

Supplementary information

Sustainable hydrothermal self-assembly of hafnium-lignosulfonate nanohybrids for highly efficient reductive upgrading of 5-hydroxymethylfurfural

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Experimental Section

Reagents

Sodium ligninsulfonate (LigS, >99.0%), HfCl₄ (>99.5%), 5-hydroxymethylfurfural (5-HMF, >99.0%), methanol (>99.5%), ethanol (>99.5%), 2-PrOH (>99.0%), 2-butanol (>99.0%), *tert*-butanol (>99.0%) and cyclohexanol (>99.0%) were purchased from Aladdin Industrial Corporation. HfO₂ (>99.5%), ZrCl₄ (>99.5%), FeCl₃ (>99.5%), AlCl₃ (>99.0%), ZnCl₂ (>99.0%), were purchased from Shanghai Macklin Biochemical Co., Ltd, China. 2-PrOH-OD (>98.0%) and 2-PrOH-d8 (>99.0%) were purchased from Sigma-Aldrich Industrial Corporation. All chemical reagents were obtained from commercial suppliers and used without further purification.

Preparation of catalysts

All metal–ligninsulfonate catalysts (M–LigS; M=Hf, Zr, Fe, Al, and Zn) were prepared from the self-assembly of ligninsulfonate with the corresponding metal chloride (i.e., HfCl₄, ZrCl₄, FeCl₃, AlCl₃, or ZnCl₂) in water under hydrothermal conditions. In a typical procedure, HfCl₄ (3.9 mmol, 1.25 g) and sodium lignosulfonate (0.625 g) were respectively dissolved in 5ml and 10ml water to form aqueous solution under ultrasound for 5 min. Subsequently, these two solutions were mixed and magnetic stirring at room temperature for 10 min. Afterwards, the mixture was transferred into 25 ml Teflon-lined stainless-steel autoclave and tightly sealed. This autoclave was placed into an oven that had been heated to 120 °C. After hydrothermal reaction for 12h, the autoclave was taken out and cooled to room temperature by running water. The as-obtained brown precipitates were centrifuged and totally washed with water and ethanol for 15-20 times until the filtrate was neutral, colourless and transparent. Finally, the obtained sample was dried in vacuum at 60 °C for 12 h to afford the Hf-LigS

catalyst.

Catalyst characterization

Scanning electron microscopy (SEM) was performed on a MERLIN SEM of ZEISS to observe the surface morphologies of different prepared catalysts. Transmission electron microscope (TEM) was conducted on a JEM-2100F with EDX analysis operated at accelerating voltage of 200 kV to observe the morphology and elemental mapping of different catalysts. N₂ adsorption–desorption isotherms of different catalysts were obtained from a Micromeritics ASAP 2020 equipment. Before testing, all the catalysts were degassed at 120 °C for 6 h. Powder X-ray diffraction patterns (XRD) of different catalysts were conducted using Rigaku diffractometer (D/MAX/III A) with Cu K α radiation ($\lambda = 1.543 \text{ \AA}$) at ambient temperature from 5 ° to 90°. Fourier transform infrared spectroscopy (FT-IR) spectra of various catalysts were recorded using a Bruker Vector33 spectrometer. The thermal stability of different samples was examined using a Mettler Toledo thermal analyser (TG) with temperature from 28 to 740 °C under flowing Ar (heating rate of 15 K min⁻¹). Diffuse reflectance UV–vis (UV–vis DRS) of solid samples were obtained on an UV-2550 spectrophotometry using barium sulfate as background standard to confirm the coordination effect. Pyridine adsorbed FT-IR spectra of different catalysts were obtained on a Nicolet380 equipment using KBr pellets in the range of 4000–400 cm⁻¹ to determine the type of acid sites. Prior to analysis, approximately 25 mg of sample was pressed into a 13 mm self-supported wafer and activated in the IR cell at 573 K for 1.0 h at 10⁻³ Pa. Following which, it was cooled to room temperature, the sample was exposed to pyridine vapor under vacuum for 20 min followed by evacuation of excess pyridine for 0.5 h. Then, the cell was heated to 383 K at a rate of 10 K min⁻¹ and kept at this temperature for 1.0 h to remove physisorbed pyridine. The concentration of the Brønsted and Lewis acid sites was calculated via Eqs. (1) and (2) respectively [9].

$$C_B = (\mu \text{ mol g}^{-1}) = \frac{1.88 \times IA_B \times R^2}{W} \quad (1)$$

$$C_L = (\mu \text{ mol g}^{-1}) = \frac{1.42 \times IA_L \times R^2}{W} \quad (2)$$

where C_B and C_L stand for the concentration of Brønsted and Lewis acid sites, respectively, IA_B and IA_L stand for the integrated absorbance peak at 1540 cm⁻¹ for Brønsted acid sites and peak at 1450 cm⁻¹ for Lewis acid sites, respectively, R stands for the radius of the self-supported disk and W stands for the weight of the sample. X-ray photoelectron spectroscopy (XPS) of various samples was examined on imaging photoelectron spectrometer (Kratos Axis Ultra DLD system) under ultrahigh vacuum. The acidity and basicity of different samples were determined through temperature-programmed desorption of NH₃ and CO₂ (NH₃/CO₂-TPD) by a Micromeritics AutoChem II 2920 equipment. Firstly, the catalyst was degassed under a flowing He (30 mL/min) at 150 °C for 2 h. Then, the system was cooled to ambient temperature under He. After the sample was adsorbed with NH₃ or CO₂, the system was purged under a flow of He at 50 °C and the TPD results were obtained from 50 °C – 300 °C

under flowing He. The hafnium and sulfur contents in the catalysts and the solution were determined with an ICP-OES equipment (Spectro Arcos FHX22).

Procedures for the CTH of 5-HMF

The CTH reaction of 5-HMF was carried out in a 25 mL pressure tube reactor under oil-heating conditions. Typically, 5-HMF (1 mmol), 2-PrOH (10 mL), and catalyst (100 mg) were added into the reactor. After that, the reactor was transferred into a preheated oil bath. After magnetically stirring for a desired time, this reactor was rapidly placed in running water. The reaction mixtures were centrifuged and collected for analysis. Identification of products was conducted using GC-MS (GCMS-QP2010 Ultra) equipped with HP-5MS capillary column (30.0 m × 250 mm × 0.25 mm). The quantification of reduction products was conducted on GC (Shimadzu Nexis GC-2030) equipped with FID detector and HP-5 capillary column (30.0 m × 250 mm × 0.25 mm).

Isotopic labelling experiments

For isotopic kinetic study of CTH of 5-HMF to BHMF, we used different deuterated 2-PrOH (2-PrOH-d8 and 2-PrOH-OD) as hydrogen source to reveal the reaction mechanism and the rate-determining step. After the reaction, the products were analyzed by GC-MS (Agilent 7890B-5977A) and ¹H NMR (JEOL-ECX 500 NMR).

Leaching and catalyst recycling experiments

In the leaching experiment, the catalyst was filtered out from the reaction system after reacting for 20min at 100 °C. Afterwards, the reaction was allowed to react for another 160 min under identical conditions without Hf-LigS catalysts. The Hf and S species leached into the reaction mixture were analyzed by ICP-OES. The reusability test of Hf-LigS catalyst was performed as follows: After the reaction proceeded at 80 °C for 1h, the solid Hf-LigS was separated by centrifugation, and washed several times with 2-PrOH. After dried under vacuum at 70 °C for 10 h, the Hf-LigS was employed for the next cycle directly under the identical reaction conditions.

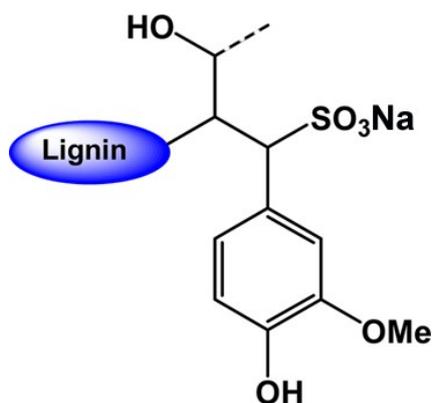


Fig. S1. Partial chemical structure of sodium liginosulfonate (LigS).

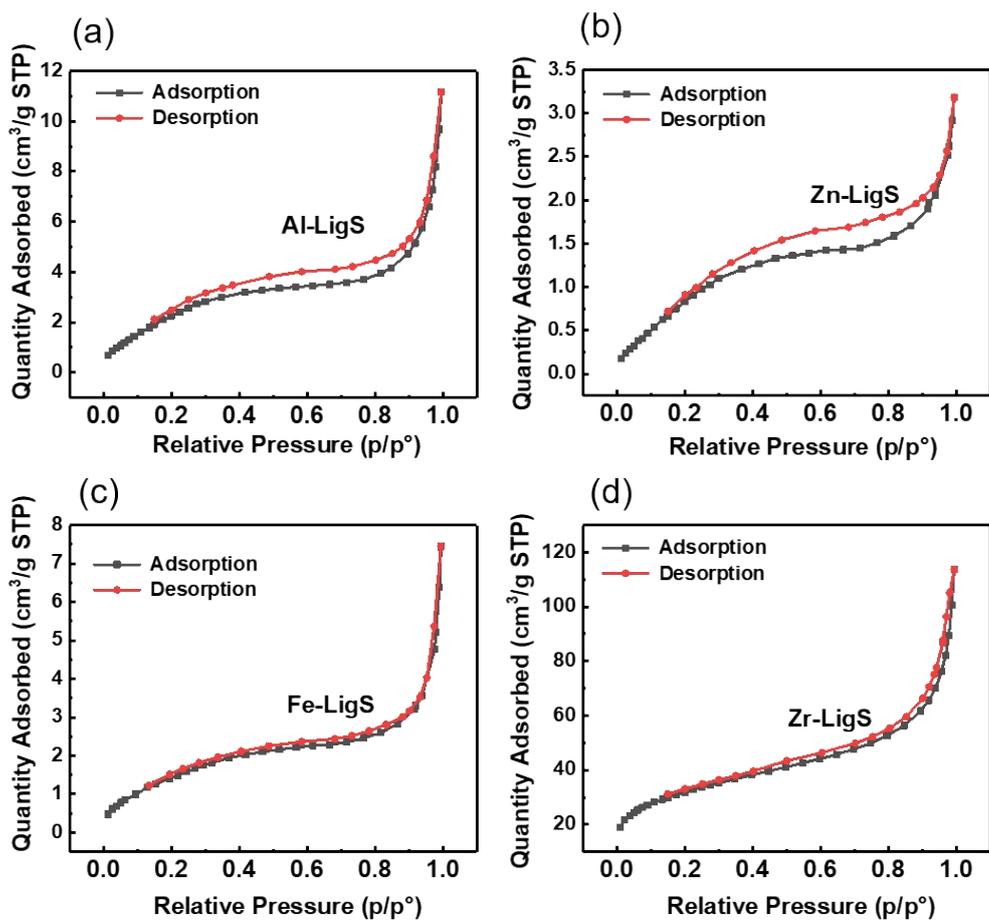


Fig. S2. N_2 adsorption–desorption isotherm of Al-LigS (a), Zn-LigS (b), Fe-LigS (c), Zr-LigS (d)

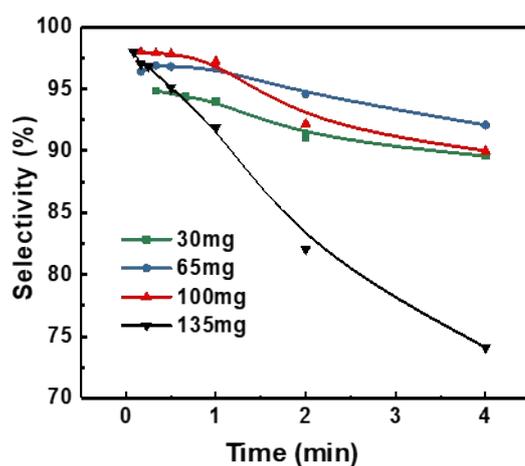


Fig. S3. Effect of Hf-LigS amount on the selectivity in CTH of 5-HMF to BHMF.

Table S1 The compositions and physical properties of various catalysts

Catalysts	Content (wt.%)						The physical properties		
	Metal ^a	Na ^a	S ^b	C ^b	H ^b	O (Calculated)	Surface area (m ² ·g ⁻¹)	Pore volume (cm ³ /g)	Average pore diameter (nm)
LS	-	3.14	3.53	43.2	4.93	45.17	0.5	-	-
HfO ₂	84.8	-	-	-	-	15.2	8.59	0.024	11.18
Hf-LigS	40.28	0.01	2.01	20.9	3.59	33.12	20.22	0.072	14.3
Zr-LigS	20.3	0.02	1.7	20.6	3.54	53.84	115.15	0.18	6.1
Fe-LigS	5.76	0.04	3.17	40.7	4.53	45.77	5.95	0.011	7.73
Zn-LigS	4.95	0.04	2.16	49.1	5.05	38.64	10.22	0.017	6.65
Al-LigS	1.26	0.03	2.42	40.2	0.75	55.31	4.4	0.005	4.47

^a Determined by ICP-OES.

^b Determined by elemental analysis.

Table S2. Base and acid properties of various catalysts ^a

Catalysts	Acidity	Basicity	Base/acid ratio
	Content (mmol/g)	Content (mmol/g)	
HfO ₂	0.01	0.00	0.10
Hf-LigS	0.56	0.36	0.64
Zr-LigS	0.57	0.32	0.56
Fe-LigS	0.90	0.29	0.32
Zn-LigS	0.79	0.26	0.33
Al-LigS	0.87	0.27	0.31
Recycled Hf-LigS	0.47	0.29	0.62

^a Basicity and acidity of the catalyst were determined with CO₂- and NH₃-TPD with a programmed temperature: heating from 50 to 300 °C at a rate of 10 °C/min and then kept at 300 °C for 60 min gas desorption.

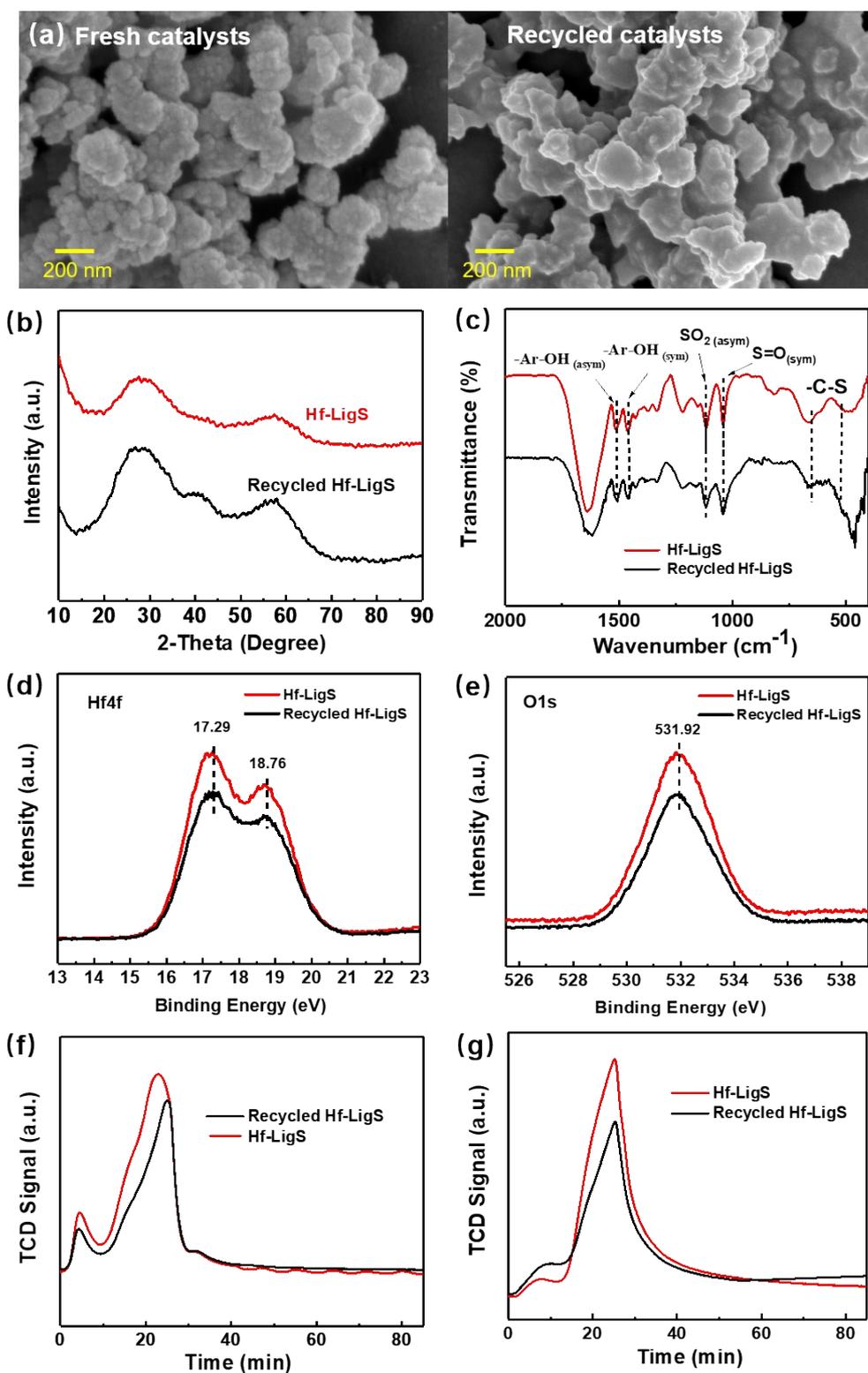


Fig. S4. Analyses of fresh and recovered Hf-LigS catalyst after seven cycles: SEM images (a), XRD patterns (b), FT-IR (c), Hf 4f XPS spectra (d), O 1s XPS spectra (e), NH₃-TPD (f) and CO₂-TPD (g).

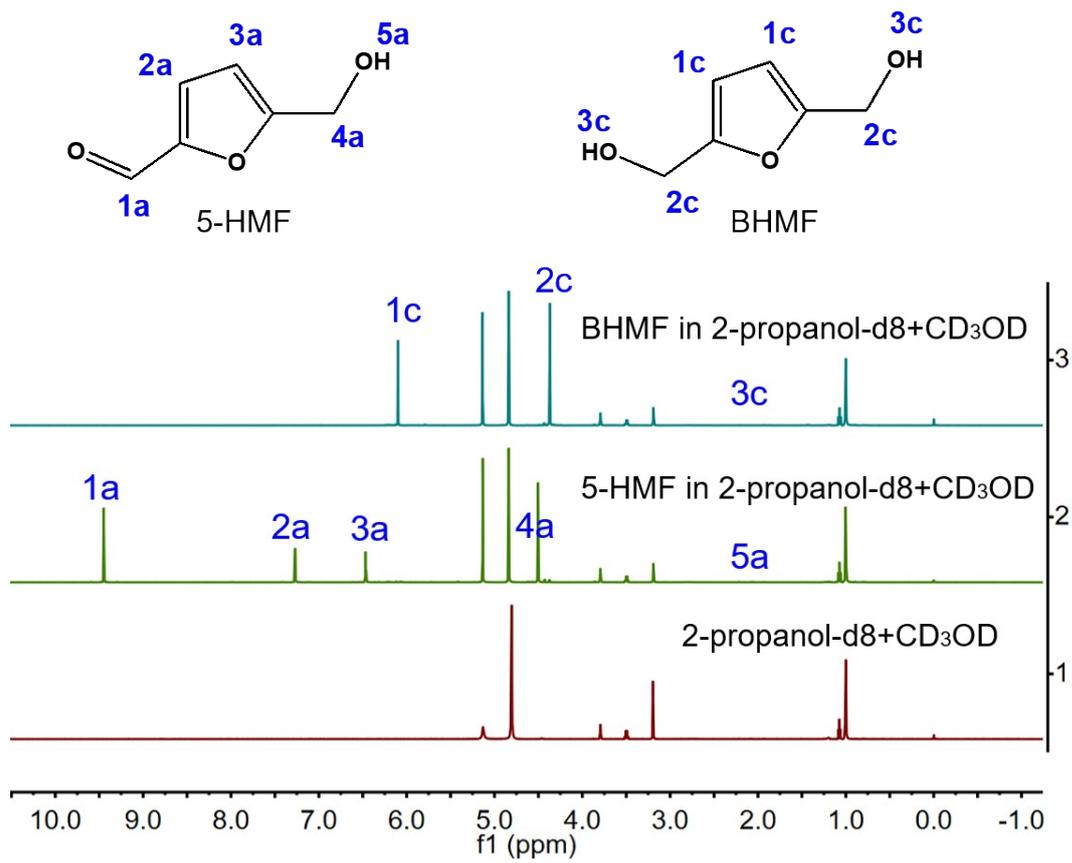


Fig. S5. ¹H NMR spectra of 5-HMF, BHMf standards and 2-propanol-d8.

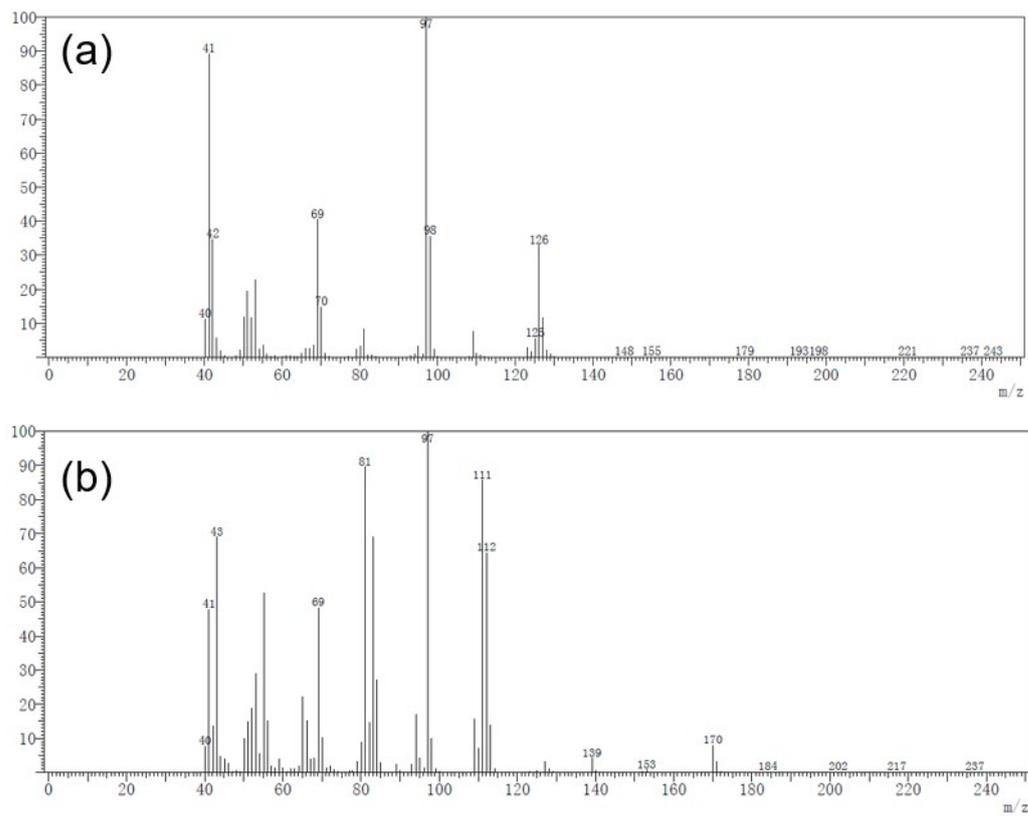


Fig. S6. MS spectra of MEFA (a) and BHM standard.

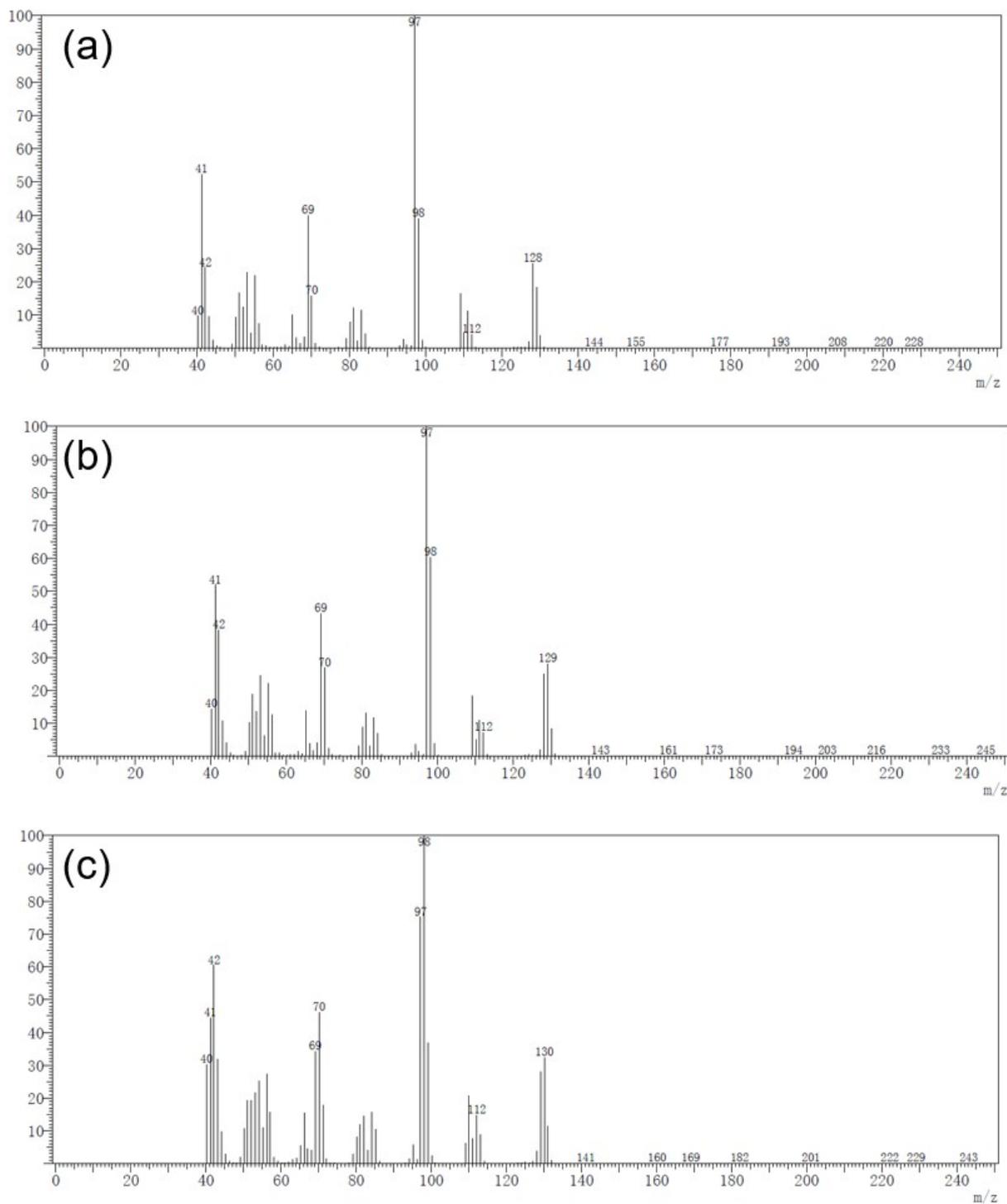


Fig. S7. MS spectra of BHMf product in 2-PrOH (a), BHMf product in 2-PrOH-OD (b) and BHMf product in 2-PrOH-d8 (c).

Table S3. Summary of different catalysts for selective reduction of 5-HMF to BHMF with 2-PrOH as H-donor in recent reported literatures.

Entry	Catalyst	Solvent	Reaction conditions and Result							Ref.
			5-HMF concentration	The amount of catalysts	Reaction temperature (°C)	Reaction time (h)	HMF Conv. (%)	BHMF Selec. (%)	Activation energy (kJ/mol)	
1	MZCCP	2-butanol	0.5g/24.5g	0.25g	140	5	99.5	96.6	-	[1]
2	ZrBa-SBA	2-propanol	0.2g/19.8g	0.1g	150	2.5	98.3	92.2		[2]
3	MZH(Zr/Fe=2)	2-Butanol	0.5g/24.5g	0.4g	150	5	98.4	91.1		[3]
4	ZrO(OH) ₂	ethanol	1g/39g	1g	150	2.5	94.1	88.9		[4]
5	γ -Fe ₂ O ₃ @HAP	2-propanol	1mmol/15ml	40mg	180	10	78.2	92.1		[5]
6	Al ₇ Zr ₃ @Fe ₃ O ₄	2-propanol	2mmol/10ml	0.08g	180	4	82.7	85.9		[6]
7	Zr-FDCA-T,	2-propanol	2mmol/10ml	100mg	140	8	97	89.7		[7]
8	Co ₃ O ₄ /MC	2-propanol	1mmol/10ml	50mg	160	6	100	99		[8]
9	Hf-LigS	2-propanol	1mmol/10ml	100mg	100	2	97.3	92.2	64.64	This work
10	Hf-LigS	2-propanol	1mmol/10ml	100mg	80	6	92.6	96.8	64.64	This work

Reference

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