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Graphical abstract

A Choline chloride/DMSO solvent for the direct synthesis of diformylfuran from carbohydrates in the presence of heteropolyacids

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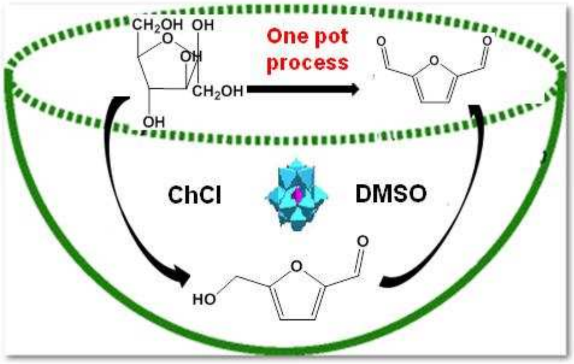

Here we report the one pot conversion of fructose to DFF in the presence of a mixture of choline chloride (ChCl) and DMSO as a solvent and Mo-Keggin heteropolyacids.

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A Choline Chloride/DMSO solvent for the direct synthesis of diformylfuran from carbohydrates in the presence of heteropolyacids

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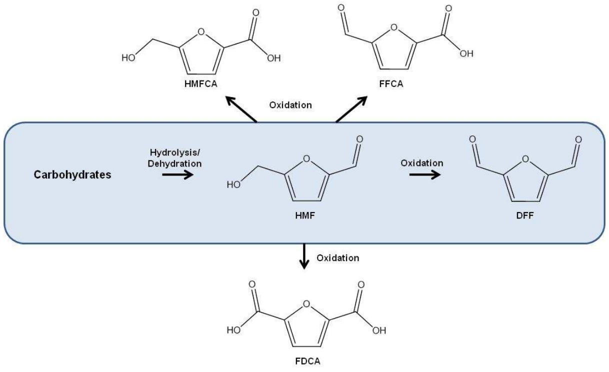
Here we demonstrate that choline chloride has a beneficial effect on the direct conversion of fructose and inulin to DFF in the presence of Mo-V containing Keggin heteropolyacid. ChCl have two beneficial effects : 1) the enhancement of the conversion of fructose to HMF and 2) a higher conversion of HMF to DFF. A yield to DFF of 84% was obtained from fructose in the optimized conditions. In this mixture inulin was also converted to DFF.

Introduction

A huge interest is nowadays given to the conversion of carbohydrates to platform molecules such as furanic compounds.[1] Among them, 2,5-diformylfuran (DFF), the partially oxidized product of 5-hydroxymethylfurfural (HMF), is considered as a key intermediate for the production of pharmaceuticals, fungicides, macrocyclic ligands, cross-linked agents and polymers.[2] The production of DFF from HMF requires the oxidation reaction to be closely controlled since a large variety of products can be obtained including 5-formyl-2-furancarboxylic acid (FFCA), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), and 2,5-furandicarboxylic acid (FDCA) as shown in Scheme 1.[3,4]



Scheme1. Oxidation of HMF

So far the reported routes for the production of DFF are mostly based on the selective oxidation of HMF using various catalysts.[5-13] However, the instability of HMF is problematic leading to costly downstream purification process. Hence, DFF is nowadays commercially available only in small quantity and at a prohibitive cost.[14]

With the aim of reducing the cost of DFF, its direct production from carbohydrates has emerged as an interesting alternative route (Scheme 1). The one pot synthesis of DFF from glucose was reported as a feasible way and involves a three step process.[15] First, glucose was isomerized to fructose in the presence of a hydrotalcite catalyst. Then, the dehydration of fructose to HMF was carried out over Amberlyst-15 and finally the oxidation of HMF to DFF occurred over a Ru/HT catalyst in *N*,*N*-dimethylformamide. The overall DFF yield was 25% under optimized conditions. An increase of the DFF yield from 25 to 49% was observed when fructose was used as a carbohydrate feed instead of glucose. Fu and co-workers have obtained 80% yield of DFF from fructose in a two-step process using successively Fe_3O_4-SBA-SO_3H and K-OMS-2 as solid catalysts in dimethylsulfoxide (DMSO).[16] Note that attempts to conduct this reaction in a one pot process failed mostly due to the dominant production of humins and other side products.

Recently, Liu and co-workers[17] have shown that DFF can be obtained from fructose in the presence of a Mo-containing Keggin heteropolyacids ($HPMo_{12}O_{40}$) under air. A DFF yield of 58% was claimed when using DMSO as a solvent. Mo-containing Keggin heteropolyacids are clearly an interesting class of catalysts for this reaction owing to their acid and redox properties allowing a bifunctional catalytic process to take place, thus minimizing the number of reaction steps.[18]

In most of reported examples dealing with the production of DFF from carbohydrates, DMSO was used as a solvent.[19] Notably, Estrine et *al.* have shown that the conversion of fructose in the presence of NaBr and DMSO led to the

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formation of 85% of DFF after 18 h at 150°C.[20] The authors claimed that the thermolysis of DMSO was responsible for the oxidation of HMF to DFF.

Here, we wish to demonstrate, that a mixture of choline chloride (ChCl) and DMSO (65/35) is an attractive media to promote the direct conversion of fructose, and even inulin, to DFF in the presence of Mo-V containing Keggin heteropolyacid catalysts. Notably, under optimized conditions, DFF was produced with a yield of 84% in a one step process. ChCl has recently attracted considerable attentions for the design of safe reaction media mainly because of its low price and biodegradability.[21] ChCl was selected here based on previous results from us and others.[22].

Experimental section

Catalyst preparation

The phosphomolybdovanadate free acids $H_{(3+n)}PMo_{(12-n)}V_nO_{40}$ (n = 0–2) were prepared according to the method previously described by Onoda et *al.*.[23] Typically, the preparation of P-Mo-V heteropoly acids involves stoichiometric amounts of vanadium oxide (V_2O_5: Alfa produkte 99.8+ %), molybdenum oxide (MoO_3: Aldrich 99+ %) and phosphoric acid (H_3PO_4: 85% wt). These chemicals were suspended in 500 ml of pre-heated water (70^oC) in a three-necked 1000 ml flask equipped with a condenser. The suspension of the metal oxides was maintained under stirring and reflux until a clear orange-red solution was obtained (nearly 48 hours). The solid product was isolated by removing the solvent under vacuum at 50^oC and dried in an oven at 110°C overnight.

Catalyst characterisation

X-ray diffraction (XRD) patterns of the Mo-Keggin catalysts were carried out with a X EMPYREAN of PANalytical instrument operated at 45 kV and 40 mA, equipped with a copper anode and a fast linear detector X'Celerator in the angular range $10° \le 2\vartheta \le 80°$. Diffuse reflectance Infra-Red spectra were recorded on a « spectrum one » spectrometer equiped with a device type ATR (Attenued Total Reflectance). The spectra were recorded between 650 and 4000 cm^{-1}. The BET surface area of catalysts were measured by nitrogen physisorption at 77 K on a with a Micromeritics Flowsorb II 2300 instrument. Before the measurement, the samples were degassed at 250 °C for 6 h. TGA/TDA analyses were performed on a TA instrument Q600, under air flow (100 ml/min) with a temperature ramp of 5°C/min from room temperature to 300°C. All the characterizations of the catalysts are reported in Fig. S1 to S9. The results obtained confirmed the structure of the heteropolyacids.

Catalytic test

The one-pot oxidation catalytic experiments starting from fructose were performed in a 10 mL one-necked glass vessel. Fructose (20 wt%, 0.4g) and catalyst (7 wt%, 0.028g) were introduced in a solvent mixture of ChCl/DMSO (2g) and was heated at the desired temperature (i.e; 120°C) under magnetic stirring and a O_2 flow (2 or 10 $mL.min^{-1}$). The stirring was maintained during the desired reaction time. After cooling to room temperature, the products were analyzed by HPLC.

Analytical methods

Yields of HMF were determined by external calibration at 25°C using a HPLC equipped with a nucleosil 100–5 C18 column (250 x 4.6 mm), a Shimadzu LC-60 20AT pump, a Shimadzu RID-10A detector and using a mixture acetonitrile/water (10:90) as mobile phase (0.8 mL.min-1).

Fructose was quantified by external calibration at 25°C using a HPLC equipped with a Shodex sugar K8-column (300 x 4.6 mm), a Shimadzu LC-60 20AT pump, a Shimadzu RID-10A detector and using water as mobile phase (1 $mL.min^{-1}$).

DFF and by products were analyzed by extrernal standard at 25°C using a HPLC equipped with a ICE-Coregel107H column (300 x 8 mm) a Varian Prostar UV-V detector (210 nm), Varian Prostar pumps (model 210) and 7mmol of sulfuric acid in water as a mobile phase (0.7 $mL.min^{-1}$).

The samples were collected periodically for HPLC analysis.

Results and dicussion

In a first set of experiments, the direct synthesis of DFF from fructose was carried out by using different mixtures of DMSO and ChCl as a solvent (Scheme 1). Otherwise noted, a solution of 20 wt% of fructose was heated at 120°C for 14 h in the presence of 7 wt% of $H_4PMo_{11}V_1O_{40}$ (HPMoV) which was used here as a bifunctional catalyst (acid/oxidant). Acid sites promote the dehydration of fructose to HMF while oxidative sites ensure the oxidation of HMF to DFF. To enhance the oxidation reaction, an oxygen flow, at a rate of 2 $mL.min^{-1}$, was employed. Different weight ratios of ChCl/DMSO ranging from 0/100 to 100/0 were first tested. Results are summarized in Figure 1. It should be noted that in all tested conditions, the yield of FDCA, a side product often observed in the production of DFF, remained lower than 2 %.

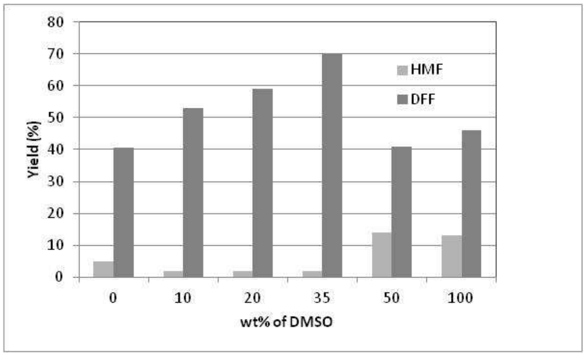

Figure 1. Synthesis of DFF from fructose at 120°C for 14h under 2 $mL.min^{-1}$ of oxygen in the presence of 7wt% of HPMoV. Effect of the ChCl/DMSO weight ratio.

In neat ChCl (a liquid fructose/ChCl deep eutectic mixture was initially formed), DFF was produced with a yield of 40% along with 5% of HMF. At high fructose conversion, the reaction media unfortunately became solid and the reaction stopped. This was ascribed to the consumption of fructose leading to a precipitation of ChCl (destruction of the liquid fructose/ChCl

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DES). In order to avoid this phenomenon and to get higher yield of DFF, DMSO was progressively added. As expected, the substitution of 10 wt% of ChCl by DMSO led to an enhancement of the DFF yield from 40% to 52% while the conversion of fructose remained total. Only HMF (1% yield) was detected as a side products indicating that other side-products were mostly humins as corroborated by the formation of black materials. When the amount of DMSO was further increased from 10 to 35 wt%, the yield of DFF was concomitantly increased from 52 to 70%. However, one should note that a further increase of the DMSO content (above 35 wt%) led to a decrease of the DFF yield from 70% to 45%.

Interestingly, addition of DMSO to ChCl has a dramatic effect on the kinetic profile of the reaction. For instance, when the reaction was stopped at 30 min, the yield of HMF (primary product) was found to be 80% in neat ChCl *versus* only 50% in neat DMSO. The initial production rate (3.42 $\mathrm{mmol_{HMF}/h}$) of HMF remained unchanged up to a ChCl/DMSO composition of 65/35 (78% yield of HMF after 30 min) but significantly dropped (2.19 $\mathrm{mmol_{HMF}/h}$) when the amount of DMSO was further increased (Fig. S10). As observed in our previous work, it seems that ChCl led to an enhancement of the initial HMF production rate presumably thanks to its ability to stabilize reaction intermediates through hydrogen bonds.

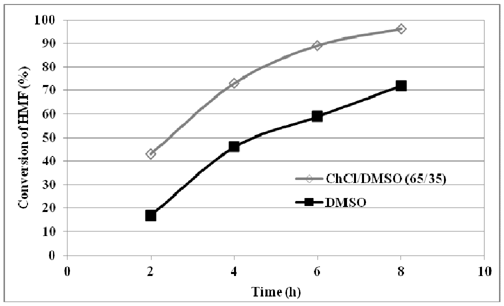

Figure 2. Oxidation of HMF to DFF in the presence of 7 wt% of HPMoV under 2 mL.min^{-1} of oxygen. Effect of the substitution of DMSO by ChCl.

To further support the beneficial effect of ChCl on the production of DFF, a similar reaction was conducted by directly starting from HMF. From the kinetic profile presented in Figure 2, it clearly appears that HMF was more rapidly converted to DFF in a ChCl/DMSO (65/35) mixture than in neat DMSO. Notably, in neat DMSO, only 72% of HMF was converted after 8 h of reaction versus 95% in a ChCl/DMSO (65/35) mixture. To explain this result, the solubility of oxygen was studied. To carry out this experiment, the oxygen gas flow content was analyzed by mass spectrometry in order to see the decrease of O2 when it will be dissolved in a mixture of 2g of solvent and 20 wt% of fructose at 120°C. An oxygen flow of 10 mL.min-1 was chosen as a reference (Fig. 3). The reaction was stopped when the oxygen content reached the initial value in the gas phase (10 mL.min^{-1}). It was interesting to see that the oxygen solubility is higher in the presence of a mixture of ChCl/DMSO than in neat DMSO. This result can explain the enhancement in the oxidation rate at high content of ChCl. Hence, a ChCl/DMSO 65/35 was optimal to get the highest yield of DFF from fructose.

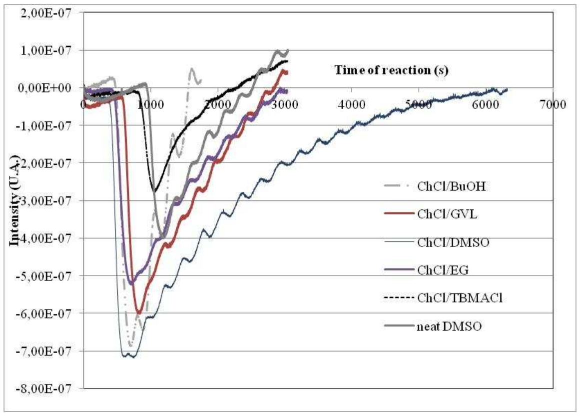

Figure 3. Solubility of O_2 in various solvent in the presence of fructose (20 wt%) at 120°C in the absence of catalyst. 10 mL.min^{-1} of O_2. Analysis of the oxygen content decrease in the gas phase by mass spectrometry analysis.

Next, the flow rate of oxygen was also studied at different ChCl/DMSO ratio. As observed in Figure 4, at 10 mL.min^{-1} of O_2, DFF was still obtained with a maximum yield of 70% at a ChCl/DMSO ratio of 65/35. Note that no significant improvement of reaction rate was observed when the O_2 flow rate was increased suggesting that fructose can be converted to DFF using a low flow rate of oxygen. Taking benefit of this advantage, the reaction was then conducted in an open air vessel. Remarkably, the yield of DFF obtained after 14h of reaction was similar (68%) than under O_2 flow which is of significant interest with respect to safety and scale up.

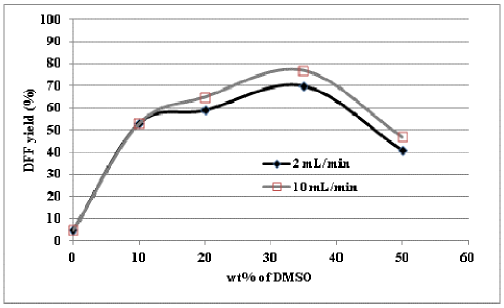

Figure 4. Synthesis of DFF from fructose in a mixture of ChCl/DMSO at 120°C in the presence of 7 wt% of HPMoV. Effect of the oxygen flow rate.

Having identifying that a ChCl/DMSO mixture of 65/35 was optimum to get the highest yield of DFF, the fructose content was then varied. All the other experimental conditions remained unchanged. Results are summarized in Table 1. As commonly observed in carbohydrate chemistry,[14, 24] when the fructose content was decreased from 20 to 5 wt%, the yield of DFF was increased from 77 to 84% (Table 1, entries 1 and 2). On the opposite, when the fructose content was increased from 20 to 50 wt%, the yield to DFF decreased from 70% to 57% (Table 1, entries 2-3). Interestingly, at such high loading, we were pleased to see that the yield of DFF was only 20% in

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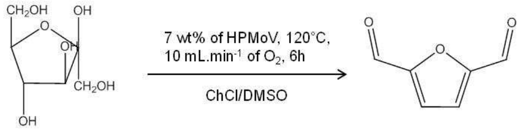
neat DMSO further reinforcing the beneficial role of ChCl on the reaction selectivity (table 1, entry 4). Such beneficial effect of ChCl on the reaction selectivity was already observed in our group notably in the production of HMF.[21] Using neat DMSO, *in situ* produced HMF was actually decomposed to the detriment of the formation of DFF.

Table 1. Conversion of fructose to DFF. Effect of the fructose content in two weight ratios of ChCl/DMSO.



Entry	Fructose content (wt%)	Catalyst content (wt%)	HMF yield (%)	DFF yield (%)
1	5	7	3	84
2	20	7	4	77
3	50	7	0	57
4	50[a]	7	0	20
5	20	5	6	65
6	20	-	60	5

[a] in neat DMSO

Next, the amount of catalyst was reduced to check the impact on the reaction selectivity. Interestingly, a reduction of the catalyst amount from 7 to 5 % obviously resulted in a decrease of the conversion rate of fructose but with no incidence on the DFF selectivity. One should notice that in the absence of any catalyst, HMF was produced with 60 % yield in the ChCl/DMSO (65/35) mixture but the yield of DFF remained lower than 5% indicating that assistance of $H_4PMo_{11}V_1O_{40}$ as a catalyst was mandatory for the oxidation of HMF to DFF (Table 1, entry 6). The catalyst-free dehydration of fructose to HMF was also previously noted by Amasekara *et al* in neat DMSO.[25] In this study, authors have demonstrated that DMSO can act as a catalyst in the dehydration of fructose to HMF, although at higher temperature (150°C) than in this work (120°C). Note that the production rate of HMF is significantly lower under catalyst free conditions suggesting that the $H_4PMo_{11}V_1O_{40}$ catalyst does have a role on the dehydration of fructose (Fig. S10).

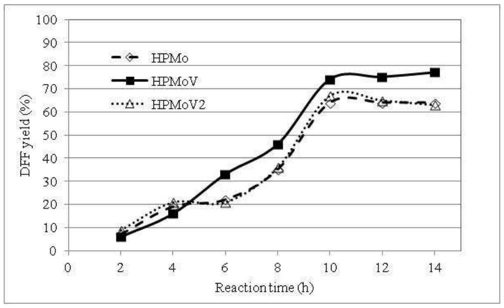
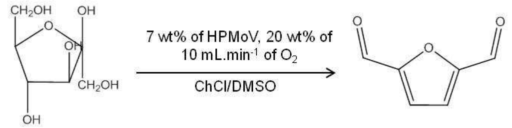


Figure 5. Effect of the catalyst nature in the synthesis of DFF from fructose (20 wt%) under 10 mL.min^{-1} of O_2 at 120°C. Solvent : mixture of ChCl/DMSO of 65/35.

Next, three different kinds of HPAs catalysts were tested and compared at 120°C in the ChCl/DMSO (65/35) mixture: $H_4PMo_{12}O_{40}$ (HPMo), HPMoV and $H_4PMo_{10}V_2O_{40}$ (HPMoV2). In Figure 5, we can observe that similar yields of DFF and reaction rate were obtained whatever the catalyst. Only a slightly higher yield of DFF was observed in the presence of HPMoV catalyst.

Table 2. Conversion of fructose to DFF. Effect of the reaction temperature in the presence of ChCl/DMSO.



Entry	Temperature (°C)	Time (h)	ChCl/DMSO weight ratio	HMF yield (%)[c]	DFF yield (%)
1	100	14	65/35	61	31
2	110	14	65/35	29	52
3	120	14	65/35	4	77
4	130	14	65/35	0	59
5	130	6	65/35	0	57
6[a]	120	14	65/35	34	37
7[a]	120	14	50/50	-	40
8[a]	100	14	50/50	22	27

[a] From 20 wt% of inulin

The temperature has also a pivotal role on the reaction (Table 2). In a mixture ChCl/DMSO (65/35), a decrease of the temperature from 120°C to 100°C decreased the reaction rate and, after 14 h of reaction, DFF was produced in only 31% yield versus 77% at 120°C which is accompanied by an increase of the HMF yield from 4 to 61%. This result indicates that if dehydration of fructose can occur at 100°C, this temperature is not optimal for an efficient oxidation of *in situ* produced HMF to DFF (Table 2, entries 1-3). Conversely, when the temperature was increased from 120 to 130°C, DFF was still obtained with 57% yield but at shorter reaction time (6h versus 14 h at 120°C, Table 2, entry 5).

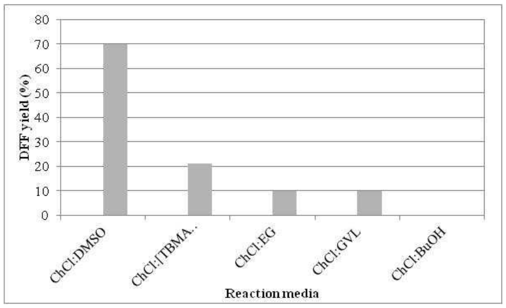


Figure 6. Conversion of fructose (20 wt%) to DFF at 120°C in the presence of HPMoV (7 wt%) under 10 mL.min-1 of O2 during 6h in the presence of a ChCl/additives weight ratio of 50/50. Effect of the nature of the solvent.

Finally, in order to collect more information on the role of DMSO, few counter experiments were performed. First of all, different additives such as tributylmethylammonium chloride ([TBMA]Cl), ethylene glycol (EG), ɣ-valerolactone (GVL), butanol (BuOH) were tested in standard conditions. As

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reported in Fig. 6, it clearly appears that the highest yield of DFF was always obtained in the presence of DMSO suggesting, in a first approximation, that DMSO does not have the only role of co-solvent. When a mixture of [TBMA]Cl/DMSO was used, the solubility of the oxygen was lower than in the presence of ChCl/DMSO and neat DMSO (Fig. 3). This lack in oxygen solubility can be responsible of the decrease of the DFF yield. For the other solvents, the solubility of oxygen is not correlated to the oxidation of HMF to DFF as shown by Fig. 3. This low DFF yield in the presence of these solvents can be due to secondary reactions that can occur between the solvent and HMF preventing its oxidation by producing ethers for example as reported in the literature.[26]

To get more insight on the reaction mechanism, the oxygen flow exiting the reactor was analyzed by means of a mass spectrometer. Interestingly, formation of Me_2S was clearly evidenced under standard conditions suggesting a partial reduction of DMSO (Fig. S13). When the catalytic reaction was carried out under helium instead of air, Me_2S was still observed but DFF was produced in a very low yield (7%). In this case, HMF was the major product (63% yield, Fig. S14) suggesting that O_2 was required to promote the oxidation of HMF to DFF. In addition, without catalyst, no Me_2S was observed indicating that reduction of DMSO to Me_2S might be catalyzed by HPMoV. Although deeper analyses would be required to fully assess the reaction mechanism with accuracy, one may propose at this stage a plausible reaction mechanism. First of all, ChCl helps to produce HMF from fructose in the presence of HPMoV, secondly DMSO was reduced to Me_2S while the catalyst oxidizes HMF to DFF. ChCl plays also the role to enhance the solubility of O_2.

Next, inulin and glucose were tested as two other carbohydrate feed. One can note that from glucose, the reaction is more challenging and our attempts to produce DFF from glucose failed even by combining HPMoV with 1.25 wt% of AlCl3, 6H2O to promote the isomerization of glucose to fructose, a critical step on the route to HMF under the same standard conditions as those described above. Under these conditions, the reaction media became solid after 14h of reaction and a DFF yield of 27% was observed along with 34% of HMF (Table 2, entry 6) from inulin. Hence in these conditions, the amount of ChCl was too high to achieve a total conversion of HMF to DFF. Hence the ChCl/DMSO was modified to a 50/50 mixture and we were pleased to see that, in this case, up to 40% yield of DFF was successfully obtained from inulin after 14 h of reaction suggesting that HPMoV is capable of hydrolyzing inulin to fructose, dehydrating fructose to HMF and then oxidizing HMF to DFF in a single reactor (Table 2, entry 6). As observed from fructose, the temperature can be decreased down to 100°C but at the expense of the reaction rate since at this temperature DFF was produced in only 22% yield along with 27% yield of HMF (Table 2, entry 7).

Conclusions

Herein, we report that mixtures of ChCl and DMSO are attractive media to promote the direct conversion of fructose to DFF in the presence of a bifunctional acid/redox catalyst *i.e.* HPMoV catalyst. Notably, yield of DFF as high as 84% were obtained from fructose. The process is also applicable to inulin from which DFF was produced with 40% yield. In addition, reaction can be conducted under air without affecting the selectivity of the reaction which is of huge interest with respect of process safety. Although clarification of the reaction definitely deserve deeper investigation, one may draw few conclusions at this stage (1) ChCl has a beneficial effect on the in situ production of HMF, (2) ChCl helps to solubilize O_2 leading to an increase in the oxidation rate reaction.

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

1 J. R. Rostrup-Nielsen, *Science*, 2005, **308**, 1421; Y. Roman-leshkov, J. N. Chheda, J. A. Dumesic, *Science*, 2006, **312**, 1933 ; H. Zhao, J. E. Holladay, H. Brown, Z.C. Zhang, *Science*, 2007, **316**, 1597; R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra,H. J. Heeres,and J. G. de Vries, Chem. Rev., 2013, **113**, 1499; A; Dutta, D. Gupta, B. Saha, A; Bhaumik, *ChemSusChem*, 2014, **7**, 928.
2 A. A. Rosatella, S. P. Simeonov, R. F. M. Frade, C. A. M. Afonso, *Green Chem.*, 2011,**13**, 754-793; K. T. Hopkins, W. D. Wilson, B. C. Bender, D. R. McCurdy, J. E. Hall, R. R. Tidwell, A. Kumar, M. Bajic, and D. W. Boykin, *J. Med. Chem.*, 1998, **41**, 3872; M. DelPoeta, W.A. Schell, C.C. Dykstra, S. Jones, R.R. Tidwell, A. Czarny, et al., *Antimicrob. Agents Chemother*,. 1998, **42**, 2495; A.S. Benahmed-Gasmi, P. Frere, M. Jubault, A. Gorgues, J. Cousseau, B. Garrigues, *Synth. Met.*, 1993, **56**, 1751; D.T. Richter, T.D. Lash, *Tetrahedron Lett.*, 1999, **40**, 6735; C. Moreau, M.N. Belgacem, A. Gandini, *Top. Catal.,*2004, **27,** 11; C. Mealares, A. Gandini, *Polym. Int,* 1996, **406**, 33; A.S. Amarasekara, D. Green, L.D. Williams, *J. Polym Eur.*, 2009, **45**, 595, and references therein.
3 X. Tong, Y. Ma, Y. Li, *Appl. Catal. A: Gen*., 2010, **385**, 1.
4 T.S. Hansen, I. Sasdaba, E.J. García-Suárez, A. Riisager, *Appl. Catal. A: Gen*., 2013, **456**, 44.
5 G.D. Yadav, R.V. Sharma, PCT Int. Appl., 2012, WO 2012073251 A1.
6 S. Yoon, J.W. Choi, H.S. Jang, J.K. Cho, J.W. Byun, W.J. Chung, S.M. Lee, Y.S. Lee, *Synlett,* 2011*,* **2**, 165.
7 A.S. Amarasekara, D. Green, E. McMillan, *Catal. Commun.*, 2008, **9**, 286.
8 J. MaZ. Du, J. Xu, Q. Chu, Y. Pang, *ChemSusChem.*, 2011, **4**, 51.
9 C. Carlini, P. Patrono, A.M.R. Galletti, G. Sbrana, V. Zima, *Appl. Catal. A: Gen*., 2005, **289**, 197.
10 G. Durand, P. Faugeras, F. Laporte, C. Moreau, M.C. Neau, G. Roux, PCT, 1996, WO96/17836.
11 O.C. Navarro, A.C. Canos, S.I. Chornet, *Top. Catal.,* 2009, **52**, 304.
12 J. Nie, H. Liu, *Pure Appl. Chem*., 2012, **84**, 765.
13 G.A. Halliday, R.J. Young Jr., V.V. Grushin, *Org. Lett*., 2003, **5**, 2003.

View Article Online
DOI: 10.1039/C5GC01336D

14 R.-J. van Putten, J. C. van der Waal,.E. de Jong,. C. B. Rasrendra,.H. J. Heeres, J. G. de Vries, *Chem. Rev.*, 2013, **113**, 1499 and references therein

15 A. Takagaki, M. Takahashi, S. Nishimura, K. Ebitani, *ACS Catal.*, 2011, **1**, 1562.

16 Z.-Z. Yang, J. Deng, T. pan, Q.-X. Guo, Y. Fu, *Green Chem.*, 2012, **14**, 2986.

17 Y. Liu, L. Zhu, J. Tang, M. Liu, R. Cheng, C. Hu, *ChemSusChem*, 2014, **7**, 3541.

18 a) J. Zhang, F. P.Xiao, J. Hao, Y. G. Wei, Dalton Trans., 2012, 41, 3599; b) T. Okuhara, *Chem. Rev.*, 2002, **102**, 3641; c) D. L. Long, R. Tsunashima, L. Cronin, *Angew. Chem. Int. Ed.*, 2010, **49**, 1736; d) C. L. Hill, *Chem. Rev.*, 1998, **98**, 1.

19 a) R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chem. Rev*. 2013, **113**, 1499; b) S. De, S. Dutta, B. Saha, *Green Chem.,* 2011, **13**, 2859; c) K.-i. Shimizu, R. Uozumi, A. Satsuma, *Catal. Commun.*, 2009, **10**, 1849;d) X. Qi, M. Watanabe, T. M. Aida, R. L. Smith, Jr., *Catal. Commun*. 2009, **10**, 1771; e) H. Yan, Y. Yang, D. Tong, X. Xiang, C. Hu, *Catal. Commun*. 2009, **10**, 1558 ; e) R. M. Musau, R. M. Munavu, *Biomass*, 1987, **13**, 67–74.

20 C. Laugel, B. Estrine, J.Le Bras,N. Hoffmann, S. Marinkovic, J. Muzar, *ChemCatChem, 2014*, **6**, 1195-1198.

21 Q. Zhang, K. De Oliveira Vigier, S. Royer, F. Jérôme, *Chemical Society Review,* 2012, **41***,* 7108.

22 F. Liu, J. Barrault, K. De Oliveira Vigier, F. Jérôme. *ChemSusChem.,* 2012, **5**, 1223.

23 T. Onoda and M. Otake, U.S. Patent, 1979, US 4 146 574.

24 F. Liu, F. Boissou, A. Vignault, L. Lemée, S. Marinkovic, B. Estrine, K. De Oliveira Vigier, F. Jérôme, *RSC Advances,* 2014, **4***, 28836 ;* C. Carlini, M. Giuttari, A. M. Raspolli Galletti, G. Sbrana, T. Armaroli, G. Busca, *Appl. Catal. A*, 1999, **183**, 295.

25 A. S. Amarasekara, L. D. Williams, C. C. Ebede, *Carbohydr. Res.*, 2008, **343**, 3021.

26 a) J. D. lewis, S. Van de Vyver, A. J. Crisci, W.R. Gunther, V. K. michaelis, R. G. Griffins, Y. Roman-Leshkov, *ChemSusChem*, 2014, **7**, 2255 ; b) P. Lanzafame, D.M. Temi, S. Perathoner, G. Centi, A. Macario, A. Aloise, G. Giordano, Catal. Today, 2011, 175, 435