sulfo groups (Table S1, Fig. S2, SI). The oxidation of the carbon surface prevented fixing sulfo groups. Treatment by H₂SO₄ at 200 °C produced on the surface of Sib-WA-S200, Sib-N32-S200 and Sib-N23-S200 a low quantity of supported sulfo groups. The amount of sulfo groups was two times lower on the surface of Sib-WA-S200, Sib-N32-S200 and Sib-N23-S200 compared to Sib-S200 (Table S1, Fig. S2, SI).

Impact of reaction conditions on cellulose hydrolysis–dehydration

Investigations of carbon catalyst activity were conducted in a flow reactor in this work (Fig. 2). To optimize reaction temperature and water pressure, the experiments without any catalyst were made. The influence of temperature on the reaction was revealed under 25 MPa water pressure and 0.5 mL min⁻¹ water flow. Non-catalytic cellulose hydrolysis–dehydration was firstly made at 180 °C. However, the total yield of the products was only 3% (Table 3, run 1). This value is lower compared to the one previously observed in the batch reactor (7%) (Gromov et al. 2018). Such low yields were explained by small reaction contact time in the flow system. In the present study, the contact time determined with the following formula was equal to 2 min (3).

$$\tau_{\text{contact}} = \frac{V_{\text{react}}}{Q_{\text{volume}}} \cdot \frac{\rho_{\text{conditions}}^{\text{H}_2\text{O}}}{\rho_{\text{syringe}}^{\text{H}_2\text{O}}} = \frac{\pi \cdot r^2 \cdot L}{Q_{\text{volume}}} \cdot \rho_{\text{conditions}}^{\text{H}_2\text{O}} \quad (3)$$

where τ_{contact} —reaction contact time, V_{react} —the volume of the reactor (mL or cm³) determined from its length (L) and radius (r), Q_{volume} —the volume flow rate, $\rho_{\text{conditions}}^{\text{H}_2\text{O}}$ and $\rho_{\text{syringe}}^{\text{H}_2\text{O}}$ —the densities of water under reaction and ambient conditions equal to 0.88 and 1 g mL⁻¹, respectively.

Because of the low yields, all the experiments were made at 200 °C. This temperature made it possible to increase the product yields and decrease the side product formation. Previously, the temperatures in the range of 200–220 °C were found to be promising for the production of water-soluble products under flow conditions (Amarasekara 2013). To evaluate the water pressure influence on the reaction, the experiments were carried out at 200 °C and water pressures of 5 and 25 MPa (Table 3, runs 2, 3). The results showed the positive impact of high pressure 25 MPa on the yields of glucose and 5-HMF. However, according to HPLC data, the oligomers were the main products at 200 °C and 25 MPa. To intensify the hydrolysis of oligosaccharides to the major product, the experiments were made under stop-slow mode. The water flow was stopped for 10, 20 and 40 min (Table 3, runs 3–6). The stop-flow conditions led to high conversion of oligomers. The yields of glucose were 10, 13 and 17% when the water flow was stopped for 10, 20 and 40 min, respectively. However, in case of 40 min, stop-flow yields of the side products and

Table 3 Product yields in cellulose hydrolysis–dehydration. Reaction conditions: flow reactor, 250 mg of cellulose, 200 mg of the catalyst, flow rate 0.5 mL·min⁻¹, experimental time 4 h

#	Catalyst	T, (°C)	P, (MPa)	τ , (min ^a)	Product yields, (%)							A_0 (mol·s ⁻¹ ·10 ⁸)	A_0^{5-HMF} (mol·s ⁻¹ ·10 ⁸)	
					Celb	Glu	Fru	5-HMF	Furf	FA ^b	LA ^b			Total
1	Blank	180	5	–	2	1	0	<1	0	0	0	0	–	–
2	Blank	200	5	–	3	6	0	1	0	0	0	0	–	–
3	Blank	200	25	–	2	8	0	2	0	<1	0	12	–	–
4	Blank	200	25	10	3	10	<1	3	0.1	0	0	16	–	–
5	Blank	200	25	20	2	13	<1	3	0.1	0	0	20	–	–
6	Blank	200	25	40	2	17	1	5	0.3	0	0	33	–	–
7	Sib	200	25	20	4	20	2	5	0.3	<1	0	33	2.23	0.40
8	Sib-S80	200	25	20	5	32	4	9	0.8	<1	<1	57	5.09	1.24
9	Sib-S150	200	25	20	5	40	4	10	0.9	1	<1	61	6.11	1.38
10	Sib-S200	200	25	20	12	48	2	7	0.9	<1	<1	71	8.34	1.04
11	Sib-WA	200	25	20	6	44	2	6	0.7	<1	0	59	7.11	0.74
12	Sib-N32	200	25	20	7	49	4	8	0.8	1	0	70	6.41	0.88
13	Sib-N23	200	25	20	6	49	5	9	0	<1	0	70	6.75	1.03
14	Sib-WA-S200	200	25	20	5	71	2	3	0.2	<1	0	81	13.8	0.52
15	Sib-N32-S200	200	25	20	5	75	3	6	1.0	<1	0	90	12.6	0.72
16	Sib-N23-S200	200	25	20	5	66	2	5	0.3	<1	0	79	11.3	0.62
17 ^c	C-S200	180	1	–	1.0	45.9	6.0	21.5	5.9	0	0	63.0	–	–

A_0 and A_0^{5-HMF} are initial rates of glucose and 5-HMF formation

a— τ —stop-flow time, b—FA is formic acid, LA is a levulinic acid, c—maximal yields described by Gromov et al. (2018)

humins were appreciable which was proven by the dark brown color of the reaction mixtures. Therefore, all the catalytic experiments were carried out under 20-min stop-flow.

Impact of catalyst acidity on cellulose hydrolysis–dehydration

The efficiency of carbon catalysts was investigated at 200 °C under 25 MPa water pressure (Table 3). The yields of the major products per hour and in total were calculated by the formulae described in experimental section. Analysis of the reaction mixtures by HPLC demonstrated that in all the catalytic experiments, glucose and 5-HMF were the main products. Cellobiose was also formed with notable yields. The formation of fructose, furfural, formic and levulinic acids was revealed. Less than 1% yield of levulinic acid was achieved in the experiments carried out in the presence of the catalysts prepared by sulfonation (Sib-S80, Sib-S150 and Sib-S200). The valuable compounds were predominantly formed during the first hour of reaction (about 70–80% of the total yield, Fig. 3).

In terms of the activity in glucose formation, all the catalysts could be divided into three groups (Fig. 4). Non-treated pure Sibunit carbon was only one catalyst in the first group. Sib sample had the lowest activity, which was slightly higher than the activity of pure water. The yields of glucose and 5-HMF reached 20% and 5%, respectively, in the presence of pure carbon.

The second group of catalysts consisted of the samples treated by sulfuric acid or oxidized by wet air or nitric acid. The yield of glucose over Sib-S200 was higher than the one over Sib-S150. Hydrolytic activity of carbon oxidized by wet air was between Sib-S150 and Sib-S200. In the presence of catalysts prepared by the HNO₃ treatment, the yields of glucose were close to each other and slightly higher than the ones achieved in the case of Sib-S200. Similar yields of glucose over sulfonated and oxidized catalysts can be explained by similar surface acidity.

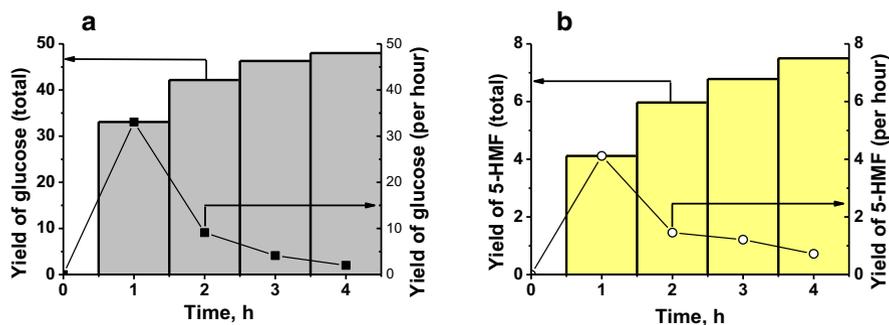


Fig. 3 Kinetic curves of accumulation of cellulose hydrolysis–dehydration products (**a**—glucose, **b**—5-HMF) in the presence of Sibunit catalyst in the flow reactor. Points—accumulation per hour. Bars—total accumulation. 250 mg of cellulose, 200 mg of Sib-WA catalyst, 200 °C, 25 MPa, flow rate 0.5 mL min⁻¹, stop-flow 20 min, experiment time 4 h

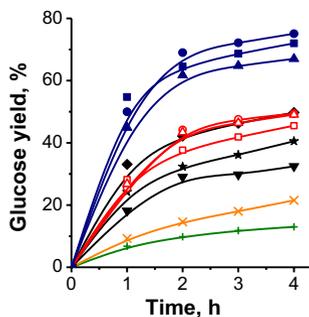


Fig. 4 Accumulation of glucose in cellulose hydrolysis–dehydration process in the presence of Sibunit solid acid catalysts. Reaction conditions: flow reactor, 250 mg of cellulose, 200 mg of the catalyst, 200 °C, 25 MPa, flow rate 0.5 mL min⁻¹, stop-flow 20 min, experiment time 4 h. +—blank, ×—Sib, pre filled inverted triangle—Sib-S80, pre filled diamond—Sib-S150, pre filled star—Sib-S200, square—Sib-WA, pre filled square—Sib-WA-S200, circle—Sib-N32, pre filled circle—Sib-N32-S200, triangle—Sib-N23, pre filled triangle—Sib-N23-S200

The third group consisted of oxidized–sulfonated carbons. Their activities were significantly (about 1.5–2 times) higher compared to the ones of oxidized and sulfonated samples.

Correlations between the glucose yield and catalyst acidity lead us to conclude that the crucial factor of the activity in the cellulose hydrolysis to glucose was the total surface acidity but not the chemical nature of the groups. Interestingly, the difference of the activities agreed with the total acidity of the catalysts (Fig. 5a). However, Sib-N32-S200 and Sib-N23-S200 demonstrated lower activity compared to Sib-WA-S200 as the efficiency of catalysts was effected by the specific surface area (Gromov et al. 2018). The glucose yield obtained in this work was reached under milder temperature conditions (200 °C).

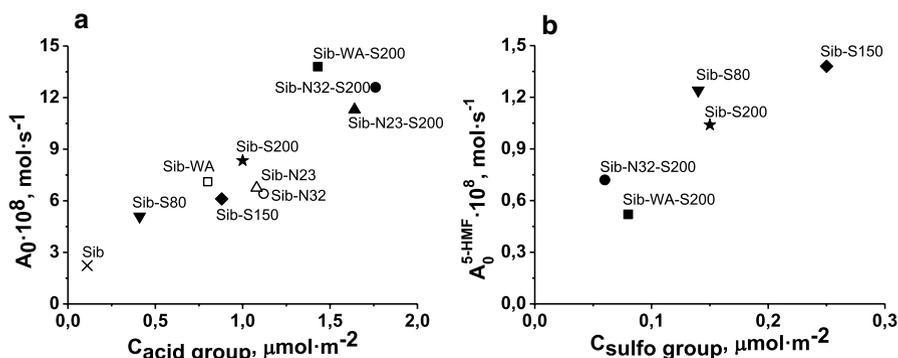


Fig. 5 Correlations between the initial reaction rate and the normalized total acidity (a) and initial rate of 5-HMF formation and amount of sulfo groups (b) the Sibunit carbon catalysts

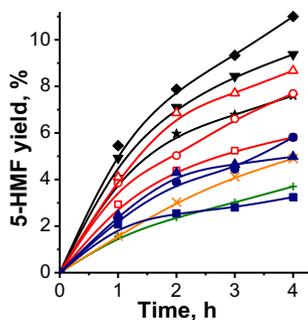


Fig. 6 Accumulation of 5-HMF in cellulose hydrolysis–dehydration process in the presence of Sibunit solid acid catalysts. Reaction conditions: flow reactor, 250 mg of cellulose, 200 mg of the catalyst, 200 °C, 25 MPa, flow rate 0.5 mL min⁻¹, stop-flow 20 min, experiment time 4 h. +—blank, ×—Sib, pre filled inverted triangle—Sib-S80, pre filled diamond—Sib-S150, pre filled star—Sib-S200, square—Sib-WA, pre filled square—Sib-WA-S200, circle—Sib-N32, pre filled circle—Sib-N32-S200, triangle—Sib-N23, pre filled triangle—Sib-N23-S200

HPLC analysis revealed the total yield of 5-HMF equal to 2–10% after the 4 h of the catalytic tests. The catalysts sulfonated by H₂SO₄ were more active in the dehydration than other samples. The activity of the sulfonated carbons increased as follows: Sib-S150 > Sib-S80 > Sib-S200 (Fig. 6). That is to say, Sib-S150 catalyst which had the highest amount of sulfo groups among all the sulfonated samples (Sib-S80, Sib-S150, Sib-S200) demonstrated the highest activity in terms of 5-HMF formation. Further, the oxidized–sulfonated samples revealed lower activity in the glucose dehydration to 5-HMF compared to oxidized ones. C-WA-S200 had the lowest activity in the dehydration, which was comparable to non-treated carbon. It can be assumed that both acid and sulfo groups were active in dehydration, but the activity of sulfo groups was noticeably higher (Fig. 5b).

Potential of Sibunit carbon catalyst under semi-flow conditions

The highest yield of glucose equal to 75% (product total yield 90%) was reached in the presence of Sib-N32-S200 catalyst in the semi-flow reactor. The concentration of glucose and total amount of products were 29 and 39 mM, respectively, at the end of the experiment. As previously reported, the highest yield of glucose was equal to 45.9% in the presence of Sibunit-based catalyst in a batch reactor at 180 °C (Gromov et al. 2018). Zhao et al. (2009, 2011) achieved 40% glucose yield under combined super- and subcritical conditions ($T=240\text{--}380$ °C). Sasaki et al. (1998) reported 75% total yield of cellulose depolymerization products in a flow reactor at 290–400 °C and pressure of 25 MPa.

Conclusion

The one-pot hydrolysis–dehydration of cellulose to glucose and 5-HMF, which are valuable compounds, has been studied. The catalysts of the process under study were based on the mesoporous graphite-like carbon material Sibunit. To evaluate the optimal method for generation of surface acid groups, the Sibunit carbon was treated by sulfonation with fuming sulfuric acid, oxidation with nitric acid or wet air, as well as additional sulfonation of oxidized carbon samples. The content of acid groups on the surface of catalysts increased by a factor of 3 to 16 compared to the non-treated pure carbon. The catalysts were tested in the cellulose hydrolysis–dehydration process under semi-flow conditions. The carbon catalysts revealed high activity with glucose and 5-HMF being the major products.

Under semi-flow conditions, oxidized–sulfonated catalysts were most perspective for glucose production from cellulose. The highest yield of glucose equal to 75% was obtained in the presence of Sibunit sample oxidized with nitric acid and sulfonated at 200 °C. For an effective cellulose hydrolysis–dehydration to 5-HMF to be carried out, a catalyst should have both high total surface acidity and high amount of sulfo groups. 10% 5-HMF yield can be achieved over Sibunit sample sulfonated at 150 °C.

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Code availability Not applicable.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Availability of data and material Not applicable.

References

- Amarasekara AS (2013) Acid hydrolysis of cellulose and hemicellulose. In: Amarasekara AS (ed) *Handbook of cellulosic ethanol*. Wiley, Beverly, pp 247–281. <https://doi.org/10.1002/9781118878750.ch7>
- Besson M, Gallezot P, Pinel C (2014) Conversion of biomass into chemicals over metal catalysts. *Chem Rev* 114:1827–1870. <https://doi.org/10.1021/cr4002269>
- Bhatnagar A, Hogland W, Marques M, Sillanpaa M (2013) An overview of the modification methods of activated carbon for its water treatment applications. *Chem Eng J* 219:499–511. <https://doi.org/10.1016/j.cej.2012.12.038>
- Bhaumik P, Dhepe PL (2016) Solid acid catalyzed synthesis of furans from carbohydrates. *Catal Rev* 58:36–112. <https://doi.org/10.1080/01614940.2015.1099894>

-
- Bobleter O (2005) Hydrothermal degradation and fractionation of saccharides. In: Dimitriu S (ed) Polysaccharides. Structural diversity and functional versatility, 2nd edn. Marcel Dekker, New York, pp 893–913
- Boehm HP (1966) Chemical identification of surface groups. *Adv Catal* 16:179–274. [https://doi.org/10.1016/S0360-0564\(08\)60354-5](https://doi.org/10.1016/S0360-0564(08)60354-5)
- Burgess R, Buono C, Davies PR, Davies RJ, Legge T, Lai A, Lewis R, Morgan DJ, Robinson N, Willock DJ (2015) The functionalisation of graphite surfaces with nitric acid: Identification of functional groups and their effects on gold deposition. *J Catal* 323:10–18. <https://doi.org/10.1016/j.jcat.2014.12.021>
- Cao L, Yu IKM, Chen SS, Tsang DCW, Wang L, Xiong X, Zhang S, Ok YS, Kwon EE, Song H, Poon CS (2018a) Production of 5-hydroxymethylfurfural from starch-rich food waste catalyzed by sulfonated biochar. *Biores Technol* 252:76–82. <https://doi.org/10.1016/j.biortech.2017.12.098>
- Cao L, Yu IKM, Tsang DCW, Zhang S, Ok YS, Kwon EE, Song H, Poon CS (2018b) Phosphoric acid-activated wood biochar for catalytic conversion of starch-rich food waste into glucose and 5-hydroxymethylfurfural. *Biores Technol* 267:242–248. <https://doi.org/10.1016/j.biortech.2018.07.048>
- Chareonlimkun A, Champreda V, Shotipruk A, Laosiripojana N (2010a) Catalytic conversion of sugarcane bagasse, rice husk and corncob in the presence of TiO₂, ZrO₂ and mixed-oxide TiO₂–ZrO₂ under hot compressed water (HCW) condition. *Biores Technol* 101:4179–4186. <https://doi.org/10.1016/j.biortech.2010.01.037>
- Chareonlimkun A, Champreda V, Shotipruk A, Laosiripojana N (2010b) Reactions of C5 and C6-sugars, cellulose, and lignocellulose under hot compressed water (HCW) in the presence of heterogeneous acid catalysts. *Fuel* 89:2873–2880. <https://doi.org/10.1016/j.fuel.2010.03.015>
- Dora S, Bhaskar T, Singh R, Naik Viswanatha D, Adhikari DK (2012) Effective catalytic conversion of cellulose into high yields of methyl glucosides over sulfonated carbon based catalyst. *Biores Technol* 120:318–321. <https://doi.org/10.1016/j.biortech.2012.06.036>
- Foo GS, Sievers C (2015) Synergistic effect between defect sites and functional groups on the hydrolysis of cellulose over activated carbon. *Chemosuschem* 8:534–543. <https://doi.org/10.1002/cssc.201402928>
- Fukuhara K, Nakajima K, Kitano M, Kato H, Hayashi S, Hara M (2011) Structure and catalysis of cellulose-derived amorphous carbon bearing SO₃H groups. *Chemosuschem* 4:778–784. <https://doi.org/10.1002/cssc.201000431>
- Gallezot P (2012) Conversion of biomass to selected chemical products. *Chem Soc Rev* 41:1538–1558. <https://doi.org/10.1039/C1CS15147A>
- Gromov NV, Medvedeva TB, Taran OP, Bukhtiyarov AV, Aymonier C, Prosvirin IP, Parmon VN (2018) Hydrothermal solubilization–hydrolysis–dehydration of cellulose to glucose and 5-hydroxymethylfurfural over solid acid carbon catalysts. *Top Catal* 61:1912–1927. <https://doi.org/10.1007/s11244-018-1049-4>
- Gromov NV, Taran OP, Semykina VS, Danilova IG, Pestunov AV, Parkhomchuk EV, Parmon VN (2017) Solid acidic NbO_x/ZrO₂ catalysts for transformation of cellulose to glucose and 5-hydroxymethylfurfural in pure hot water. *Catal Lett* 147:1485–1495. <https://doi.org/10.1007/s10562-017-2056-y>
- Gromov NV, Taran OP, Sorokina KN, Mischenko TI, Sivakumar U, Parmon VN (2016) New methods for the one-pot processing of polysaccharide components (cellulose and hemicelluloses) of lignocellulose biomass into valuable products. Part 1: methods for biomass activation. *Catal Ind* 8:176–786. <https://doi.org/10.1134/S2070050416020057>
- Guo F, Fang Z, Xu CC, Smith RL Jr (2012a) Solid acid mediated hydrolysis of biomass for producing biofuels. *Prog Energy Combust Sci* 38:672–690. <https://doi.org/10.1016/j.pecs.2012.04.001>
- Guo H, Qi X, Li L, Smith RL Jr (2012b) Hydrolysis of cellulose over functionalized glucose-derived carbon catalyst in ionic liquid. *Biores Technol* 116:355–359. <https://doi.org/10.1016/j.biortech.2012.03.098>
- Janaun J, Ellis N (2011) Role of silica template in the preparation of sulfonated mesoporous carbon catalysts. *Appl Catal A* 394:25–31. <https://doi.org/10.1016/j.apcata.2010.12.016>
- Jiang C-W, Zhong X, Luo Z-H (2014) An improved kinetic model for cellulose hydrolysis to 5-hydroxymethylfurfural using the solid SO₄²⁻/Ti-MCM-41 catalyst. *RSC Advances* 4:15216–15224. <https://doi.org/10.1039/C4RA00167B>
- Kim K-H, Ihm S-K (2011) Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: a review. *J Hazard Mater* 186:16–34. <https://doi.org/10.1016/j.jhazmat.2010.11.011>

-
- Kitano M, Yamaguchi D, Suganuma S, Nakajima K, Kato H, Hayashi S, Hara M (2009) Adsorption-enhanced hydrolysis of β -1,4-glucan on graphene-based amorphous carbon bearing SO_3H , COOH , and OH groups. *Langmuir* 25:5068–5075. <https://doi.org/10.1021/la8040506>
- Lai D-m, Deng L, Li J, Liao B, Guo Q-x, Fu Y (2011) Hydrolysis of cellulose into glucose by magnetic solid acid. *Chemosuschem* 4:55–58. <https://doi.org/10.1002/cssc.201000300>
- Levec J, Pintar A (2007) Catalytic wet-air oxidation processes: a review. *Catal Today* 124:172–184. <https://doi.org/10.1016/j.cattod.2007.03.035>
- Li S, Gu Z, Bjornson BE, Muthukumarappan A (2013) Biochar based solid acid catalyst hydrolyze biomass. *J Environ Chem Eng* 1:1174–1181. <https://doi.org/10.1016/j.jece.2013.09.004>
- Li Y, Shen S, Wang C, Peng X, Yuan S (2018) The effect of difference in chemical composition between cellulose and lignin on carbon based solid acids applied for cellulose hydrolysis. *Cellulose* 25:1851–1863. <https://doi.org/10.1007/s10570-018-1693-7>
- Likhoholov VA (2001) Catalysis by novel carbon-based materials. In: Centi G, Wichterlová B, Bell AT (eds) *Catalysis by unique metal ion structures in solid matrices from science to application*. Kluwer Academic Publishers, Netherlands, pp 295–306
- Liu X-Y, Huang M, Ma H-L, Zhang Z-Q, Gao J-M, Zhu Y-L, Guo X-Y (2010) Preparation of a carbon-based solid acid catalyst by sulfonating activated carbon in a chemical reduction process. *Mol J* 15:7188–7196. <https://doi.org/10.3390/molecules15107188>
- Liu Z, Fu X, Tang S, Cheng Y, Zhu L, Xing L, Wang J, Xue L (2014) Sulfonated magnetic carbon nanotube arrays as effective solid acid catalysts for the hydrolyses of polysaccharides in crop stalks. *Catal Commun* 56:1–4. <https://doi.org/10.1016/j.catcom.2014.06.022>
- Loppinet-Serani A, Aymonier C (2014) Hydrolysis in near- and supercritical water for biomass conversion and material recycling. In: Fan M (ed) *Supercritical fluid technology for energy and environmental applications*. Elsevier, Boston, pp 139–156. <https://doi.org/10.1016/B978-0-444-62696-7.00007-1>
- Mukherjee A, Dumont M-J, Raghavan V (2015) Review: Sustainable production of hydroxymethylfurfural and levulinic acid: challenges and opportunities. *Biomass Bioenerg* 72:143–183. <https://doi.org/10.1016/j.biombioe.2014.11.007>
- Murzin D, Salmi T (2012) Catalysis for lignocellulosic biomass processing: methodological aspects. *Catal Lett* 142:676–689. <https://doi.org/10.1007/s10562-012-0812-6>
- Nakajima K, Hara M (2012) Amorphous carbon with SO_3H groups as a solid Bronsted acid catalyst. *ACS Catal* 2:1296–1304. <https://doi.org/10.1021/cs300103k>
- Nakajima K, Okamura M, Kondo JN, Domen K, Tatsumi T, Hayashi S, Hara M (2008) Amorphous carbon bearing sulfonic acid groups in mesoporous silica as a selective catalyst. *Chem Mater* 21:186–193. <https://doi.org/10.1021/cm801441c>
- Nandiwale KY, Galande ND, Thakur P, Sawant SD, Zambre VP, Bokade VV (2014) One-pot synthesis of 5-hydroxymethylfurfural by cellulose hydrolysis over highly active bimodal micro/mesoporous H-ZSM-5 catalyst. *ACS Sustain Chem Eng* 2:1928–1932. <https://doi.org/10.1021/sc500270z>
- Onda A, Ochi T, Yanagisawa K (2008) Selective hydrolysis of cellulose into glucose over solid acid catalysts. *Green Chem* 10:1033–1037. <https://doi.org/10.1039/B808471H>
- Onda A, Ochi T, Yanagisawa K (2009) Hydrolysis of cellulose selectively into glucose over sulfonated activated-carbon catalyst under hydrothermal conditions. *Top Catal* 52:801–807. <https://doi.org/10.1007/s11244-009-9237-x>
- Pang J, Wang A, Zheng M, Zhang T (2010) Hydrolysis of cellulose into glucose over carbons sulfonated at elevated temperatures. *Chem Commun* 46:6935–6937. <https://doi.org/10.1039/c0cc02014a>
- Perez S, Mazeau K (2005) Conformation, structures, and morphologies of celluloses. In: Dimitriu S (ed) *Polysaccharides. Structural diversity and functional versatility*, 2nd edn. Marcel Dekker, New York, pp 41–64
- Pestunov AV, Kuzmin AO, Yatsenko DA, Pravdina MK, Taran OP (2015) The mechanical activation of crystal and wooden sawdust cellulose in various fine-grinding mills. *J Sib Federal Univ Chem* 8:386–400. <https://doi.org/10.17516/1998-2836-2015-8-3-386-400>
- Rogalinski T, Ingram T, Brunner G (2008a) Hydrolysis of lignocellulosic biomass in water under elevated temperatures and pressures. *J Supercrit Fluids* 47:54–63. <https://doi.org/10.1016/j.supflu.2008.05.003>
- Rogalinski T, Liu K, Albrecht T, Brunner G (2008b) Hydrolysis kinetics of biopolymers in subcritical water. *J Supercrit Fluids* 46:335–341. <https://doi.org/10.1016/j.supflu.2007.09.037>

-
- Sasaki M, Kabyemela B, Malaluan R, Hirose S, Takeda N, Adschiri T, Arai K (1998) Cellulose hydrolysis in subcritical and supercritical water. *J Supercrit Fluids* 13:261–268. [https://doi.org/10.1016/S0896-8446\(98\)00060-6](https://doi.org/10.1016/S0896-8446(98)00060-6)
- Shen S, Wang C, Han Y, Cai B, Li H (2014) Influence of reaction conditions on heterogeneous hydrolysis of cellulose over phenolic residue-derived solid acid. *Fuel* 134:573–578. <https://doi.org/10.1016/j.fuel.2014.06.023>
- Shrotri A, Kobayashi H, KaikinH YM, Fukuoka A (2017) Cellulose hydrolysis using oxidized carbon catalyst in a plug-flow slurry process. *Ind Eng Chem Res* 56:14471–14478. <https://doi.org/10.1021/acs.iecr.7b03918>
- Suganuma S, Nakajima K, Kitano M, Yamaguchi D, Kato H, Hayashi S, Hara M (2008) Hydrolysis of cellulose by amorphous carbon bearing SO₃H, COOH, and OH groups. *J Am Chem Soc* 130:12787–12793. <https://doi.org/10.1021/ja803983h>
- Suganuma S, Nakajima K, Kitano M, Yamaguchi D, Kato H, Hayashi S, Hara M (2010) Synthesis and acid catalysis of cellulose-derived carbon-based solid acid. *Solid State Sci* 12:1029–1034. <https://doi.org/10.1016/j.solidstatesciences.2010.02.038>
- Takagaki A, Nishimura M, Nishimura S, Ebitan K (2011) Hydrolysis of sugars using magnetic silica nanoparticles with sulfonic acid groups. *Chem Lett* 40:1195–1197. <https://doi.org/10.1246/cl.2011.1195>
- Takagaki A, Tagusagawa C, Domen K (2008) Glucose production from saccharides using layered transition metal oxide and exfoliated nanosheets as a water-tolerant solid acid catalyst. *Chem Commun* 48:5363–5365. <https://doi.org/10.1039/b810346a>
- Takagaki A, Toda M, Okamura M, Kondo JN, Hayashi S, Domen K, Hara M (2006) Esterification of higher fatty acids by a novel strong solid acid. *Catal Today* 116:157–161. <https://doi.org/10.1016/j.cattod.2006.01.037>
- Taran OP, Descorme C, Polyanskaya EM, Ayusheev AB, Besson M, Parmon VN (2013) Sibunit based catalytic materials for the deep oxidation of organic ecotoxicants in aqueous solutions. III: wet air oxidation of phenol over oxidized carbon and Ru/C catalysts. *Catal Ind* 5:164–174. <https://doi.org/10.1134/S2070050413020104>
- Taran OP, Polyanskaya EM, Ogorodnikova OL, Descorme C, Besson M, Parmon VN (2011a) Sibunit-based catalytic materials for the deep oxidation of organic ecotoxicants in aqueous solution: I. Surface properties of the oxidized sibunit samples. *Catal Ind* 2:381–386. <https://doi.org/10.1134/S2070050410040136>
- Taran OP, Polyanskaya EM, Ogorodnikova OL, Descorme C, Besson M, Parmon VN (2011b) Sibunit-based catalytic materials for the deep oxidation of organic ecotoxicants in aqueous solutions. II: wet peroxide oxidation over oxidized carbon catalysts. *Catal Ind* 3:161–169. <https://doi.org/10.1134/S2070050411020152>
- Toles CA, Marshall WE, Johns MM (1997) Granular activated carbons from nutshells for the uptake of metals and organic compounds. *Carbon* 35:1407–1414. [https://doi.org/10.1016/S0008-6223\(97\)00073-0](https://doi.org/10.1016/S0008-6223(97)00073-0)
- Van de Vyver S, Geboers J, Jacobs PA, Sels BF (2011) Recent advances in the catalytic conversion of cellulose. *ChemCatChem* 3:82–94. <https://doi.org/10.1002/cctc.201000302>
- Van Pelt AH, Simakova OA, Schimming SM, Ewbank JL, Foo GS, Pidko EA, Hensen EJM, Sievers C (2014) Stability of functionalized activated carbon in hot liquid water. *Carbon* 77:143–154. <https://doi.org/10.1016/j.carbon.2014.05.015>
- van Putten R-J, van der Waal JC, de Jong E, Rasrendra CB, Heeres HJ, de Vries JG (2013) Hydroxymethylfurfural, a versatile platform chemical made from renewable resources. *Chem Rev* 113:1499–1597. <https://doi.org/10.1021/cr300182k>
- Wang H, Zhang C, He H, Wang L (2012) Glucose production from hydrolysis of cellulose over a novel silica catalyst under hydrothermal conditions. *J Environ Sci* 24:473–478. [https://doi.org/10.1016/S1001-0742\(11\)60795-X](https://doi.org/10.1016/S1001-0742(11)60795-X)
- Watanabe M, Aizawa Y, Iida T, Nishimura R, Inomata H (2005) Catalytic glucose and fructose conversions with TiO₂ and ZrO₂ in water at 473 K: relationship between reactivity and acid-base property determined by TPD measurement. *Appl Catal A Gen* 295:150–156. <https://doi.org/10.1016/j.apcata.2005.08.007>
- Xiong X, Yu IKM, Chen SS, Tsang DCW, Cao L, Song H, Ok YS, Zhang S, Poon CS (2018) Sulfonated biochar as acid catalyst for sugar hydrolysis and dehydration. *Catal Today* 314:52–61. <https://doi.org/10.1016/j.cattod.2018.02.034>

-
- Yang F, Liu Q, Bai X, Du Y (2011a) Conversion of biomass into 5-hydroxymethylfurfural using solid acid catalyst. *Biores Technol* 102:3424–3429. <https://doi.org/10.1016/j.biortech.2010.10.023>
- Yang F, Liu Q, Yue M, Bai X, Du Y (2011b) Tantalum compounds as heterogeneous catalysts for saccharide dehydration to 5-hydroxymethylfurfural. *Chem Commun* 47:4469–4471. <https://doi.org/10.1039/c0cc05138a>
- Yu Y, Lou X, Wu H (2008) Some recent advances in hydrolysis of biomass in hot-compressed water and its comparisons with other hydrolysis methods. *Energy Fuel* 22:46–60. <https://doi.org/10.1021/ef700292p>
- Zhao Y, Lu W-J, Wang H-T, Li D (2009) Combined supercritical and subcritical process for cellulose hydrolysis to fermentable hexoses. *Environ Sci Technol* 43:1565–1570. <https://doi.org/10.1021/es803122f>
- Zhao Y, Wang H-T, Lu W-J, Wang H (2011) Combined supercritical and subcritical of cellulose for fermentable hexose production in a flow reaction system. *Chem Eng J* 166:868–872. <https://doi.org/10.1016/j.cej.2010.11.058>