## A catalytic system for the selective conversion of cellulose to 5-hydroxymethylfurfural under mild conditions

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Conversion of cellulose to 5-hydroxymethylfurfural (5-HMF), one of the most promising products derived by conversion of renewable raw materials, has been studied. When performing the process in ionic liquids, addition of small amounts of Brønsted acids was found to allow the adaption of the catalytic system to be used under mild conditions, which is particularly important for the industrial processing of cellulose. Highest yield of 5-HMF (44%) was obtained by carrying out the conversion of cellulose at 100 °C for 12 h with a modified catalytic system based on  $CrCl_3 \cdot 6H_2O$  and  $H_2SO_4$ .

Key words: 5-hydroxymethylfurfural, carbohydrates, cellulose, ionic liquids, catalysis.

Natural plant biomass containing mainly various polysaccharides and lignine (lignocellulosic biomass), is one of the most effective and ecological renewable energy sources.<sup>1</sup> Both biomass *per se*<sup>2</sup> and products of its modification<sup>3</sup> may be used for energy generation. World resources of carbohydrates are enormous,<sup>4</sup> therefore search for methods of the most effective application of lignocellulosic biomass as an alternative to traditional natural resources presents one of the important scientific trends.

Presently, biomass processing to generate biofuel is developed;<sup>5,6</sup> however, treatment comprising the conversion to the products of fine organic synthesis aimed on the products of high molecular complexity<sup>7,8</sup> is studied insuf-

ficiently. Earlier, the possibility of a selective conversion of cellulose to 5-hydroxymethylfurfural (5-HMF), which is one of the key platform compounds<sup>9</sup> obtained by the renewable resource processing, was shown. The product of its reduction, namely, 2,5-dimethylfurane (2,5-DMF) is one of the most advanced components of liquid biofuel.<sup>10–12</sup> Symmetrical derivatives of 5-HMF, particularly, 2,5-diformylfurane (2,5-DFF)<sup>13</sup>, 2,5-furanedicarboxylic acid (2,5-FDCA) and 2,5-bishydroxymethylfurane (2,5-BHMF), have found application in biopolymer synthesis<sup>14</sup> (Scheme 1).

Cellulose is a hardly soluble stereoregular polymer. During its processing to 5-HMF, ionic liquids (ILs)<sup>9</sup>



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showed their high efficiency as a reaction medium, wherein the problems of development of environmentally friendly technologies using ILs has become of particular importance.<sup>15,16</sup> It was found, that upon conversion of cellulose in imidazolium ILs the side processes of polymer (humins) formation as well as hydrolysis of 5-HMF to levulinic and formic acids are minimized.<sup>9</sup> Various synthetic methods to produce 5-HMF from cellulose using functionalized ionic liquids,<sup>17</sup>, strong Lewis acids,<sup>18–23</sup> nano-sized catalysts,<sup>24,25</sup> as well as under photocatalysis conditions<sup>26</sup> have been studied. However, high yields of the product (above 50%) were obtained under high temperature conditions,<sup>19</sup> in the presense of expensive reagents,<sup>27</sup> under microwave irradiation,<sup>28,29</sup> as well as using a significant (exceeding 30%) amount of a catalyst.<sup>20</sup>

According to the literature data, in the process of 5-HMF formation from celulose three main stages may be recognized: 1) cellulose hydrolysis to D-glucopyranose, 2) cycloisomerization of D-glucopyranose to D-fructofuranose, and 3) dehydration of the latter yielding 5-HMF.<sup>20</sup> Earlier, the use of chromium chlorides was shown to be one of the most effective approaches to obtain 5-HMF from cellulose, as it does not require the isolation of the intermediate products.<sup>9</sup> The yield of the target product is generally high (the total yield is 50-55%, average yield at each stage is  $\sim 80\%$ ), but the hydrolysis process has a lowest selectivity<sup>30</sup> and requires high temperatures (120–130 °C and higher).<sup>18–20</sup> Studies on modification of the chromium chloride/ionic liquid catalytic system are directed mainly on the increasing of the 5-HMF yield by using various additives, however in most cases these operations do not result in a considerable increase in the vield of the target products.<sup>9</sup>

The present study is aimed on the development of mild procedure for selective conversion of cellulose to 5-HMF potentially suitable for the processing of lugnocellulosic biomass. A possibility to modify the known catalytic systems based on chromium chlorides for application at reduced temperatures without significant loss in the total selectivity of the process has been examined.

## **Results and Discussion**

One of the possible approaches to universal catalysts is the formation of adaptive catalytic systems which properties are tuned according to a given reaction depending on its conditions.<sup>31</sup> For the studied process such a system may comprise the main catalyst **A**, active only at high temperatures, as well as cocatalyst **B**, which presence enables the reaction with catalyst **A** to proceed at lower temperatures (Scheme 2).

As a model catalyst for the conversion of cellulose to 5-HMF,  $CrCl_3 \cdot 6H_2O$  was used showing high efficiency in performing the reaction in [BMIM][Cl]<sup>19,20</sup> (BMIM is 1-butyl-3-methylimidazolium chloride). The highest



Scheme 2

product yield (52%) was obtained maintaining the reaction mixture comprising 10% of a catalyst at 130 °C during 3 h (Table 1, run 5). We studied the possibility to perform the conversion of 5-HMF under milder conditions by using various cocatalysts promoting the stage of cellulose hydrolysis without the considerable loss in the total selectivity. Studies aimed on the search for such systems were carried out at 120 °C maintaining the reaction mixture comprising  $CrCl_3 \cdot 6H_2O$ , cocatalyst and [BMIM][Cl] for 1 h. Under these conditions in the absence of a cocatalyst, the rate of formation of 5-HMF is sufficiently low enabling the comparative analysis of the performance of the catalytic systems (see Table 1).

Some Brønsted acids are known to catalyze effectively the cellulose hydrolysis to glucose<sup>32</sup> as well as fructose dehydration to 5-HMF.<sup>33</sup> At the first step, a series of acids differing in the nature and  $pK_a$  was used as cocatalysts: acetic ( $pK_a = 4.8$ ), citric ( $pK_a = 3.1$ ; 4.8; 6.4), camphorsulphonic (CSA) ( $pK_a = 1.2$ ), *p*-toluenesulphonic (TsOH) ( $pK_a = -2.8$ ), and sulphuric ( $pK_a = -3$ ; 2) acids

**Table 1.** Catalytic conversion of cellulose to 5-HMF and effectof Brønsted acids<sup>a</sup>

Run	Cocatalyst (amount)	<i>T</i> /°C	<i>t</i> /h	Yield of 5-HMF <sup>b</sup> (%)
1	_	100	12	<1
2	—	110	6	5
3	—	120	1	22
4	—	120	4	47
5	—	130	4	52
6	MeCOOH (0.1 equiv.)	120	1	24
7	MeCOOH (0.1 equiv.)	110	4	28
8	Citric acid (0.05 equiv.)	120	1	32
9	Citric acid (0.05 equiv.)	100	12	37
10	CSA (0.1 equiv.)	120	1	37
11	CSA (0.1 equiv.)	110	4	27
12	TsOH (0.1 equiv.)	120	1	34
13	TsOH (0.1 equiv.)	110	6	38
14	Amberlyst 15 (0.1 equiv.)	120	1	35
15	Amberlyst 15 (0.1 equiv.)	110	4	43
16	$H_2SO_4$ (0.025 equiv.)	120	1	39
17	$H_2SO_4$ (0.025 equiv.)	100	12	44

<sup>*a*</sup> Reaction conditions: cellulose (50 mg), [BMIM][Cl] (0.5 g), CrCl<sub>3</sub>·6H<sub>2</sub>O (0.1 equiv.).

<sup>b</sup> According to <sup>1</sup>H NMR spectroscopy data (DMSO-d<sub>6</sub>).



Scheme 3

*i*. H<sub>2</sub>SO<sub>4</sub>, CrCl<sub>3</sub>·H<sub>2</sub>O, 100 °C or 130 °C.

as well as Amberlyst  $15^{\text{(B)}}$  (p $K_a < 1$ ). The data obtained after optimizing the reaction conditions are given in Table 1. The values of the 5-HMF yields for each reaction were determined from the integral intensity ratio of the signals of an ionic liquid and 5-HMF in the <sup>1</sup>H NMR spectra. To evaluate the accuracy of calculation of the product yield from the <sup>1</sup>H NMR spectroscopy data for the reaction mixture obtained on carrying out the reaction in the absence of cocatalysts, the target product was isolated in the yield of 49% (see Experimental and Table 1, run 5).

In all experiments, cellulose was added to a prepared solution of cocatalysts in IL, since an addition of a catalyst to the cellulose solution elongated considerably its dissolution time because of a drastic increase in the medium viscosity. The experiments performed demonstrated that strong acids are most effective at low temperatures and moderate concentrations while the acids of medium strength show the highest activity at intermediate temperature and concentration of a cocatalyst (see Table 1, runs 8-17). By using weak acids, no considerable increase in the yield of the target product was observed (runs 6 and 7). The highest yield of 5-HMF was obtained in the presence of 2.5% H<sub>2</sub>SO<sub>4</sub> maintaining the reaction mixture at 100 °C for 12 h (run 17). Without cocatalyst at this temperature, the product is formed only in trace amounts (run 1). Also, it was found that the significant amount (more than 3 equiv. relative to cellulose) of water in the reaction mixture as well as the complete removal of water from the reaction mixture (carrying out the synthesis in vacuo) decreases the reaction rate. Thus, using  $CrCl_3 \cdot 6H_2O/H^+$ catalytic system in the synthesis of 5-HMF from cellulose, requires no addition of water.

The mechanism of cellulose conversion to 5-HMF in the presence of chromium chlorides (Scheme 3;  $H_2SO_4$ shows highest selectivity at the stage of cellulose hydrolysis at 100 °C; while at 130 °C, CrCl<sub>3</sub> is the most effective) suggests the hydrolysis of the Lewis acid-activated glycosidic bond at the first stage.<sup>20</sup> In this process, CrCl<sub>3</sub> demonstrates low activity at 100 °C, whereas in the presence of  $H_2SO_4$  hydrolysis can be performed even at lower temperatures.<sup>32</sup> Subsequently, CrCl<sub>3</sub> is involved in cycloisomerization of D-glucopyranose to give a pyranose form of D-fructose, which dehydration yields the target product. Both catalysts can catalyze the last stage of the process at 100  $^{\circ}$ C.<sup>9</sup>

Thus, in the present study it was found that by using small amounts of strong Brønsted acids, effective catalytic systems can be obtained. The suggested catalytic systems are adaptable to the temperature conditions of the 5-HMF synthesis from cellulose without a considerable loss in the total selectivity of the process. Optimization gave a modified catalytic system based on  $CrCl_3 \cdot 6H_2O$  and  $H_2SO_4$ , which application gave the highest yield of 5-HMF (44%) in cellulose conversion at 100 °C for 12 h. This approach has a high potential in an industrial processing of lignocellulosic biomass under mild conditions.

## **Experimental**

All reagents and solvents used in the study are commercially available. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker Avance III instrument at the <sup>13</sup>C nuclei, respectively; residual solvent signals were used as an internal standards.

Synthesis of 5-HMF from cellulose in the presence of  $CrCl_3 \cdot 6H_2O$ . A mixture of [BMIM][Cl] (500 mg) and  $CrCl_3 \cdot 6H_2O$  (7.4 mg, 0.028 mmol) was homogenized at 80 °C for 30 min, then cellulose (50 mg, 0.28 mmol, based on D-glucose) was added and the resulting mixture was stirred for 4 h at 130 °C. The product was isolated from the ionic liquid by the repeated extraction with EtOAc; after evaporation of the solvent 17 mg (49%) of red-brown oil was obtained, which crystallizes on cooling.

Catalytic conversion of cellulose to 5-HMF in the presence of Brønsted acids (general procedure). A mixture of [BMIM][Cl] (500 mg),  $CrCl_3 \cdot 6H_2O$  (7.4 mg, 0.028 mmol) and the corresponding amount of a cocatalyst was homogenized at 80 °C for 30 min, then cellulose (50 mg, 0.28 mmol, based on D-glucose) was added and the resulting mixture was stirred for 1–12 h at 100–120 °C (see Table 1). The yield of the product was determined from the <sup>1</sup>H NMR spectra (DMSO-d<sub>6</sub>).

**5-Hydroxymethylfurfural.** <sup>1</sup>H NMR (DMSO-d<sub>6</sub>)  $\delta$ : 9.55 (s, 1 H, C(O)H); 7.49 (d, 1 H, CH-furane, J = 3.5 Hz); 6.60 (d, 1 H, CH-furane, J = 3.5 Hz); 5.53 (t, 1 H, OH, J = 5.9 Hz); 4.51 (d, 2 H, CH<sub>2</sub>OH, J = 6.1 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-d<sub>6</sub>),  $\delta$ : 177.9 (C(O)H); 162.2, 151.8 (C, furane); 124.3, 109.7 (CH, furane); 56.0 (CH<sub>2</sub>OH). Found (%): C, 57.08; H, 4.79. C<sub>6</sub>H<sub>6</sub>O<sub>3</sub>. Calculated (%): C, 57.14; H, 4.80.

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