PAPER

Check for updates

Synthesis of 5-hydroxymethylfurfural from monosaccharides catalyzed by superacid VNU-11–SO$_4$ in 1-ethyl-3-methylimidazolium chloride ionic liquid†

Linh Ho Thuy Nguyen,‡[abc] Huong Thi Vo,‡[ac] Ha Bich Phan,‡[abd] Minh Huy Dinh Dang,[abc] Tan Le Hoang Doan [iD] *[bc] and Phuong Hoang Tran [iD] *[ac]

Superacid VNU-11–SO$_4$, a modified metal–organic framework by post-synthetic treatment with a sulfuric acid solution, has been considered as a promising heterogeneous catalyst in the isomerization of glucose to fructose and further dehydration to form 5-hydroxymethylfurfural (HMF) due to its possession of both Lewis and Brønsted acid sites. In this work, we focused on using VNU-11–SO$_4$ for the optimization of the conversion of fructose and glucose into HMF using an ionic liquid as a green solvent. The highest yields of HMF from glucose and fructose could be obtained in 28% (140 °C, 8 h) and 86% (110 °C, 3 h), respectively, with the use of VNU-11–SO$_4$ catalyst in 1-ethyl-3-methylimidazolium chloride ionic liquid. Recycling examination of the catalyst showed only a slight decrease in the HMF yield, implying its potential industrial application in biomass transformation.

1. Introduction

5-Hydroxymethylfurfural is a useful furan ring that can produce an important intermediate to biofuels and commodity chemicals.[1–3] In recent years, the preparation of HMF from carbohydrates has been extensively studied. Generally, HMF is mainly produced *via* dehydration reactions of monosaccharides using homogeneous (*e.g.*, H$_2$SO$_4$, HCl, AlCl$_3$, and CrCl$_3$) or heterogeneous catalysts (*e.g.*, zirconium oxide, zeolites, metal–organic frameworks) in a biphasic system.[3–10] Although the homogeneous acidic catalysts are efficient in the process,[11] some methods suffer from intrinsic drawbacks, *e.g.*, an expensive catalyst with high loading, long reaction time, low yield, difficulty in the recovery of catalyst, and toxic reactants. The heterogeneous catalysts prove prominent advantages of stability and reusability promising as potential alternatives.[12–15] Besides, water, dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), *N*-methyl pyrrolidone (NMP), acetonitrile, ionic liquids (ILs), deep eutectic (DES) and biphasic systems have proven as suitable solvents for the

dissolution of sugar.[16,17] Among these, ILs and DES are becoming increasingly important due to the unique properties related to design flexible structure and reusability.[16,18–20]

Metal–organic frameworks (MOFs) are attracted considerable interest in porous crystalline materials composed of organic ligands and inorganic metal clusters. These materials have been received with widespread attention for several fields, including gas storage and separation,[21,22] catalysis,[23,24] sensing,[25,26] drug delivery,[27,28] proton, and ion conduction.[29,30] With the prominent features such as low density, the large pore sizes, and thermal stability, MOFs have recently appeared as ability heterogeneous catalytic for organic transformations.[31,32] In HMF production, the materials had multi-utility catalytic simultaneously shown better activity and selectivity for the isomerization/dehydration of glucose, in particular, Lewis acidity, Brønsted acidity, and uniform structured nanoscale cavities in MOF could be readily introduced for biomass conversion.[33–37] Sulfated MOF-808 and VNU-11 were known as the first superacid MOF on Zr- and Hf-MOF by anchoring sulfate groups onto the metal clusters of secondary building units. The coexisting Brønsted and Lewis acidities in superacid MOF were also capable of catalyzing reaction, including Friedel–Crafts acylation, esterification, isomerization, and heterocyclization.[38,39] The reaction proceeded smoothly and afforded the expected product in high yield in the presence of superacid MOF and ionic liquid under mild condition.

Herein, we demonstrate a strategy using superacid VNU-11–SO$_4$ for the preparation of HMF from monosaccharides in ILs (Scheme 1). The VNU-11–SO$_4$ was proved to be an efficient

ᵃDepartment of Organic Chemistry, Faculty of Chemistry, University of Science, Ho Chi Minh City, 721337, Vietnam. E-mail: thphuong@hcmus.edu.vn

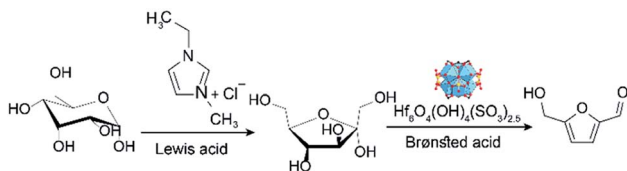*ᵇCenter for Innovative Materials and Architectures (INOMAR), Ho Chi Minh City, 721337, Vietnam*

ᶜVietnam National University-Ho Chi Minh City, Ho Chi Minh City, 721337, Vietnam

ᵈInstitute of Public Health, Ho Chi Minh City, 700000, Vietnam

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0ra08261a

‡ These authors contributed equally.

Scheme 1 The glucose conversion into HMF using superacid MOF in ionic liquids.

catalyst for dehydration of glucose and fructose into HMF in 1-ethyl-3-methylimidazolium chloride ([Emim]Cl). To the best of our knowledge, this is the first report of utilizing VNU-11–SO$_4$ in the conversion of monosaccharides to HMF in ionic liquids.

2. Experimental

2.1. Materials and instrumentations

All chemicals were purchased commercial suppliers and used without further purification. HPLC analyses were recorded on Agilent Technologies 1260 Infinity high-performance liquid chromatography InertSustain C18 (4.6 × 150 mm) column, the size of particles is 5 μm, equipped with a UV photodiode array detector. For more details about chemicals and instruments, please see in ESI.†

2.2. Preparation of VNU-11–SO$_4$

VNU-11 and VNU-11–SO$_4$ were synthesized from reported literature.[34] A mixture of HfOCl$_2$·8H$_2$O (7.5 mmol, 3.10 g) and the tricarboxylic acid H$_3$BTC (2.5 mmol, 537 mg) in 320 mL solvent mixture of DMF and formic acid (v/v = 1 : 1) were added in 500 mL capped bottle and heated in an oven at 120 °C for 3 days under static conditions. After cooling the bottle to room temperature, the precipitates were collected by centrifugation. The products were washed with DMF, deionized water, and anhydrous acetone separately 3 times for three days. Then, the material was dried under reduced pressure at room temperature for 24 h and at 150 °C for 24 h to collect activated VNU-11.

To obtain VNU-11–SO$_4$, activated VNU-11 (200 mg, 0.109 mmol) was treated with 20 mL of H$_2$SO$_4$ 0.1 M and for 24 h. After 24 h, the solid was centrifuged and washed with 60 mL deionized water in 3 times per day for three days. Then, the sample was washed quickly, exchanged with 100 mL anhydrous acetone and immersed in 20 mL anhydrous chloroform for 3 days (3 times per day). Finally, VNU-11–SO$_4$ was dried under reduced pressure at room temperature for 24 h and at 150 °C for 24 h to collect activated VNU-11–SO$_4$.

2.3. Preparation of DESs

The deep eutectic solvents (DESs), a new type of ionic liquids, including choline chloride/phenol (DES 1), choline chloride/ethylene glycol (DES 2) were prepared through the procedure reported in our previous literature.[13,40] DESs were synthesized easily by the formation of hydrogen bonding between phenol or ethylene glycol with choline chloride (please see in Section 3, ESI†).

2.4. Catalytic study

In a typical experiment, glucose or fructose (1 mmol) was dissolved in [Emim]Cl (6 mmol), and then the VNU-11–SO$_4$ catalyst (20 mg) was added. The reaction mixture was heated in a magnetic stirrer with an oil bath for 24 h. Samples were taken from the reaction mixture at a period of time for HPLC analysis to study the effect of catalyst, reaction times, and reaction temperatures on the yield of the product. The isolation of HMF from [Emim]Cl was performed by liquid–liquid extraction with a mixture of ethyl acetate/diethyl ether. The structure of HMF was characterized by ^{1}H NMR and MS.

3. Results and discussion

3.1. Catalysts characterization of VNU-11–SO$_4$

The VNU-11 and VNU-11–SO$_4$ were synthesized with a modification of the previous method and the detailed procedure reported in ESI.†[38] The Hf-MOFs were prepared *via* the reaction between hafnium salt and H$_3$BTC in *N,N*-dimethylformamide as a solvent, and formic acid as a modulator. After the removal of the guest molecules by evacuation at 150 °C for 24 h, the structure of the material was determined by PXRD patterns and N$_2$ sorption isotherms to confirm the successful activation and phase purity of the materials (Fig. 1a and d). TGA measurements were carried out for the VNU-11 pristine and VNU-11–SO$_4$ sample under airflow (Fig. 1b).

The TGA curve of VNU-11 and VNU-11–SO$_4$ showed two distinct weight loss steps, corresponding to the evaporation of organic solvents and water adsorbed on the surface (~3% and 10% for VNU-11 and VNU-11–SO$_4$, respectively) and to the decomposition of the framework (29.2% and 24.9% at 250–600 °C for VNU-11 and VNU-11–SO$_4$, respectively). The temperature range of 600–800 °C of the VNU-11–SO$_4$ sample was shown the decomposition of the anhydrous compound Hf(SO$_4$)$_2$ to give the end product HfO$_2$ of decomposition.[41] In the range
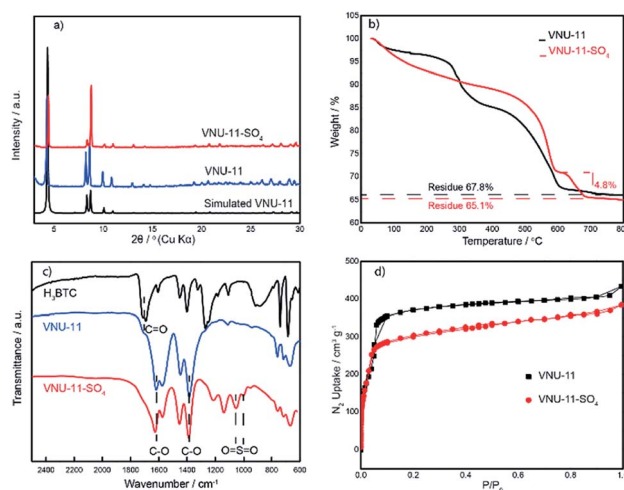

Fig. 1 (a) PXRD patterns, (b) TGA curves, (c) FT–IR and (d) N$_2$ isotherms of VNU-11 (blue) and VNU-11–SO$_4$ (red) samples. The filled and opened symbols represent the adsorption and desorption processes, respectively.

temperature 600–700 °C, the mass loss was 4.8%, which corresponded to a release of SO_2. This value was consistent with the percentage of theoretical mass SO_2 lost from VNU-11–$(SO_4)_{2.5}$ (4.2%).

Fig. 1c shows the FT-IR spectra of the H_3BTC, VNU-11, and VNU-11–SO_4 samples. The characteristic peaks in the range of 1610–552 cm^{-1} in the VNU-11 spectrum were ascribed to C=O vibrations (1610 cm^{-1}), C–O stretching (1400 cm^{-1}), and Zr–O modes (760 cm^{-1}). The presence of sulfonic groups in the VNU-11–SO_4 structure resulted in identical signals at approximately 1000 and 1050 cm^{-1}. The acidities of VNU-11–SO_4 were characterized by using the Hammett indicator test. The color change observed of VNU-11–SO_4 in 2,4-dinitrofluorobenzene as with a value of $Ho \leq -14.5$ indicated a higher acidity than the original VNU-11 as well as sulfuric acid ($Ho = -12$).

3.2. Catalytic study

3.2.1. Optimization of solvent and catalyst loading.
As reported in the literature, fructose or glucose is often used in the synthesis of HMF. Glucose molecules need to undergo the isomerization and finish with the dehydration to form HMF. In addition, organic solvents such as DMSO, IL 1-butyl-3-methyl-imidazolium chloride [Bmim]Cl, IL 1-ethyl-3-methyl-imidazolium chloride [Emim]Cl, were effective solvents for this reaction. To evaluate the role of catalytic active sites in each conversion, the reactions were investigated by heating fructose or glucose at reflux with the screening solvents and amount of VNU-11–SO_4 (Table 1).

The catalytic activity of the VNU-11–SO_4 catalyst was investigated for dehydration of fructose under screening the amount of catalyst from 0–30 mg in [Emim]Cl and DMSO. A high HMF yield of 90% could be achieved under 1 mmol fructose, 6 mmol [Emim]Cl as solvent at 80 °C for 24 h when using 0.025 mmol (30 mg) of VNU-11–SO_4 (Table 1, entry 4), but the conversion of glucose was not more than 30% at 140 °C for 3 h (Table 1, entry

10). As seen in Table 1, the HMF was not detected in the absence of the catalyst (Table 1, entry 1). This can be seen that the strong acidity of the SO_3H group in superacid VNU-11–SO_4 could promote for dehydration of fructose to achieve the high HMF yield and the catalytic system between [Emim]Cl and Hf-clusters could further an isomerization of glucose to fructose.

Next, the influence solvents on the HMF production were tested, and the results were shown in Table 1. The investigation indicated the highest HMF yield was obtained in [Emim]Cl (Table 1, entries 4 and 7), which was higher than the results achieved in DMSO (Table 1, entries 5 and 12). Deep eutectic solvents, a new type of ionic liquids, were also tested as the solvents in the present method, but the low yields of HMF were observed by using DES 1 and DES 2 (Table 1, entries 13 and 14). The reaction did not proceed in the absence of a solvent (Table 1, entry 11). The high yield of HMF in [Emim]Cl could be explained by the high concentration of chloride anion in the reaction mixture to assist with the isomerization of glucose to fructose of Lewis acid sites on VNU-11–SO_4.[42] Therefore, [Emim]Cl was used as the solvent for glucose conversion to HMF.

3.2.2. Optimization of temperature and reaction time.
After finding the positive role of [Emim]Cl for these reactions, the optimization of the effects of temperature (80–140 °C) and reaction times (0.5–24 h) was screened in both cases of fructose and glucose. For the dehydration of fructose, when the temperature was raised from 80–140 °C, the yield of 5-HMF increased significantly and reached an 82% yield of 5-HMF at 140 °C. The results in Fig. 2 demonstrated that the highest yield of HMF was found at 80 °C and 24 h. At the higher temperature 110 °C, the yield of 83% HMF stead increased after 3 h, uphold magnitude in 2 h, and then slipped from 80% to 70% at the time reaction prolong from 6 h to 24 h. The same phenomenon almost occurred at 140 °C, but the magnitude of a stronger decline than at 110 °C. Reduce the HMF yield could be caused by the decomposition of 5-HMF at the high temperature. The synthesis of HMF from fructose was also carried out on

Table 1 Optimization of solvent and catalytic loading in the synthesis of 5-HMF^a

Entry	Monosaccharides	Solvents	VNU-11–SO_4 (mg)	HMF yield (%)
1	Fructose^b	[Emim]Cl	0	0
2		[Emim]Cl	10	51.0
3		[Emim]Cl	20	86.5
4		[Emim]Cl	30	90.5
5		DMSO	30	18.5
6	Glucose^c	[Emim]Cl	0	0
7		[Emim]Cl	10	14.5
8		[Emim]Cl	20	14.8
9		[Emim]Cl	25	23.7
10		[Emim]Cl	30	28.5
11		No solvent	10	0
12		DMSO	10	7.6
13		DES 1^d	10	5.9
14		DES 2^e	10	3.5

^{a} Reaction condition: 1 mmol of fructose or glucose, 6 mmol solvent. ^{b} At 80 °C for 24 h. ^{c} At 140 °C for 3 h. ^{d} Deep eutectic solvent between choline chloride and phenol was prepared at a 1 : 4 molar ratio. ^{e} Deep eutectic solvent between choline chloride and ethylene glycol was prepared at a 1 : 2 molar ratio.
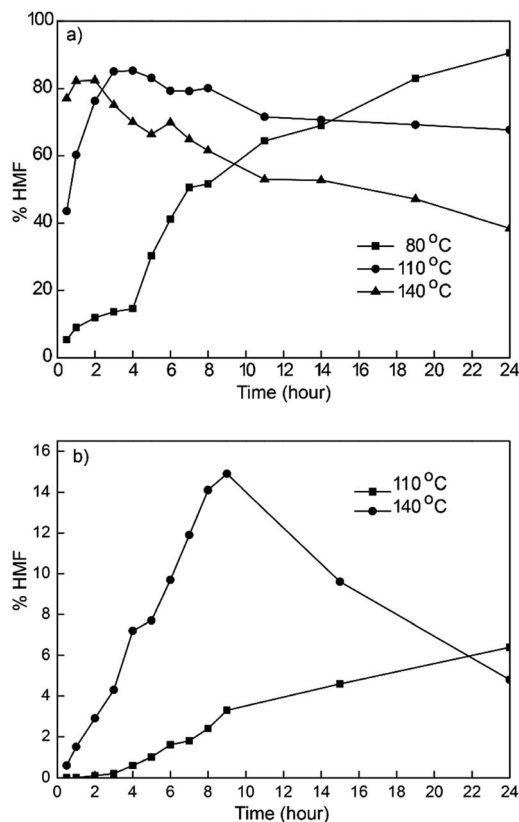
Fig. 2 The effect of temperature and time reaction of fructose (a) and glucose (b) conversion to HMF. Reaction condition: 1 mmol mono-saccharides, 6 mmol [Emim]Cl and 30 mg VNU-11–SO$_4$.

a 10 mmol scale, and the HMF yield was almost the same as that on the 1 mmol scale (84.2% *vs.* 90.5%).

In a previous study, high temperatures were essential for the dehydration of glucose. Fig. 2 shows the effect of time (110–140 °C) and temperature (0.5 –24 h) on the yield of HMF from the conversion of glucose in [Emim]Cl.

The best result of glucose conversion was obtained in 140 °C with 28.5% HMF yield for 8 h. A further increase in reaction

time resulted in a noticeable decrease in HMF yield, presumably due to the decomposition of HMF (Fig. 2). At the lower temperature (110 °C), the yield of HMF increased slowly to 14% when extending the reaction time up to overnight, and the reaction did not proceed at 80 °C.

It is essential to compare our work with previous literature using MOFs as catalysts. The HMF yield from fructose was demonstrated in Table 2 (entries 1–7). The efficiency of the VNU-11–SO$_4$ catalyst showed better activity than other MOFs, HMF yield of 86% could be achieved at 110 °C for only 3 h. In [Emim]Cl solvent, the activity of Brønsted acid MOF as PTA(3.0)/MIL-101 and VNU-11–SO$_4$ were efficient for this reaction at the low temperature. The tolerable increase of HMF yields with longer reaction may be due to the sparing decomposition of HMF.

The summary for the progression of glucose conversion over a variety of catalysts and solvent was shown in Table 2, entries 8–12. At the high temperature of 160 °C, UiO-66 provided the desired product in a moderate yield (37%) of HMF in a mixture of DMSO and water. MIL-101(Cr)–SO$_3$H gave a much higher yield of HMF for 7 h at 150 °C, compared with the yield using VNU-11–SO$_4$ at 140 °C for 8 h.

3.2.3. Recyclability of VNU-11–SO$_4$. The recyclability of the catalyst VNU-11–SO$_4$ was investigated in the reaction for the
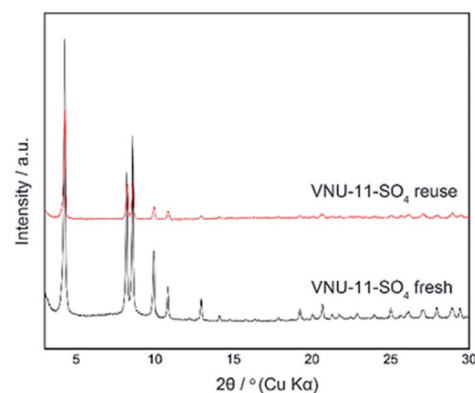

Fig. 3 PXRD analysis of VNU-11–SO$_4$ fresh (black) and after (red) the glucose conversion.

Table 2 The comparison of catalysts for the conversion of monosaccharides to HMF

Entry	React	Catalyst	Solvent	Time (h)	Temperature (°C)	HMF yield (%)	Ref.
1	Fructose	**VNU-11–SO$_4$**	**[Emim]Cl**	**24**	**80**	**90.5**	**This work**
2		**VNU-11–SO$_4$**	**DMSO**	**24**	**80**	**18.5**	**This work**
3		PTA (3.0)/MIL-101	[Emim]Cl	1	80	63	43
4		NUS-6 (Hf)	DMSO	3.5	100	98	34
5		**VNU-11–SO$_4$**	**[Emim]Cl**	**3**	**110**	**86**	**This work**
6		**VNU-11–SO$_4$**	**DMSO**	**3**	**110**	**31.2**	**This work**
7		MIL-101(Cr)–SO$_3$H	DMSO	1	120	90	6
8	Glucose	**VNU-11–SO$_4$**	**[Emim]Cl**	**8**	**140**	**28.5**	**This work**
9		PO$_4$/Nu-1000	Water/THF	5	140	25	44
10		MIL-101(Cr)–SO$_3$H	GVC : water	7	150	39.7	45
11		UiO-66	DMSO	0.5	160	28	1
12		UiO-66	DMSO/water	0.5	160	37	1
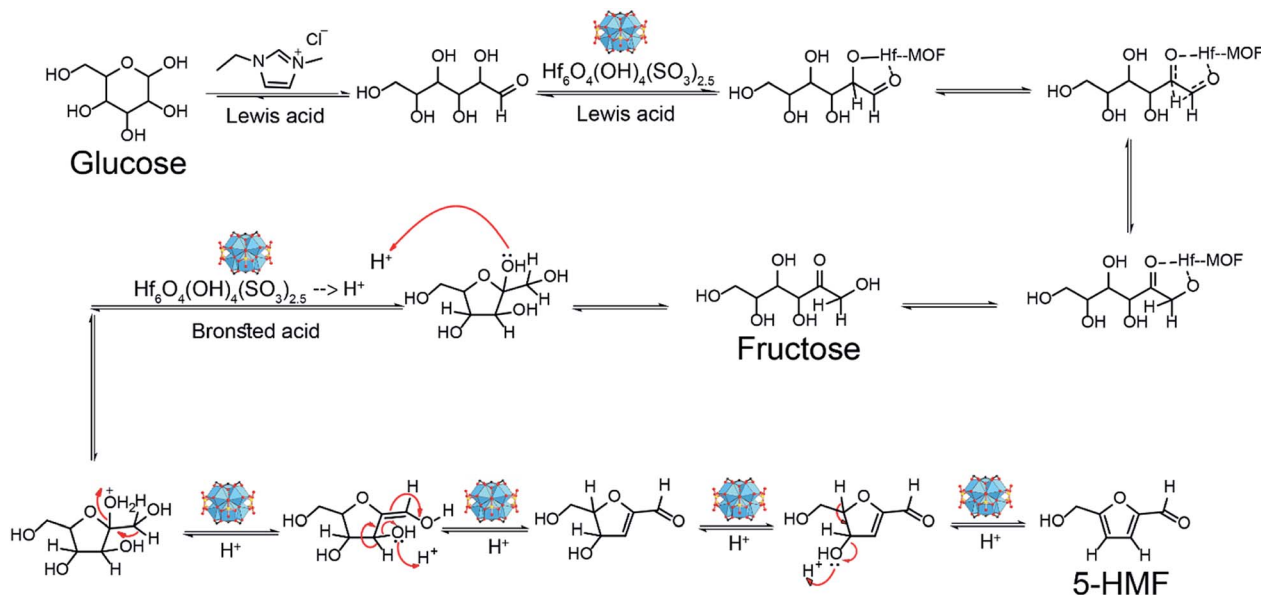
Scheme 2 Dehydration reaction between glucose under VNU-11(Hf) catalyst and [Emim]Cl solvent.

synthesis of HMF. After completion of the reaction, the mixture was diluted with organic solvents and VNU-11–SO$_4$ was collected *via* centrifugation, washed with dichloromethane and acetone, dried in reduced pressure. PXRD patterns of the fresh and reused catalysts after the three cycles indicated the structure of VNU-11–SO$_4$ has remained mostly unchanged (Fig. 3). The S=O coordination in the structure after the reaction was confirmed by FT-IR (Fig. S2, ESI†) to deny the possibility of the leaching SO$_4$ from the catalyst in the reaction mixture.

The leaching test was examined by ICP-OES and the hafnium content in the reaction mixture was less than 2 ppm, indicating negligibly slight leaching occurred from the catalyst. The recovered VNU-11–SO$_4$ was reused three times with a slight decrease in the HMF yield. The recyclability of VNU-11–SO$_4$ promises the potential application in industrial processes.

Based on the previous reports[13,46] and our work, the isomerization of glucose and dehydration of fructose into HMF in the presence of [Emim]Cl solvent were demonstrated the sample evidence of VNU-11–SO$_4$ as both of Brønsted and Lewis sites in the reaction mechanism (Scheme 2). In the first step, glucose was dissolved in [Emim]Cl solvent and isomerized to fructose by Lewis sites of VNU-11–SO$_4$. Then, SO$_3$H groups of superacid MOF acted as Brønsted acid for the dehydration process to obtain HMF.

4.   Conclusion

The heterogeneously catalytic capability of superacid MOF was tested in dehydration of glucose and fructose to HMF in [Emim]Cl ionic liquid and DMSO. As a result, the VNU-11–SO$_4$ showed a highly efficient conversion of glucose to fructose and further formation of HMF. Moreover, VNU-11–SO$_4$ could be recycled three times without a significant decrease in reactivity. Compared to other MOFs, VNU-11–SO$_4$ was a better catalyst and

exhibited excellent performance in the 28% and 90% yield towards HMF from large amount of glucose and fructose, respectively, at the low temperature. This is the first example of HMF synthesis catalyzed by superacid MOF in ionic liquids. The method is a promising route for the large-scale production of HMF from biomass.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1 J. Gong, M. J. Katz and F. M. Kerton, *RSC Adv.*, 2018, **8**, 31618–31627.

2 H. Xia, S. Xu, H. Hu, J. An and C. Li, *RSC Adv.*, 2018, **8**, 30875–30886.

3 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**, 1499–1597.

4 F. Menegazzo, E. Ghedini and M. Signoretto, *Molecules*, 2018, **23**, 2201.

5 W. Guo, H. J. Heeres and J. Yue, *Chem. Eng. J.*, 2020, **381**, 122754.

6 J. Chen, K. Li, L. Chen, R. Liu, X. Huang and D. Ye, *Green Chem.*, 2014, **16**, 2490–2499.

7 A. A. Rosatella, S. P. Simeonov, R. F. M. Frade and C. A. M. Afonso, *Green Chem.*, 2011, **13**, 754.

8 Y. Yang, C.-w. Hu and M. M. Abu-Omar, *Green Chem.*, 2012, **14**, 509–513.

9 J. Yang, K. De Oliveira Vigier, Y. Gu and F. Jérôme, *ChemSusChem*, 2015, **8**, 269–274.

10 K. Zeng, Z. Huang, J. Yang and Y. Gu, *Chin. J. Catal.*, 2015, **36**, 1606–1613.

11 P. Körner, D. Jung and A. Kruse, *Green Chem.*, 2018, **20**, 2231–2241.

12 L. T. Mika, E. Cséfalvay and Á. Németh, *Chem. Rev.*, 2018, **118**, 505–613.

13 P. H. Tran and P. V. Tran, *Fuel*, 2019, **246**, 18–23.

14 J. Tuteja, S. Nishimura and K. Ebitani, *Bull. Chem. Soc. Jpn.*, 2012, **85**, 275–281.

15 W. Niu, D. Wang, G. Yang, J. Sun, M. Wu, Y. Yoneyama and N. Tsubaki, *Bull. Chem. Soc. Jpn.*, 2014, **87**, 1124–1129.

16 S. Körner, J. Albert and C. Held, *Front. Chem.*, 2019, **7**, 661.

17 F. D'Anna, S. Marullo, P. Vitale, C. Rizzo, P. Lo Meo and R. Noto, *Appl. Catal., A*, 2014, **482**, 287–293.

18 J. Zhang, Y. Xiao, Y. Zhong, N. Du and X. Huang, *ACS Sustainable Chem. Eng.*, 2016, **4**, 3995–4002.

19 C. Wu, L.-H. Lu, A.-Z. Peng, G.-K. Jia, C. Peng, Z. Cao, Z. Tang, W.-M. He and X. Xu, *Green Chem.*, 2018, **20**, 3683–3688.

20 L.-Y. Xie, S. Peng, L.-H. Lu, J. Hu, W.-H. Bao, F. Zeng, Z. Tang, X. Xu and W.-M. He, *ACS Sustainable Chem. Eng.*, 2018, **6**, 7989–7994.

21 H. Li, K. Wang, Y. Sun, C. T. Lollar, J. Li and H.-C. Zhou, *Mater. Today*, 2018, **21**, 108–121.

22 O. V. Gutov, W. Bury, D. A. Gomez-Gualdron, V. Krungleviciute, D. Fairen-Jimenez, J. E. Mondloch, A. A. Sarjeant, S. S. Al-Juaid, R. Q. Snurr, J. T. Hupp, T. Yildirim and O. K. Farha, *Chem.–Eur. J.*, 2014, **20**, 12389–12393.

23 Y. Bai, Y. Dou, L.-H. Xie, W. Rutledge, J.-R. Li and H.-C. Zhou, *Chem. Soc. Rev.*, 2016, **45**, 2327–2367.

24 L. H. T. Nguyen, T. T. T. Nguyen, P. H. Tran, Y. Kawazoe, H. M. Le and T. L. H. Doan, *J. Catal.*, 2019, **374**, 110–117.

25 P. Kumar, A. Deep and K.-H. Kim, *TrAC, Trends Anal. Chem.*, 2015, **73**, 39–53.

26 D.-K. Nguyen, J.-H. Lee, T. L.-H. Doan, T.-B. Nguyen, S. Park, S. S. Kim and B. T. Phan, *Appl. Surf. Sci.*, 2020, **523**, 146487.

27 P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J.-S. Chang, Y. K. Hwang, V. Marsaud, P.-N. Bories, L. Cynober, S. Gil, G. Ferey, P. Couvreur and R. Gref, *Nat. Mater.*, 2010, **9**, 172–178.

28 L. He, Y. Liu, J. Lau, W. Fan, Q. Li, C. Zhang, P. Huang and X. Chen, *Nanomedicine*, 2019, **14**, 1343–1365.

29 H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 1230444.

30 A. U. Czaja, N. Trukhan and U. Muller, *Chem. Soc. Rev.*, 2009, **38**, 1284–1293.

31 V. I. Isaeva, O. M. Nefedov and L. M. Kustov, *Catalysts*, 2018, **8**, 368.

32 V. Pascanu, G. González Miera, A. K. Inge and B. Martín-Matute, *J. Am. Chem. Soc.*, 2019, **141**, 7223–7234.

33 Z. Xue, M.-G. Ma, Z. Li and T. Mu, *RSC Adv.*, 2016, **6**, 98874–98892.

34 Z. Hu, Y. Peng, Y. Gao, Y. Qian, S. Ying, D. Yuan, S. Horike, N. Ogiwara, R. Babarao, Y. Wang, N. Yan and D. Zhao, *Chem. Mater.*, 2016, **28**, 2659–2667.

35 Z. Hu and D. Zhao, in *Elaboration and Applications of Metal-Organic Frameworks*, 2018, pp. 495–518, DOI: 10.1142/9789813226739_0012.

36 R. Insyani, D. Verma, S. M. Kim and J. Kim, *Green Chem.*, 2017, **19**, 2482–2490.

37 Y.-T. Liao, B. M. Matsagar and K. C. W. Wu, *ACS Sustainable Chem. Eng.*, 2018, **6**, 13628–13643.

38 L. H. T. Nguyen, T. T. Nguyen, H. L. Nguyen, T. L. H. Doan and P. H. Tran, *Catal. Sci. Technol.*, 2017, **7**, 4346–4350.

39 J. Jiang, F. Gándara, Y.-B. Zhang, K. Na, O. M. Yaghi and W. G. Klemperer, *J. Am. Chem. Soc.*, 2014, **136**, 12844–12847.

40 P. T. Nguyen, T.-D. T. Nguyen, V. S. Nguyen, D. T.-X. Dang, H. M. Le, T.-C. Wei and P. H. Tran, *J. Mol. Liq.*, 2019, **277**, 157–162.

41 S. Genieva, R. Yankova, G. Baikusheva-Dimitrova and N. Halachev, *J. Therm. Anal. Calorim.*, 2016, **124**, 1595–1600.

42 D.-J. Tao, Z. Cheng, F.-F. Chen, Z.-M. Li, N. Hu and X.-S. Chen, *J. Chem. Eng. Data*, 2013, **58**, 1542–1548.

43 Y. Zhang, V. Degirmenci, C. Li and E. J. M. Hensen, *ChemSusChem*, 2011, **4**, 59–64.

44 M. Yabushita, P. Li, T. Islamoglu, H. Kobayashi, A. Fukuoka, O. K. Farha and A. Katz, *Ind. Eng. Chem. Res.*, 2017, **56**, 7141–7148.

45 Y. Su, G. Chang, Z. Zhang, H. Xing, B. Su, Q. Yang, Q. Ren, Y. Yang and Z. Bao, *AIChE J.*, 2016, **62**, 4403–4417.

46 I. Elsayed, M. Mashaly, F. Eltaweel, M. A. Jackson and E. B. Hassan, *Fuel*, 2018, **221**, 407–416.