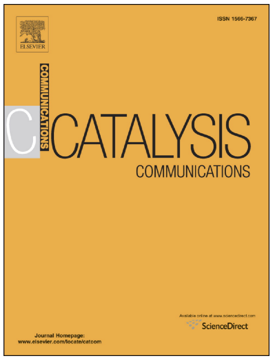

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Catalytic conversion of furfuryl alcohol or levulinic acid into alkyl levulinates using a sulfonic acid-functionalized hafnium-based MOF

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Abstract

Biomass conversion using reusable solid acid catalysts are highly desirable to comply with the principles of green chemistry. Here, we report a sulfonic acid-functionalized hafnium-based metal-organic framework (MOF), UiO-66(Hf)-SO_3H, as an efficientsolid acidcatalyst for the alcoholysis of furfuryl alcohol (FA) andesterification of levulinic acid (LA) affording alkyl levulinates (ALs). Among the as prepared UiO-66 based MOFs(UiO-66(Hf), UiO-66(Hf)-NH_2, UiO-66(Hf)-SO_3H and UiO-66(Zr)-SO_3H), UiO-66(Hf)-SO_3H holds highest Brønsted acidity and therefore exhibits excellent catalytic activity towards production of ALs. The highest Brønsted acidity in UiO-66(Hf)-$SO_3H$is the result of the covalently bound sulfonic acid groups present inorganic linkers along with the ligated hydroxyl groups (Hf-μ_3-OH) to the Hf metal clusters.

Keywords: Furfuryl alcohol; Alkyl levulinates; Levulinic acid; Hafnium-based; metal-organic framework.

1.Introduction

Rapid consumption of fossil resources and environmental concerns over carbon footprint have triggered global research initiatives in the field of catalytic conversion of biomass into chemicals[1]. Development of highly efficient and cost-effective catalytic processes for biomass conversions are desirable in order to replace fossil-based fuels and chemicals with biomass derived fuels and chemicals[2,3]. Alkyl levulinates (ALs) have been attractive due to their versatile applicationssuch as a greener solvents, fuel & food additives and renewable starting materials[4]. The unique properties of ALs such as high octane number, flash point stability and lower toxicity make them ideal oxygenates for blending in gasoline[5].Along withhigh octane number,the greater solubility of levulinate ester in gasoline or diesel is desirable as less soluble alkyl levulinatescan separate from gasoline or diesel at cold temperatures. Levulinate esters of higher molecular-weight alcohols have better solubility in gasoline and diesel[4,5]. In this regard, isopropyl levulinate (IPL) having highoctane number and high solubility in gasoline and dieselbecomes the choice of material to be used as fuel additive.ALs can be obtained from various biomass-based compounds (Fig. S1 ESI). In general, acid catalyzed esterification of LAproduces ALs [6]. However, considering the high cost of LA, commercial production of ALs utilizing cheaply available starting materialssuch as cellulose [7] and FA [8]is desirable.

Earlier research for the production of ALs involved the use of strong mineral acids such as HCl and H_2SO_4 [9],however, the associated problems such as reactor corrosion, catalyst separation and neutralization limit their applications. Considering the environmental aspects, solid Brønsted acid catalyzed ring opening reaction of FA in alcohols has become the meaningfull approach to produce ALs. In this view,various solid acid catalysts such as zeolites [10], metal supported silicates [11], metal oxides [12], heteropoly acids [13], sulphated zirconia [14] and sulfonic acid functionalized materials including graphene [15], silica[16] and carbon [17]have been developed reporting moderate to excellent catalytic activity in production of ALs.

The unique properties of MOFssuch as exceptional porosity, high thermal and chemical stability andability to undergo post synthetic modificationsmake them promising materials for heterogeneous catalysis [18,19]. Brønsted acidity in MOFs can be introduced by various methods[20]. The use of sulfonated ligands has been the most popular approach to introduce the $-SO_3H$ group in MOFs. One of the most successful examples is MIL-101-SO_3H, demonstrated for cellulose hydrolysis [21], and alcoholysis of FA[22]. However, the harsh synthetic conditions and severe toxicity of chromium reagent greatly limit their applications.Hence, -SO_3H functionalized Zr-based MOFshave received considerable attention in biomass conversions [23]. Hf and Zr being chemical twins, share similar properties. The, Hf-based MOFs exhibit exceptional thermal and chemical stability [24,25]. Brønsted acidity in Hf-based MOFs can be incorporated using sulfonated ligands during their synthesis and the presence of Hf-μ_3-OH groups provides additional Brønsted acidity due to the higher dissociation energy of Hf-O bond (802 kJ/mol) as compared to Zr-O bond (766 kJ/mol) [26]. Recently, Hu et al. [27] have reported the Hf-based MOF for the conversion of fructose into 5-hydroxymethylfurfural (HMF).

Herein, for the first time we report direct hydrothermally prepared sulfonic acid-functionalized UiO-66(Hf)-SO_3H, as an efficient catalyst for the conversion of FA or LA into ALs. Due to the presence of both organic and inorganic Brønsted acidic sites, UiO-66(Hf)-SO_3H shows superior performance than that of UiO-66(Zr)-SO_3H towards the production of ALs.Reaction conditions and activity of the present catalytic system have been compared with other reported catalysts for alcoholysis of FA and the results are summarized in Table S1 (ESI).

2. Experimental

The detailed information regarding materials, methods, catalyst preparations and procedures for alcoholysis of FA and esterification of LA are provided in ESI. The graphical representation of the hydrothermal synthesis of UiO-66(Hf)-SO_3H is shown in Fig. 1.

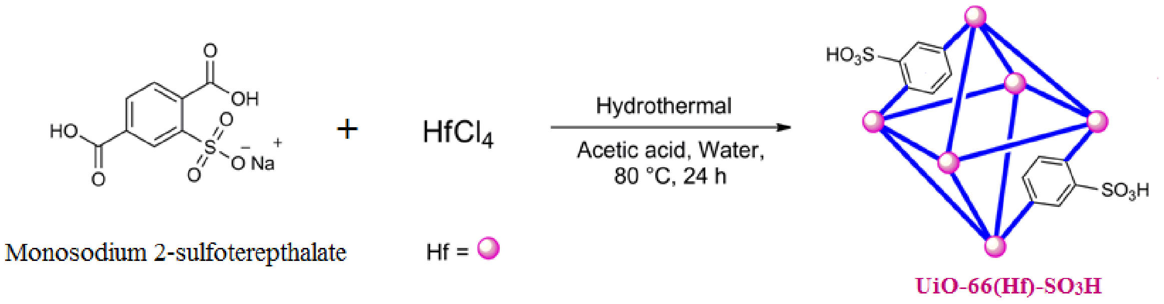

Fig. 1. Hydrothermal synthesis of UiO-66(Hf)-SO_3H.

3. Results and Discussion

3.1 Catalyst characterization

The crystallinity of the as prepared MOFs was initially examined by powder XRD. The PXRD patterns (Fig. S2, ESI) of UiO-66(Hf), UiO-66(Hf)-NH_2, UiO-66(Hf)-SO_3H and UiO-66(Zr)-SO_3H bear close similarity to the earlier reports [25,27]. The sharp XRD peaks at 2θ value of 3.34°, 5.54°, 7.72° and 8.88° (Fig. S2 d) suggest for the cubic crystal structure of UiO-66(Hf)-SO_3H. As inthe earlier report [27], UiO-66(Hf)-SO_3H and UiO-66(Zr)-SO_3H are isostructural having molecular formula of $C_{120}O_{291}S_{15}M_{21}H_{386}\{[M_6O_4(OH)_8L]_{3.5}.xH_2O\}$,where M is either Hf or Zr. Thus, XRD results confirm the successful formation of highly crystalline MOFs.

The chemical analysis of UiO-66(Hf)-SO_3H was studied by XPS (Fig. S3).The surveys scan (Fig. S3a) containing peaks corresponding to Hf, S, C and O element only, indicates the high purity of UiO-66(Hf)-SO_3H. Absence of peak corresponding to Na elementsignifies the complete protonation of the ligand during the synthesis of MOF. The formation of Hf-O chemical bond between Hf metal clusters and organic linkers was confirmed fromthe peaks presentat 225 eV and 214.5 eV (Fig. S3b) assigned to the Hf 4d5/2 and Hf 4d3/2 [28]. The Hf 4f peaks appeared at 20.7 eV and 19.4 eV and were assigned to Hf 4f5/2 and Hf 4f7/2 (Fig. S3 c). The Hf 4f peaks in UiO-66(Hf)-SO_3H appeared at higher binding energies (Fig. S3c) as compared to the Hf 4f peaks in HfO_2 (Hf 4f5/2 at 18.5 eV and Hf 4d7/2 at 16.9 eV), indicating thestrong Lewis acidity of UiO-66(Hf)-SO_3H [29]. The S 2p high-resolution scan (Fig. S3d) shows two peaks at 170.5 eV (S 2p1/2) and 169.6 eV (S 2p3/2) consistent with the presence of -SO_3H groups in UiO-66(Hf)-SO_3H.

The presence of completely protonated -SO_3H groups in UiO-66(Hf)-SO_3H was further confirmed by FTIR analysis (Fig. S4). The FTIR bands at 1230 cm^{-1} and 1180 cm^{-1}(Fig. S4c,d) can be attributed to the symmetric and asymmetric stretching vibrations of O=S=O, respectively [30].

The FE-SEM images (Fig. S5) and TEM images (Fig. S6a,b) reveal the polyhedral morphology of UiO-66(Hf)-SO_3Hhaving average particle size of 1 μm. HR-TEM analysis (Fig. S6c,d) indicate the high crystallinity of the material with lattice spacing of ~0.3 nm representing the (110) crystal plane of UiO-66(Hf)-SO_3H.

Elemental composition and distribution of the as-synthesized UiO-66(Hf)-SO_3 were studied by HAADF-STEM.. The mapping result (Fig. S7 and Fig. S8, ESI) confirmed the uniform distribution of elements throughout the crystal.

The N_2 physical adsorption/desorption isotherms (Fig. S9, ESI) indicate the high porosity of UiO-66(Hf)-SO_3H, possessing a BET surface area of 510 $m^2\ g^{-1}$. The total pore volume of the material was 0.64 $cm^{-3}g^{-1}$.

The high thermal stability of UiO-66(Hf)-SO_3H was confirmed byTG analysis. TGA result (Fig. S10, ESI) shows weight loss of the material in two steps. The first weight loss by about 10% in the temperature range of 50-250 °C could be possibly due to the removal of residual solvents and Hf-μ_3-OH groups from the MOF. The second weight loss by about 25% above 400 °C can be assigned to the collapse of framework structure due to the degradation of organic matter.

The Brønsted acid concentrations in various as synthesised MOFs were obtained by acid-base titration experiment and results are summarised in Table 1. Saturated aqueous solution of NaCl was used for ion-exchange to release the acidic protons from MOFs in the solution,which was subsequently titrated with 0.1 M NaOH to quantify the acidic protons exchanged out in the previous step. Among the as synthesised MOFs, UiO-66(Hf)-SO_3H exhibits highest Brønsted acidity due to the higher concentration of acidic protons (14.3 mol)per mole of MOF.

3.2 Catalytic conversion of furfuryl alcohol into alkyl levulinates

3.2.1 Screening of the as-prepared catalysts

The presence of completely protonated -SO_3H groups suggest that UiO-66(Zr)-SO_3H and UiO-66(Hf)-SO_3H should be the efficient solid acid catalyst for alcoholysis of FA (Scheme S1). The catalytic activity of as-prepared UiO-66-based MOFs was evaluated towards the alcoholysis of FA to isopropyl levulinate (IPL) using isopropyl alcohol, and the obtained results are given in Table 1. Initially, UiO-66(Hf) was used as a catalyst which afforded 8% yield of IPL (Table 1, entry 1), whereas no formation of IPL was observed when UiO-66(Hf)-$NH_2$was used as a catalyst (Table 1, entry 2). These results clearly indicate the catalytic inactivity of Lewis acidic as well as Lewis basic sites towards the alcoholysis of FA. It was interesting to observe that the use of UiO-66(Zr)-SO_3H as a catalyst provided 52% yield of

IPL with 77% conversion of FA (Table 1, entry 4). This is because of the Brønsted acidity in UiO-66(Zr)-SO_3H arising from the dangling -SO_3H groups. The reaction afforded 88% yield of IPL with quantitative conversion of FA when UiO-66(Hf)-SO_3H was used as the catalyst. This can be attributed to the presence of stronger Brønsted acidity in UiO-66(Hf)-SO_3H, which is also confirmed by the acid-base titration experiment. The acid-base titration results (Table 1) reveal the higher concentration of acidic protons in UiO-66(Hf)-SO_3H (14.3 mol) as compared to the UiO-66(Zr)-SO_3H (13.1 mol) per mole of the MOFs. The higher concentration of Brønsted acidity in UiO-66(Hf)-SO_3H might be contributed tothe ligated hydroxyl groups (Hf-μ_3-OH) besides the dangling -SO_3H groups inthe organic ligands [27]. Another reaction without any catalyst under similar conditions provided negligible yield of IPL (Table 1, entry 5), indicating the role of the catalyst. Hence, it is concluded that UiO-66(Hf)-SO_3H with highest Brønsted acidity among the as-prepared MOFs is the most active catalyst for the alcoholysis of FA.

Table 1. Screening of various UiO-66-based catalysts for the conversion of FA into isopropyl levulinate.[a]

Entry	Catalyst	Mole of acidic proton per mole of MOF $[H^+]$/mol mol^{-1}	FA [b] Conversion (%)	IPL [c] Yield (%)	FE [d] Yield (%)
1	UiO-66(Hf)	0	13	8	-
2	UiO-66(Hf)-NH_2	0	5	-	-
3	UiO-66(Hf)-SO_3H	14.3	100	88	-
4	UiO-66(Zr)-SO_3H	13.1	77	52	23
5	-	-	6	-	-

[a] Reaction conditions: FA, 1 mmol; catalyst, 100 mg; isopropyl alcohol, 20 mL; temperature, 120 °C; reaction time, 4h.

[b] FA, furfuryl alcohol. [c] IPL, isopropyl levulinate. [d] FE, furfuryl ether.

3.2.2 Effect of catalyst loading

The effect of UiO-66(Hf)-SO_3H loading was studied and results are presented in Fig. 2.By decreasing the loading of UiO-66(Hf)-SO_3H to 0.4 mol %resulted in lowering the conversion of FA (87%) and IPL yield (47%),possibly due to the reduced catalytic sites availablefor the reaction. Increased catalyst loading afforded higher yield of the product, and maximum yield of IPL (88%) was obtained using 0.8 mol % of catalyst. Further increasing the catalyst loading to 1.0 mol % resulted into a slightly decrease in the yield of IPL (83%) due to the side reactions.

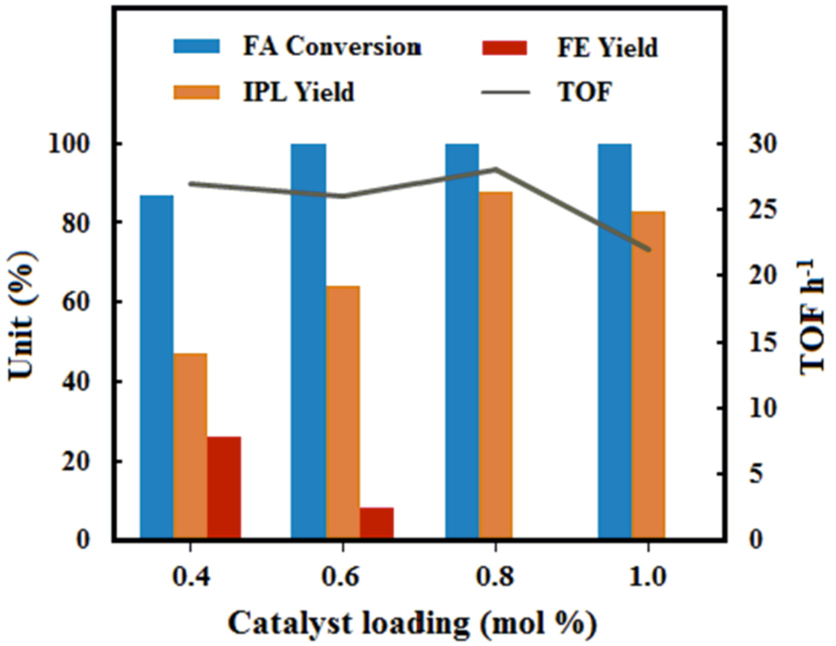

Fig. 2. Effect of catalyst loading on alcoholysis of furfuryl alcohol. Reaction Conditions: FA, 1 mmol; UiO-66(Hf)-SO_3H, 0.4 – 1.0 mol %; isopropyl alcohol, 20 mL; temperature, 120 °C; reaction time, 4h.

3.2.3 Effect of reaction temperature

The reaction temperature (Fig. 3) has significant role inthe alcoholysis of FA. At the lowest temperature studied, that is 90 °C,a 92% conversion of FA was achieved corresponding to a 65% yield of IPL along with 25% yield of FE. Increasing the reaction temperature to 100 °C, complete conversion of FA was seen with 73% yield of IPL, whereas the yield of FE was dropped to 12%, result which indicates the consumption of FE during the progress of reaction. Further increase in temperature resulted into an increased yield of IPL and afurther decrease in the yield of FE. The maximum yield of IPL (88%) was achieved at 120 °C with negligible amount of FE indicating that the FE is the dominant intermediate in alcoholysis of FA in our case and elsewhere[22,31].

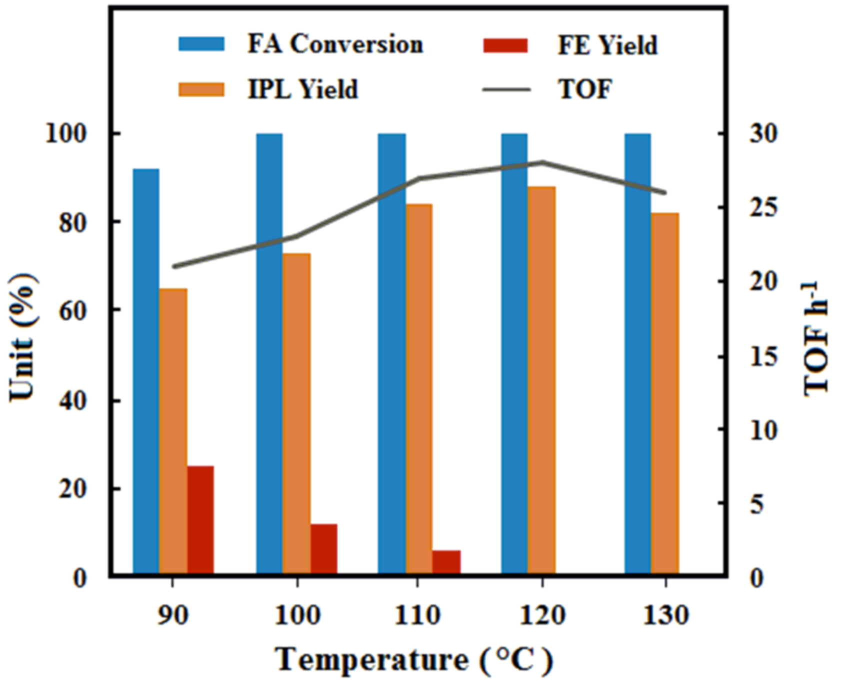

Fig. 3. Effect of reaction temperature on alcoholysis of furfuryl alcohol. Reaction Conditions: FA, 1 mmol; UiO-66(Hf)-SO_3H, 0.8 mol %; isopropyl alcohol, 20 mL; temperature, 90-130 °C; reaction time, 4h.

3.2.4 Effect of reaction time

As summarized in Fig. S11, reaction monitoring after 1h shows 85% conversion of FA with 12% of IPL and 64% of FE yields. Continuing the reaction for another 1h provided 92% conversion of FA, the yield of IPL was increased to 47%, whereas the yield of FE was decreased significantly to 40%, indicating the consumption of FE during the course of the reaction. The complete conversion of FA was achieved after 3h providing 72% yield of IPL along with 23% yield of FE. The reaction after 4h revealed complete consumption of FE affording the maximum yield of IPL,ca. 88%. Hence, these results suggest the conversion of FA into FE as an intermediate, which further gets converted into IPL successively as reaction time increases.

3.2.5 Preparation of different alkyl levulinates

To establish the general applicability of UiO-66(Hf)-SO_3H as an efficient solid acid catalyst for the production of ALs, a range of different ALs have been prepared fromthe alcoholysis of FA using various aliphatic alcohols under optimized reaction conditions. As presented in Table 2, alcoholysis of FA in methanol as well as in ethanol produced the corresponding ALs in lower yields, 48% and 62%, respectively, due to the formation of large amount of intermediates (B and C in Fig. S14),which slowlygets converted into product. The alcoholysis of FA in propanol resulted in suppressed formation of intermediates, affording 76% and 88% yield of desired products in 1-propanol and 2-propanol, respectively. It was observed that alcohols having longer carbon chain lengths (4, 5 and 6 carbons) provided a lower yield of the corresponding products. The presence of large carbon chain might have created the steric crowding near the hydroxyl group of alcohol, which probably reduced their efficient nucleophilic attack during the progress of reaction.

Table 2. Conversion of furfuryl alcohol into different alkyl levulinates.[a]

Entry	Alcohol	Product	Yield (%)[b]
1	methanol	methyl levulinate	48
2	ethanol	ethyl levulinate	62
3	1-propanol	1-propyl levulinate	76
4	2-propanol	2-propyl levulinate	88
5	1-butanol	1-butyl levulinate	72
6	2-butanol	2-butyl levulinate	66
7	1-pentanol	1- pentyl levulinate	64
8	1-hexanol	1- hexyl levulinate	57

[a] Reaction conditions: FA, 1 mmol; UiO-66(Hf)-SO_3H, 0.8 mol %; alcohol, 20 mL; temperature, 120 °C; reaction time, 4h.

[b]Yield was calculated by GC-MS.

3.3 Catalytic conversion of levulinic acid into alkyl levulinates

The catalytic activity of UiO-66(Hf)-SO_3H was also studied towards the esterification of LA (Scheme S2, ESI). Optimization of various reaction parameters provided 86% yield of the desired product with 93% conversion of LA at 120 °C in 2h using 0.8 mol % of the catalyst (Table 3, entry 2). As summarized in Table 3, different alkyl levulinates were obtained in good yields from the esterification of LA in various alcohols using UiO-66(Hf)-SO_3H as a catalyst. These results indicate the wide applicability of UiO-66(Hf)-SO_3H as an efficient solid Brønsted acid catalyst.

Table 3. Catalytic conversion of levulinic acid into alkyl levulinates.[a]

Entry	Solvent	Temperature (°C)	Time (h)	LA Conversion (%)	AL Yield[b] (%)
1	methanol	100	2	78	65
2	methanol	120	2	93	86
3	methanol	140	2	93	87
4	methanol	120	1.5	86	73
5	methanol	120	2.5	94	85
6	ethanol	120	2	90	85
7	1-propanol	120	2	87	78
8	2-propanol	120	2	88	80

[a] Reaction conditions: LA, 1 mmol; UiO-66(Hf)-SO_3H, 0.8 mol %; alcohol, 20 mL; temperature, 120 °C; reaction time, 2h.

[b] Yield was calculated by GC-MS.

3.4 Catalyst reusability

Besides the good catalytic activity, reusability is also an important factor considered while catalyst selection, especially in industry. The reusability of UiO-66(Hf)-SO_3H was demonstrated by recycling the catalyst for four times in the production of IPL from the alcoholysis of FA. After each catalytic run, the catalyst was isolated by centrifugation and washed three times with isopropyl alcohol and dried under vacuum at 100 °C for 12h and then used for the next run. Isolation of the catalyst from reaction mixture by centrifugation provided the maximum recovery of the catalyst (90 mg) with 10 mg loss of the catalyst after recycling for four times. The reusability of UiO-66(Hf)-SO_3H was also studied towards esterification of LA. As represented in Fig. 4, the yield of IPL during alcoholysis of FA was decreased from 88% to 73% after the fourth recycle of UiO-66(Hf)-SO_3H. The slight loss in catalytic activity can be attributed to the adsorption of some oligomerized products on the catalyst surface [31,32]. The catalyst UiO-66(Hf)-SO_3H exhibited excellent catalytic recyclability towards esterification of LA (Fig. 4).The XRD (Fig. S12, ESI) and FEG-SEM analysis (Fig. S13, ESI) of UiO-66(Hf)-SO_3H catalyst recycled for four times shows retention of its crystallinity and polyhedral morphology, respectively. These results suggest high stability of the UiO-66(Hf)-SO_3H catalyst during recycling towards alcoholysis of FA.

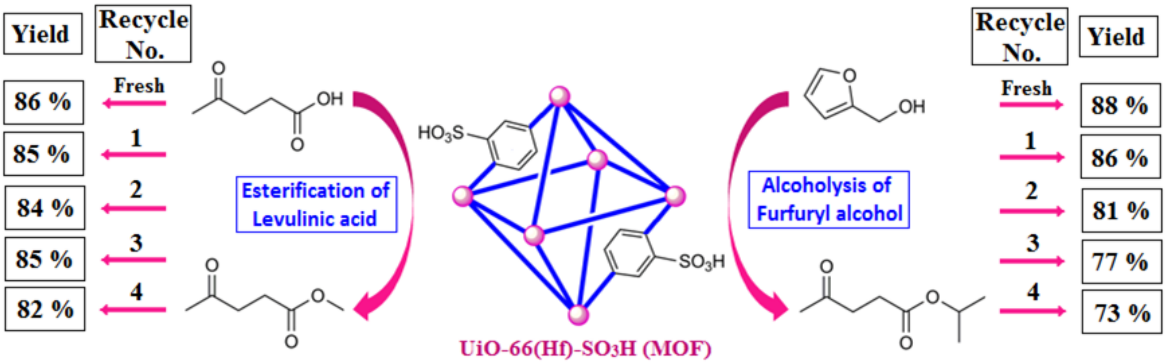

Fig. 4. Reusability of UiO-66(Hf)-SO_3H.

3.5 Plausible reaction mechanism

On the basis of the identified intermediates and earlier reports [13,17,31], a plausible reaction mechanism for the alcoholysis of FA using UiO-66(Hf)-SO_3H as a catalyst has been proposed and shown in Fig. S14. The detailed discussions have been provided in ESI.

4. Conclusions

The two sulfonic acid-functionalized MOFs, UiO-66(Hf)-SO_3H and UiO-66(Hf)-SO_3H wereprepared by direct hydrothermal synthesis and used for the alcoholysis of FA to produce ALs. Among the as-prepared sulfonic acid-functionalized MOFs, UiO-66(Hf)-SO_3H exhibited excellent catalytic performance providing 88% of IPL with quantitative conversion of FA at 120 °C in 4h. The superior catalytic activity of UiO-66(Hf)-SO_3H was attributed to its stronger Brønsted acidity resulting from the ligated hydroxyl groups of hafnium metal clusters besides the presence of sulfonic acid groups. Furthermore, the UiO-66(Hf)-SO_3H can be used as an efficient Brønsted acid catalyst for esterification of LA to afford ALs. Our results have demonstrated the efficient production of alkyl levulinates from biomass derived renewable and abundant molecules.

Acknowledgements

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References

[1] P. Gallezot, Conversion of biomass to selected chemical products, Chem. Soc. Rev. 41 (2012) 1538–1558. doi:10.1039/C1CS15147A.

[2] C. Nguyen-Huy, J.S. Kim, S. Yoon, E. Yang, J.H. Kwak, M.S. Lee, et al., Supported Pd nanoparticle catalysts with high activities and selectivities in liquid-phase furfural hydrogenation, Fuel. 226 (2018) 607–617. doi:10.1016/j.fuel.2018.04.029.

[3] S.S.R. Gupta, M.L. Kantam, Selective hydrogenation of levulinic acid into γ-valerolactone over Cu/Ni hydrotalcite-derived catalyst, Catal. Today. 309 (2018) 189–194. doi:10.1016/j.cattod.2017.08.007.

[4] A. Démolis, N. Essayem, F. Rataboul, Synthesis and Applications of Alkyl Levulinates, ACS Sustain. Chem. Eng. 2 (2014) 1338–1352. doi:10.1021/sc500082n.

[5] E. Christensen, A. Williams, S. Paul, S. Burton, R.L. McCormick, Properties and Performance of Levulinate Esters as Diesel Blend Components, Energy & Fuels. 25 (2011) 5422–5428. doi:10.1021/ef201229j.

[6] K.Y. Nandiwale, S.K. Sonar, P.S. Niphadkar, P.N. Joshi, S.S. Deshpande, V.S. Patil, et al., Catalytic upgrading of renewable levulinic acid to ethyl levulinate biodiesel using dodecatungstophosphoric acid supported on desilicated H-ZSM-5 as catalyst, Appl. Catal. A Gen. 460–461 (2013) 90–98. doi:10.1016/j.apcata.2013.04.024.

[7] J. Dai, L. Peng, H. Li, Intensified ethyl levulinate production from cellulose using a combination of low loading H 2 SO 4 and Al(OTf) 3, Catal. Commun. 103 (2018) 116–119. doi:10.1016/j.catcom.2017.10.007.

[8] D. Zhao, P. Prinsen, Y. Wang, W. Ouyang, F. Delbecq, C. Len, et al., Continuous Flow Alcoholysis of Furfuryl Alcohol to Alkyl Levulinates Using Zeolites, ACS Sustain. Chem. Eng. 6 (2018) 6901–6909. doi:10.1021/acssuschemeng.8b00726.

[9] C. Chang, G. Xu, X. Jiang, Production of ethyl levulinate by direct conversion of wheat straw in ethanol media, Bioresour. Technol. 121 (2012) 93–99. doi:10.1016/j.biortech.2012.06.105.

[10] T.M. Lima, C.G.S. Lima, A.K. Rathi, M.B. Gawande, J. Tucek, E.A. Urquieta-González, et al., Magnetic ZSM-5 zeolite: a selective catalyst for the valorization of furfuryl alcohol to γ-valerolactone, alkyl levulinates or levulinic acid, Green Chem. 18

(2016) 5586–5593. doi:10.1039/C6GC01296E.

[11] M.M. Antunes, S. Lima, P. Neves, A.L. Magalhães, E. Fazio, F. Neri, et al., Integrated reduction and acid-catalysed conversion of furfural in alcohol medium using Zr,Al-containing ordered micro/mesoporous silicates, Appl. Catal. B Environ. 182 (2016) 485–503. doi:10.1016/j.apcatb.2015.09.053.

[12] D. Ren, J. Fu, L. Li, Y. Liu, F. Jin, Z. Huo, Efficient conversion of biomass-derived furfuryl alcohol to levulinate esters over commercial α-Fe 2 O 3, RSC Adv. 6 (2016) 22174–22178. doi:10.1039/C5RA24319J.

[13] S.R. B., K.K. P., D.L. D., L. N., One pot selective transformation of biomass derived chemicals towards alkyl levulinates over titanium exchanged heteropoly tungstate catalysts, Catal. Today. 309 (2018) 269–275. doi:10.1016/j.cattod.2017.05.040.

[14] M.S. Tiwari, A.B. Gawade, G.D. Yadav, Magnetically separable sulfated zirconia as highly active acidic catalysts for selective synthesis of ethyl levulinate from furfuryl alcohol, Green Chem. 19 (2017) 963–976. doi:10.1039/C6GC02466A.

[15] S. Zhu, C. Chen, Y. Xue, J. Wu, J. Wang, W. Fan, Graphene Oxide: An Efficient Acid Catalyst for Alcoholysis and Esterification Reactions, ChemCatChem. 6 (2014) 3080–3083. doi:10.1002/cctc.201402574.

[16] S. An, D. Song, Y. Sun, Q. Zhang, P. Zhang, Y. Guo, Conversion of Furfuryl Alcohol to Levulinic Acid in Aqueous Solution Catalyzed by Shell Thickness-Controlled Arenesulfonic Acid-Functionalized Ethyl-Bridged Organosilica Hollow Nanospheres, ACS Sustain. Chem. Eng. 6 (2018) 3113–3123. doi:10.1021/acssuschemeng.7b03133.

[17] D. Song, S. An, B. Lu, Y. Guo, J. Leng, Arylsulfonic acid functionalized hollow mesoporous carbon spheres for efficient conversion of levulinic acid or furfuryl alcohol to ethyl levulinate, Appl. Catal. B Environ. 179 (2015) 445–457. doi:10.1016/j.apcatb.2015.05.047.

[18] M. Rimoldi, A.J. Howarth, M.R. DeStefano, L. Lin, S. Goswami, P. Li, et al., Catalytic Zirconium/Hafnium-Based Metal–Organic Frameworks, ACS Catal. 7 (2017) 997–1014. doi:10.1021/acscatal.6b02923.

[19] J.H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, et al., A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with

Exceptional Stability, J. Am. Chem. Soc. 130 (2008) 13850–13851. doi:10.1021/ja8057953.

[20] J. Jiang, O.M. Yaghi, Brønsted Acidity in Metal–Organic Frameworks, Chem. Rev. 115 (2015) 6966–6997. doi:10.1021/acs.chemrev.5b00221.

[21] G. Akiyama, R. Matsuda, H. Sato, M. Takata, S. Kitagawa, Cellulose Hydrolysis by a New Porous Coordination Polymer Decorated with Sulfonic Acid Functional Groups, Adv. Mater. 23 (2011) 3294–3297. doi:10.1002/adma.201101356.

[22] X.-F. Liu, H. Li, H. Zhang, H. Pan, S. Huang, K.-L. Yang, et al., Efficient conversion of furfuryl alcohol to ethyl levulinate with sulfonic acid-functionalized MIL-101(Cr), RSC Adv. 6 (2016) 90232–90238. doi:10.1039/C6RA19116A.

[23] Y. Kuwahara, H. Kango, H. Yamashita, Catalytic Transfer Hydrogenation of Biomass-Derived Levulinic Acid and Its Esters to γ-Valerolactone over Sulfonic Acid-Functionalized UiO-66, ACS Sustain. Chem. Eng. 5 (2017) 1141–1152. doi:10.1021/acssuschemeng.6b02464.

[24] M.J. Cliffe, W. Wan, X. Zou, P.A. Chater, A.K. Kleppe, M.G. Tucker, et al., Correlated defect nanoregions in a metal–organic framework, Nat. Commun. 5 (2014) 4176. doi:10.1038/ncomms5176.

[25] S. Rojas-Buzo, P. García-García, A. Corma, Catalytic Transfer Hydrogenation of Biomass-Derived Carbonyls over Hafnium-Based Metal-Organic Frameworks, ChemSusChem. 11 (2018) 432–438. doi:10.1002/cssc.201701708.

[26] M.H. Beyzavi, R.C. Klet, S. Tussupbayev, J. Borycz, N.A. Vermeulen, C.J. Cramer, et al., A Hafnium-Based Metal–Organic Framework as an Efficient and Multifunctional Catalyst for Facile CO 2 Fixation and Regioselective and Enantioretentive Epoxide Activation, J. Am. Chem. Soc. 136 (2014) 15861–15864. doi:10.1021/ja508626n.

[27] Z. Hu, Y. Peng, Y. Gao, Y. Qian, S. Ying, D. Yuan, et al., Direct Synthesis of Hierarchically Porous Metal–Organic Frameworks with High Stability and Strong Brønsted Acidity: The Decisive Role of Hafnium in Efficient and Selective Fructose Dehydration, Chem. Mater. 28 (2016) 2659–2667. doi:10.1021/acs.chemmater.6b00139.

[28] Y. Il Song, C.-M. Yang, L. Ku Kwac, H. Gun Kim, Y. Ahm Kim, Atomic layer

coating of hafnium oxide on carbon nanotubes for high-performance field emitters, Appl. Phys. Lett. 99 (2011) 153115. doi:10.1063/1.3650471.

[29] H. Li, T. Yang, Z. Fang, Biomass-derived mesoporous Hf-containing hybrid for efficient Meerwein-Ponndorf-Verley reduction at low temperatures, Appl. Catal. B Environ. 227 (2018) 79–89. doi:10.1016/j.apcatb.2018.01.017.

[30] M.G. Goesten, J. Juan-Alcañiz, E. V. Ramos-Fernandez, K.B. Sai Sankar Gupta, E. Stavitski, H. van Bekkum, et al., Sulfation of metal–organic frameworks: Opportunities for acid catalysis and proton conductivity, J. Catal. 281 (2011) 177–187. doi:10.1016/j.jcat.2011.04.015.

[31] D. Song, S. An, Y. Sun, Y. Guo, Efficient conversion of levulinic acid or furfuryl alcohol into alkyl levulinates catalyzed by heteropoly acid and ZrO 2 bifunctionalized organosilica nanotubes, J. Catal. 333 (2016) 184–199. doi:10.1016/j.jcat.2015.10.018.

[32] T. Kim, R.S. Assary, R.E. Pauls, C.L. Marshall, L.A. Curtiss, P.C. Stair, Thermodynamics and reaction pathways of furfuryl alcohol oligomer formation, Catal. Commun. 46 (2014) 66–70. doi:10.1016/j.catcom.2013.11.030.

Highlights

- Efficient production of alkyl levulinates using a reusable solid acid catalyst.
- Sulfonic acid-functionalized MOF, UiO-66(Hf)-SO_3H holds strong Brønsted acidity.
- Alcoholysis of furfuryl alcohol and esterification of levulinic acid.
- UiO-66(Hf)-SO_3H shows excellent catalytic activity and recyclability.