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# A heteropoly acid ionic crystal containing Cr as an active catalyst for dehydration of monosaccharides to produce 5-HMF in water†

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Cs<sub>2</sub>[Cr<sub>3</sub>O(OOCC<sub>2</sub>H<sub>5</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>2</sub>[α-SiW<sub>12</sub>O<sub>40</sub>], a chromium-based heteropoly acid (HPA) ionic crystal, was demonstrated to be an active heterogeneous catalyst for production of 5-hydroxymethylfurfural (HMF) from fructose or glucose. The dependencies of catalytic activity on reaction parameters such as solvent, temperature and reaction time were investigated and the reaction conditions were optimized. Based on fructose, the yield of HMF reaches 86% and 56% when using DMSO and water as solvents, respectively. Starting from glucose, a yield of HMF up to 48% can be achieved for both aqueous and DMSO media. The catalyst was successfully recycled 5 times.

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## Introduction

Gradual exhaustion of available fossil feedstocks prompts the search for renewable raw materials.<sup>1</sup> Renewable and abundant cellulosic biomass is a promising alternative for substitution of fossil resources in the chemical industry.<sup>2</sup> C<sub>6</sub> monosaccharides are readily available *via* hydrolysis of cellulose and hemicelluloses.<sup>3</sup> Dehydration of these monosaccharides results in formation of HMF which is a promising platform substance for production of fuels and chemicals.

Dehydration of saccharides takes place in the presence of catalysts with Brønsted acidic functionalities.<sup>4</sup> The yield of HMF is very sensitive to reaction parameters such as substrate, solvent, catalyst and temperature. The reaction is hampered by subsequent transformations of HMF, *i.e.* formation of humins or hydrolysis of HMF into levulinic acid and formic acid. Since some organic solvents stabilize HMF molecules protecting them from destruction, the yield of the product depends on the choice of solvent as follows: ionic liquids > polar organic solvents (especially DMSO) > water. Despite nearly quantitative yields of HMF in ionic liquids<sup>5–8</sup> and DMSO,<sup>4,9</sup> these solvents are hardly applicable in large scale owing to difficulties with recovery of HMF,<sup>9,10</sup> high cost and toxicity. From ecological and economical points of view, water is the solvent of choice for production of HMF.

However, the yields of HMF in aqueous medium are restricted to *ca.* 35%<sup>4</sup> owing to the acid-catalyzed rehydration of HMF leading to levulinic acid and formic acid. Only application of rather complex procedures, *i.e.* reactive extraction<sup>2</sup> or adsorption<sup>11,12</sup> of HMF, helps to improve the yield of this product. The highest yields of HMF are obtained when using fructose as substrate, whereas hydrolysis of cellulose gives rise to glucose. Although glucose is an economically more suitable substrate for production of HMF, the acidic dehydration of glucose is very unselective and yields only *ca.* 20% of HMF.<sup>4</sup> In general, a successful conversion of glucose into HMF requires first the isomerization into fructose with subsequent dehydration of the latter in the presence of a tandem catalytic system for these subsequent reactions, *e.g.* a combination of chromium salts (Lewis acid for glucose–fructose isomerization) with ionic liquids (Brønsted acid for dehydration of fructose into HMF) results in 60–80% yield of HMF based on glucose.<sup>13</sup> The same approach was accomplished by combining a solid Lewis acid Sn-beta zeolite with a Brønsted acid such as HCl or Amberlyst.<sup>14</sup> HMF was obtained in *ca.* 60% yield from glucose applying an extraction-assisted process<sup>8,15,16</sup> or using organic solvents.<sup>17</sup> Alternatively, a combination of a basic catalyst for glucose isomerization and acid-catalyzed dehydration of fructose might be performed in cascade<sup>18</sup> or even one-pot<sup>19,20</sup> processes. Definitely, the design of a heterogeneous catalyst bearing Lewis and Brønsted acidic sites would be highly desirable considering not only recyclability, reduced corrosion potential, and waste formation but also optimized reaction integration for a technical application. From this point of view, the derivatives of HPAs<sup>21–23</sup> are suitable candidates for bifunctional catalysts. Lewis acidity can be introduced to HPAs by exchange of

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protons for transition metals. Such catalysts were successfully tested for hydrolysis of cellobiose and cellulose,<sup>24</sup> production of biodiesel, and conversion of cellulose into HMF.<sup>25–28</sup> Focusing on the synthesis of HMF, we have recently demonstrated the catalytic activity of dodeca-tungstophosphoric acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) and its cesium or silver salts<sup>29,30</sup> for the dehydration of fructose or glucose into HMF. Dehydration of fructose over  $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$  was performed in a biphasic water/methylisobutylketone (MIBK) system at 120 °C for 60 min yielding 78% of HMF. Owing to the Lewis acidity of the catalyst, a transformation of glucose was also possible, but required harsher conditions: 76% yield of HMF was obtained at 130 °C for 4 h in the same biphasic system. Although HMF can be produced in rather high yield in the biphasic system, it would be advantageous to elaborate a bifunctional catalyst with Lewis-Brønsted acidity for the manufacture of HMF in aqueous medium.  $\text{Cs}_2[\text{Cr}_3\text{O}(\text{OOCCH}_2)_6(\text{H}_2\text{O})_3]_2[\alpha\text{-SiW}_{12}\text{O}_{40}]$  ( $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$ ), a chromium-based polyoxometalate (POM) ionic crystal, is a suitable candidate for water-tolerant catalyst for HMF synthesis. Chromium atoms are responsible for the Lewis acidity of this catalyst, while the Brønsted acidity can be generated from the HPA molecules' dissociation of coordinated water under the polarizing effect of the cation.<sup>31</sup>  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  was firstly reported by the Mizuno group<sup>32</sup> as a channel-selective material with hydrophilic and hydrophobic pores. The narrowest and widest openings of the hydrophobic channel are 4.0 Å and 5.2 Å, respectively. Importantly, incorporation of Cr into the easily separable solid catalyst diminishes the hazardous effect of  $\text{Cr}^{3+}$ . Therefore, in this work, we tested  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  as catalyst for HMF formation based on fructose and glucose as substrates in combination with DMSO and water as solvents.

## Experimental

### Catalyst preparation and investigation

Solvents and reagents were obtained from commercial sources and were used without further purification.  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  was prepared following literature studies.<sup>33,34</sup>  $\text{Cs}_2[\text{Cr}_3\text{O}(\text{OOCCH}_2)_6(\text{H}_2\text{O})_3]_2[\alpha\text{-SiW}_{12}\text{O}_{40}]$  was prepared according to a previously reported procedure.<sup>32</sup> IR spectra (4000–400  $\text{cm}^{-1}$ ) were recorded in KBr discs on a Nicolet Magna 560 IR spectrometer. Elemental analyses were carried out using a Leeman Plasma Spec (I) ICP-ES. The data on elemental analysis reveal a good agreement of the calculated composition for  $\text{Cs}_2[\text{Cr}_3\text{O}(\text{OOCCH}_2)_6(\text{H}_2\text{O})_3]_2[\alpha\text{-SiW}_{12}\text{O}_{40}]$  (W, 48.78; Cr, 6.90; Cs, 5.88; Si, 0.62 wt.%) with the obtained results (W, 49.37; Cr, 6.83; Cs, 5.85; Si, 0.61 wt.%).

Acidity of  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  was evaluated by a combination of spectroscopic and Hammett methods.<sup>35,36</sup> A sample of catalyst (100 mg) and Hammett indicator (*p*-nitroaniline, 50 mg) were dispersed in  $\text{H}_2\text{O}$  (20 mL). The mixture was sealed, stirred for 12 h at room temperature and subsequently separated by filtration. The concentration of *p*-nitroaniline in the filtrate was measured by using a Cary 500 UV/Vis/NIR spectrophotometer at  $\lambda = 380$  nm.

### Catalytic experiments

The catalytic experiments were performed under nitrogen atmosphere in a Parr reactor (volume 50 mL). A mixture of a monosaccharide (0.3 g) and a given amount of the catalyst was added into 10 g of solvent. The mixture was stirred and heated up. The reaction was stopped by rapid cooling of the reactor in an ice bath. The catalyst  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  was separated by centrifugation and rinsed with water three times. The catalyst was dried at 80 °C for 3 h to remove water.

### Analysis

The consumption of saccharides was measured by means of high-performance liquid chromatography (HPLC, Shimadzu LC-10A) conducted on a system equipped with a refractive index detector. The saccharides were quantified by HPLC with an Aminex HPX-87H column, using MilliQ water (pH = 5.5) as the mobile phase at a flow rate of 0.6  $\text{mL min}^{-1}$  and a column temperature of 30 °C. The concentration of HMF in aqueous phase was determined by HPLC with an ION-300H column using a 2 : 8 v/v methanol : water (pH = 2) eluent at a flow rate of 0.7  $\text{mL min}^{-1}$  and a column temperature of 30 °C using a UV detector. The concentration of HMF in the organic phases was determined by gas chromatography using an Agilent 6890 system equipped with an Agilent 19091J-416 capillary column and a flame ionization detector. Qualitative analysis was performed by gas chromatography-mass spectrometry (GC-MS, Agilent 5970) with scan parameters as follows: low mass 20.0, high mass 700.0, and threshold 150.

## Results and discussion

### Fructose dehydration reactions

The heteropoly acids  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  and  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  were characterized and studied as catalysts for fructose dehydration into HMF.  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  is a soluble Brønsted acid with an acid content of 1.34  $\text{mmol g}^{-1}$ .<sup>37</sup>  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  is a solid bifunctional catalyst with dual Brønsted-Lewis acidity. The contents of Brønsted acid and Lewis acid sites were obtained from titration and the FT-IR spectra of pyridine adsorption.<sup>38</sup> The Brønsted acidity of  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  evaluated by means of sorption of *p*-nitroaniline is equal to 0.89  $\text{mmol g}^{-1}$ , while the Lewis acidity of 0.54  $\text{mmol g}^{-1}$  was estimated from the ratio of the intensities of peaks corresponding to Brønsted sites at 1540 and 1639  $\text{cm}^{-1}$  and those corresponding to Lewis sites at 1450 and 1610  $\text{cm}^{-1}$  in the IR spectra of pyridine adsorption. Similar concentrations of acidic sites were found for  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  and  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ .  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  contains hydrophilic channels with diameters comparable with the dimensions of fructose (*ca.* 5 Å).<sup>39</sup> Therefore we expected fructose to be adsorbed in these micropores. The IR spectra of  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  and the spectra after adsorption of fructose confirmed the adsorption of the substrate on the catalyst (Fig. S1†). IR vibration bands at 982  $\text{cm}^{-1}$  ( $\nu_{\text{as}} \text{W-O}_d$ , terminal oxygen bonding to W atom), 920  $\text{cm}^{-1}$  ( $\nu_{\text{as}} \text{Si-O}$ ), 876  $\text{cm}^{-1}$  ( $\nu_{\text{as}} \text{W-O}_b$ , edge-shared oxygen connecting W), 792  $\text{cm}^{-1}$

( $\nu_{\text{as}}$  W–O<sub>c</sub>, corner-shared oxygen connecting W<sub>3</sub>O<sub>13</sub> units), and 540 cm<sup>−1</sup> ( $\nu_{\text{as}}$  Cr–O) were detected for the parent material Cs<sub>2</sub>Cr<sub>3</sub>SiW<sub>12</sub> (Fig. S1b†). A shift to higher frequencies occurred after adsorption of fructose (Fig. S1a†) with 984 cm<sup>−1</sup>, 936 cm<sup>−1</sup>, and 878 cm<sup>−1</sup> and a wide band located at 738 to 806 cm<sup>−1</sup> indicating an interaction between fructose and the SiW<sub>12</sub>O<sub>40</sub> anion. We screened the catalytic activity of Cs<sub>2</sub>Cr<sub>3</sub>SiW<sub>12</sub> and H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> using water, DMSO and MIBK as solvents at 130 °C for 30 min (Table 1). The conversion of fructose is nearly the same for all solvents with a decreasing selectivity for HMF in the following order: DMSO > MIBK > water. This tendency is not surprising as DMSO is known to stabilize HMF, while water gives rise to levulinic and formic acids as by-products.<sup>4,9</sup> H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> was more catalytically active compared to Cs<sub>2</sub>Cr<sub>3</sub>SiW<sub>12</sub> owing to the higher Brønsted acidity. Nevertheless, a comparable conversion of fructose in the presence of both HPAs indicates Cs<sub>2</sub>Cr<sub>3</sub>SiW<sub>12</sub> as a very promising solid catalyst for this process.

Taking into account that the subsequent hydration of HMF is catalyzed by H<sup>+</sup>, optimization of the Brønsted acidic functionality is an important factor for HMF selectivity. We presumed that HMF is more stable in the presence of solid Cs<sub>2</sub>Cr<sub>3</sub>SiW<sub>12</sub> than over highly acidic soluble H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>. Fig. 1 shows that the decomposition of HMF into levulinic acid and formic acid slows down over Cs<sub>2</sub>Cr<sub>3</sub>SiW<sub>12</sub> compared to H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>. Moreover, the hydrophobic channels of the Cs<sub>2</sub>Cr<sub>3</sub>SiW<sub>12</sub> ionic crystal probably also contribute to the protection of HMF, as the less polar HMF molecule exhibits a high affinity for hydrophobic sorption sites.<sup>40</sup>

The activity of Cs<sub>2</sub>Cr<sub>3</sub>SiW<sub>12</sub> for fructose dehydration was studied at different temperatures and reaction times using DMSO as solvent (Fig. S2†). The reaction was carried out at 110, 120, 130 and 140 °C. Increasing temperature accelerates the dehydration of fructose. Interestingly, at 110 and 120 °C the reaction stops after 2 h at a fructose conversion of ca. 75% and further increasing the reaction time does not significantly improve the conversion pointing towards deactivation of the catalyst. Probably, at temperatures lower than 130 °C the organic substrates or/and products are strongly adsorbed on the surface of the catalyst causing deactivation. For higher temperatures, desorption is enhanced, and at 130 and 140 °C, full conversion of fructose can be achieved within 1.5 h. Interestingly, degradation of HMF was observed for temperatures above 130 °C, while the product was stable at a lower temperature. Decomposition of HMF in the presence of

acidic catalysts is expected, taking into account the high reactivity and tendency of HMF to resinification.<sup>4,9</sup> Fig. 2 shows temperature- and time-dependent HMF yields over Cs<sub>2</sub>Cr<sub>3</sub>SiW<sub>12</sub> in aqueous medium. The trends observed for DMSO are in agreement with the findings for the water-based system. In both solvents, the highest yields of HMF are reached at 130 °C within 1.5–2 h and equal 83% and 48% in DMSO and water, respectively. Longer reaction times do not improve the formation of HMF, mainly due to catalyst deactivation (at  $T < 130$  °C) or preferential formation of soluble polymers and humins (at  $T > 130$  °C).

Literature reports suggest that HMF yield and selectivity depend on the starting fructose concentrations (Fig. 3). The formation of humins is one of the side reactions of fructose dehydration. The yield of humins can be as high as 35% for 18 wt.% fructose solution and 20% for 4.5 wt.% fructose solution.<sup>9</sup> Surprisingly, the HPA is catalytically active and produces HMF in nearly equal yields based on fructose concentrations as high as 30 wt.%. The reactions were performed at 130 °C for 30 min with yields of HMF in DMSO and water of ca. 45% and 34%, respectively. A further increase of the fructose concentration to 50 wt.% results in a decrease of the HMF yield accompanied by extensive formation of a brown precipitate. Nevertheless, even when using 50 wt.% of substrate, a rather high catalytic activity of Cs<sub>2</sub>Cr<sub>3</sub>SiW<sub>12</sub> is observed.

### Glucose dehydration reactions

HMF production from glucose is more challenging compared to that from fructose. Thus, a Brønsted acid such as H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> demonstrates poor catalytic activity for the conversion of glucose, producing HMF in yields of 10–29% in DMSO and 8–14% in an aqueous medium (Fig. 4). Owing to the presence of chromium in the framework, Cs<sub>2</sub>Cr<sub>3</sub>SiW<sub>12</sub> can serve as a bifunctional catalyst with Brønsted and Lewis acidity. The yield of HMF in the presence of Cs<sub>2</sub>Cr<sub>3</sub>SiW<sub>12</sub> is much higher than over H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> and reaches ca. 56% and 48% in DMSO and water, respectively. The optimal conditions for the reaction are 140 °C and 4 h. Interestingly, the HMF yield in DMSO considerably decreases from 83% to 56% when using glucose as substrate instead of fructose. At the same time, the HMF yield is the same (48%) for both substrates when water serves as solvent. In addition to HMF, levulinic and formic acids were detected by HPLC as by-

**Table 1** The activity and selectivity of different catalysts for fructose dehydration<sup>a</sup>

Catalysts	Solvent	Conversion (%)	Yield (%)	Selectivity (%)
H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub>	DMSO	87.6	47.3	54.0
	MIBK	89.2	44.9	50.3
	Water	91.4	19.7	21.5
Cs <sub>2</sub> Cr <sub>3</sub> SiW <sub>12</sub>	DMSO	76.6	45.1	58.9
	MIBK	78.3	36.2	46.2
	Water	73.2	33.4	45.6

<sup>a</sup> Reaction conditions: 0.3 g of fructose, 0.007 mmol of catalyst, 10 g of solvent, 130 °C, 30 min.

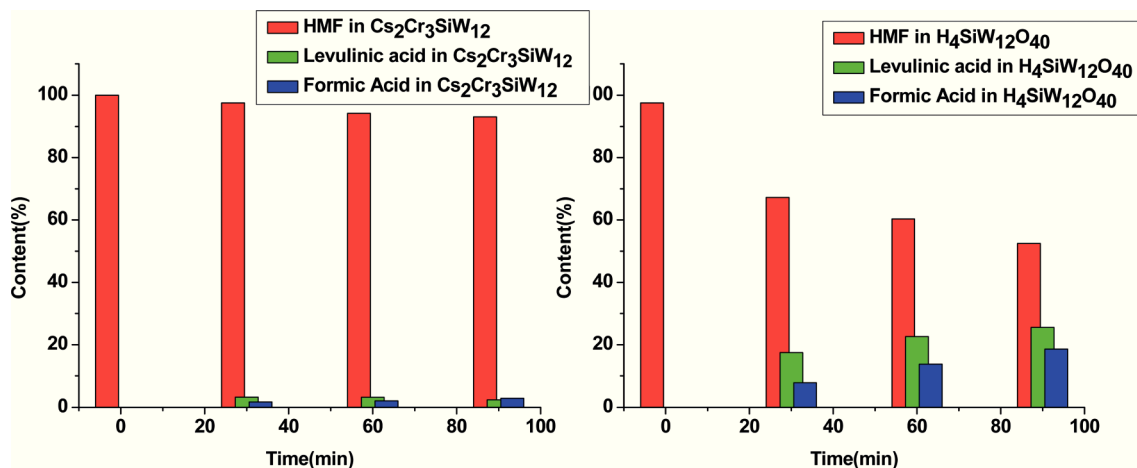


Fig. 1 Stability of HMF over (left) Cs<sub>2</sub>Cr<sub>3</sub>SiW<sub>12</sub> and (right) H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> catalysts at 130 °C.

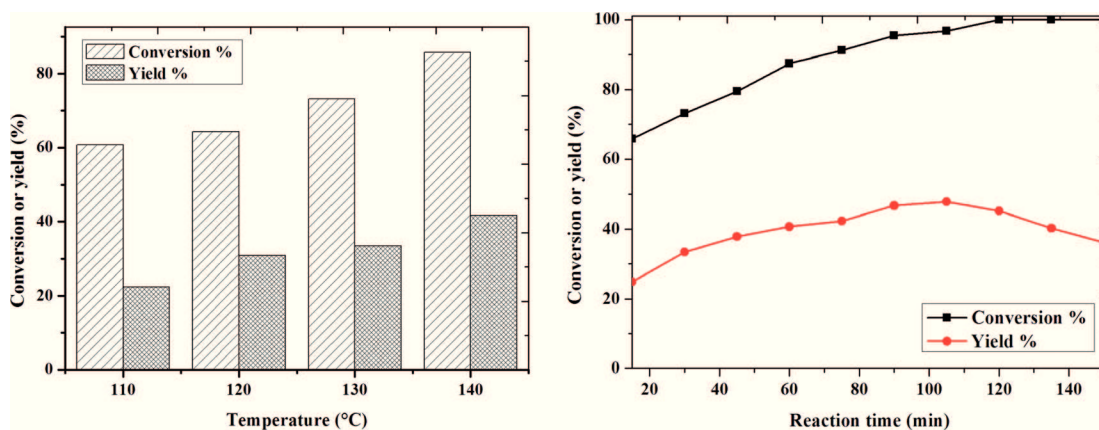


Fig. 2 Influence of temperature and reaction time at 130 °C on conversion of fructose. Reaction conditions: 0.3 g of fructose, 0.007 mmol of catalyst, 10 g of water, 130 °C, 30 min.

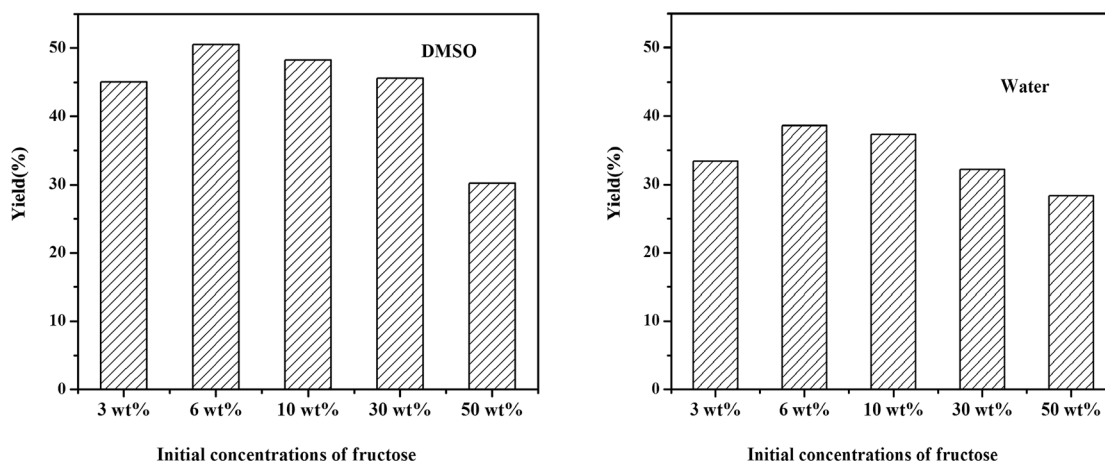


Fig. 3 Influence of initial concentration of fructose on HMF yield in water and DMSO solvents. Reaction conditions: 10 g of solvent, 0.007 mmol of catalyst, 130 °C, 30 min.

products. Moreover, formation of humins was observed. Overall, these results emphasize the excellent efficiency of

Cs<sub>2</sub>Cr<sub>3</sub>SiW<sub>12</sub> for isomerization of glucose into fructose in aqueous medium. However, the productivity of fructose



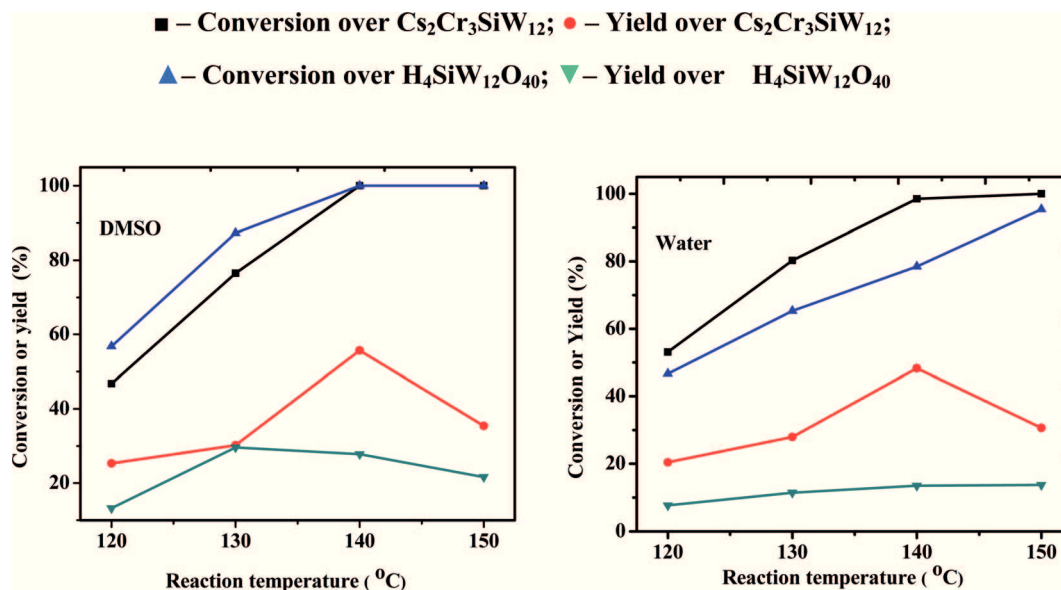


Fig. 4 Glucose conversion and HMF yield in the presence of  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  and  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ . Reaction conditions: 0.3 g of glucose, 10 g of solvent, 0.056 mmol of catalyst, 4 h.

formation over  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  in DMSO is obviously much lower than in water. Remarkably, a sole bifunctional catalyst  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  enables the aqueous-phase production of HMF based on glucose in yields of 48% compared to a maximum of 60% yield reported in the literature for rather complex systems composed of mixtures of a Lewis acid, a Brønsted acid, a saturated aqueous solution of NaCl, and an organic solvent for reactive extraction of HMF.<sup>15,16</sup>

#### Reusability of the catalyst

Recyclability is a crucial parameter of a catalyst.  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  was separated from the product mixture by centrifugation and reused after washing with water. The catalyst was successfully recycled 5 times for synthesis of HMF based on

fructose in DMSO (Fig. 5) and water (Fig. 6) with only a minor decrease in catalytic activity. The leaching of  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  into water after five recycling runs of the catalyst was *ca.* 4.7 wt.% determined by UV-spectroscopy. The IR spectrum of the recycled  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  (Fig. S1c†) basically corresponds to the parent material. It contains the vibration bands at  $\nu_{\text{as(W-O)}}$  976  $\text{cm}^{-1}$ ,  $\nu_{\text{as(W-O-W)}}$  896  $\text{cm}^{-1}$ ,  $\nu_{\text{as(W-O-W)}}$  806  $\text{cm}^{-1}$  and  $\nu_{\text{as(Cr-O)}}$  521  $\text{cm}^{-1}$ , indicating that the original frameworks of HPAs are not destroyed after the reaction. However, some shifts of the bands in the IR spectrum and the appearance of new bands indicate minor structural changes. For instance, we failed to identify the position of a weak band corresponding to  $\nu_{\text{as(Si-O)}}$  and located at *ca.* 920  $\text{cm}^{-1}$ . Nevertheless, the catalytic activity of the material was not dramatically affected by recycling. Probably, these changes in IR spectrum take place due to strong adsorption

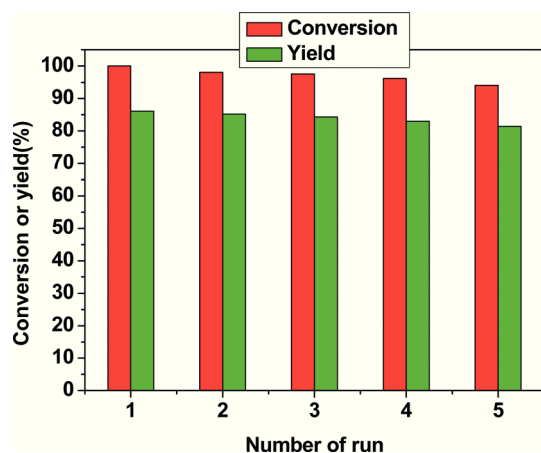


Fig. 5 Catalyst activity in five reaction cycles. Reaction conditions: 0.3 g of fructose, 10 g of DMSO, 0.007 mmol of catalyst, 130 °C, 90 min.

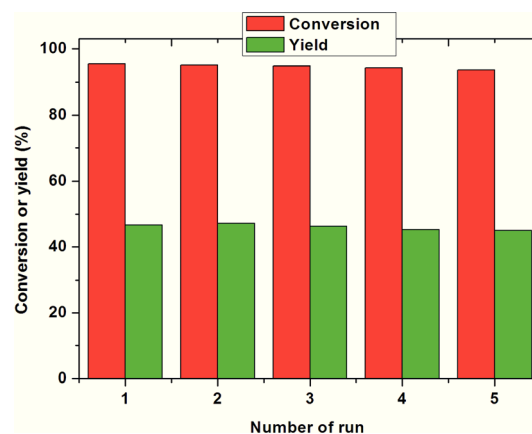


Fig. 6 Catalyst activity in five reaction cycles. Reaction conditions: 0.3 g of fructose, 10 g of water, 0.007 mmol of catalyst, 130 °C, 90 min.

of fructose or products. The future work will aim to search for a more efficient regeneration procedure for  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  than washing with water. Noteworthy, ease at recycling of the solid  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  is a great advantage of this catalyst over classical HPAs. For example, we failed to perform a recyclability test of  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  which is soluble in high-boiling DMSO. Moreover  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  is not sufficiently soluble in potential extracting solvents (e.g. diethyl ether), therefore cannot be easily isolated.

To investigate whether the catalytic process is homogeneously or heterogeneously catalyzed, a leaching test was performed.  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  was thermostated at 130 °C in aqueous medium for 90 minutes without addition of fructose. Afterwards the catalyst was separated from the liquid phase by centrifugation. Then fructose was added to the aqueous supernatant, and the reaction was carried out for 30 min at 130 °C resulting in fructose conversion and HMF yields of 11.8% and 3.5%, respectively. Conversion of fructose and yield of HMF in the blank experiment without HPA were 11.4% and 3.2%, accordingly. This result demonstrates that  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  catalyzes dehydration of fructose heterogeneously.

## Conclusion

The heteropoly acid ionic crystal  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  has been studied as a catalyst for the selective conversion of fructose and glucose into HMF in DMSO and water. The activity of  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  is comparable to that of  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  for dehydration of fructose to HMF. However, HMF is more stable in the presence of  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  than over  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  owing to lower Brønsted acidity of the former and possible stabilization of low polar HMF molecules in the hydrophobic channels of the ionic crystal.  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  produces HMF in high yields based on fructose solutions with initial concentrations of 3–30 wt.%. Temperatures higher than 130 °C are required to avoid deactivation of the catalyst via strong adsorption of the substrate and/or products. The yields of HMF from fructose and glucose in DMSO media are 83% and 56%, respectively. The catalyst is very active in aqueous medium producing HMF from glucose and fructose in nearly the same yield of 48%. This result suggests  $\text{Cs}_2\text{Cr}_3\text{SiW}_{12}$  as a very efficient catalyst for aqueous-phase glucose-based synthesis of HMF. The catalyst was recycled 5 times with only minor loss of activity.

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