Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Conversion of highly concentrated fructose into 5-hydroxymethylfurfural by acid-base bifunctional HPA nanocatalysts induced by choline chloride

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Experimental

The Hammett acid strength was measured by exposing samples (0.1g) to benzene solutions of a known amount of selected Hammett indicators (methyl violet, pKa = +0.8; anthraquinone, pKa = -8.2; 2,4,6-trinitroaniline, pKa = -10.1; p-nitrotoluene, pKa = -11.35; p-nitrochlorobenzene, pKa = -12.7; 2,4- dinitrotoluene, pKa = -13.75; 2,4-dinitrofluorobenzene, pKa = -14.52). UV-Vis spectra of the air dried samples were recorded to quantify the amount of indicator adsorbed on the surface of the catalyst. And the Hammett base strength was also determined in the same method, which was measured by exposing samples of catalysts (0.1g) to benzene solutions of a known amount of selected Hammett indicators (bromothymol blue, pKa = 7.2; phenolphthalein, pKa = 9.3; 2,4,6-Trinitrobenzene amine, pKa = 12.2; 2,4-dinitraniline, pKa = 15.0; 4-chloride-2–nitroaniline, pKa = 17.2).

The acid capacity of $Ly_{3-x}H_xPW$ and $H_3PW_{12}O_{40}$ was measured by titration. A sample of catalyst (0.1g) was stirred with 2M NaCl (20 mL). After 24 h, Filter to remove the solid, the filtrate was measured by titration with NaOH (0.05 M). The indicator was phenolphthalein.[1-2]

1 D. E. Lopez, K. Suwannakarn, D. A. Bruce, J. G. Goodwin Jr. , J. Catal. 2007, 247, 43 –50.

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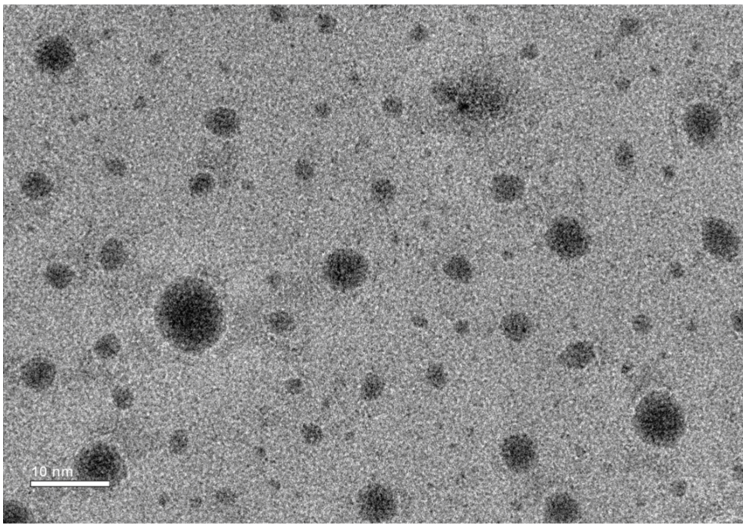


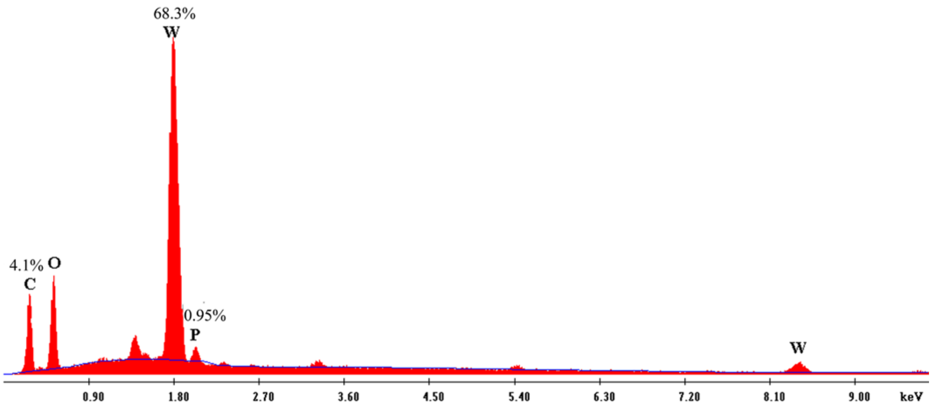


Fig. S1 The TEM image and the Energy dispersive X-ray spectroscopic data of $(C_6H_{15}O_2N_2)_2HPW_{12}O_{40}$

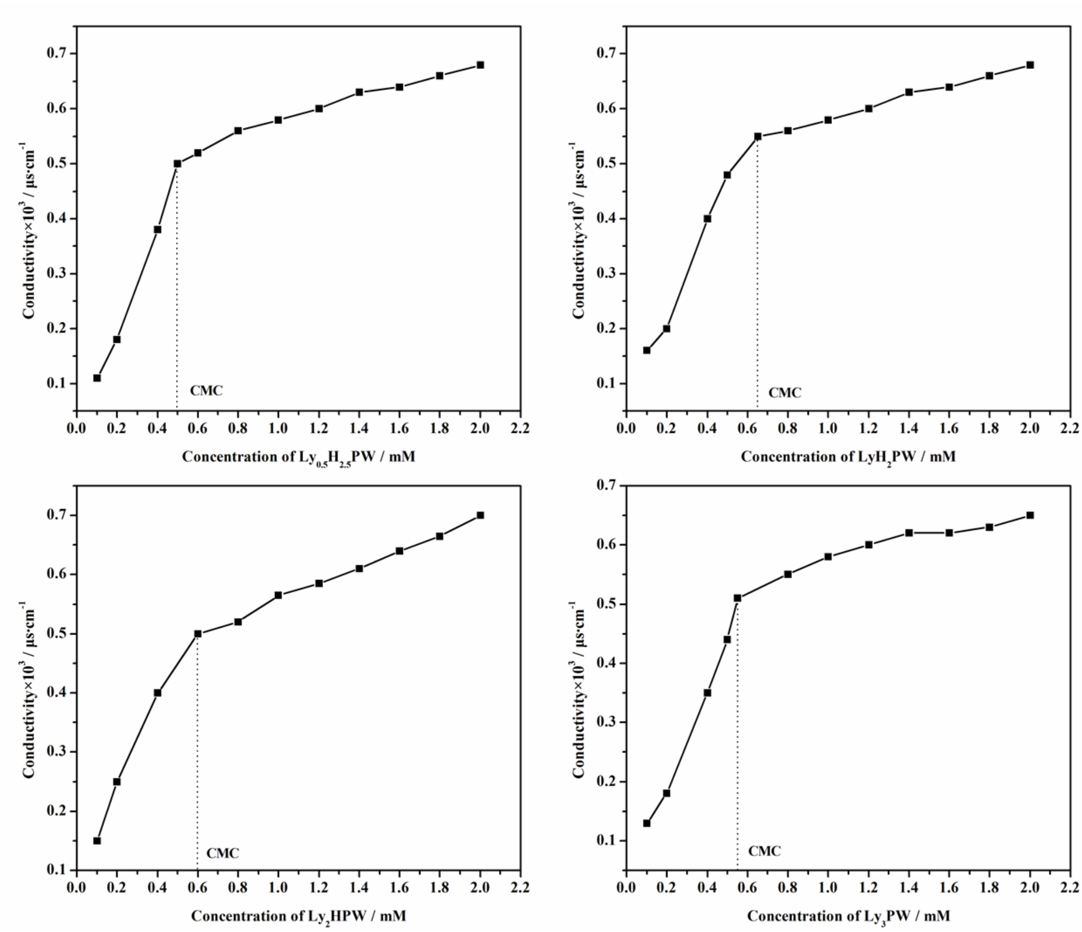


Fig. S2 The CMC of $Ly_{3-x}H_xPW$ in room temperature

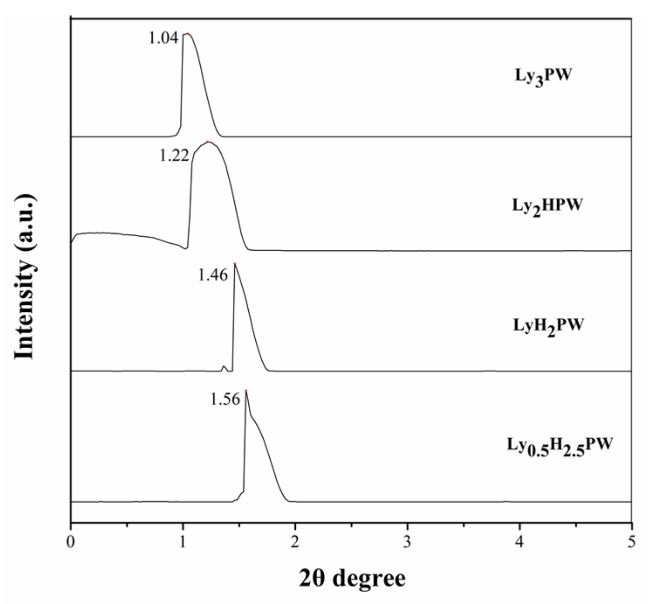


Fig. S3 Low-angle XRD patterns of $Ly_{3-x}H_xPW$.

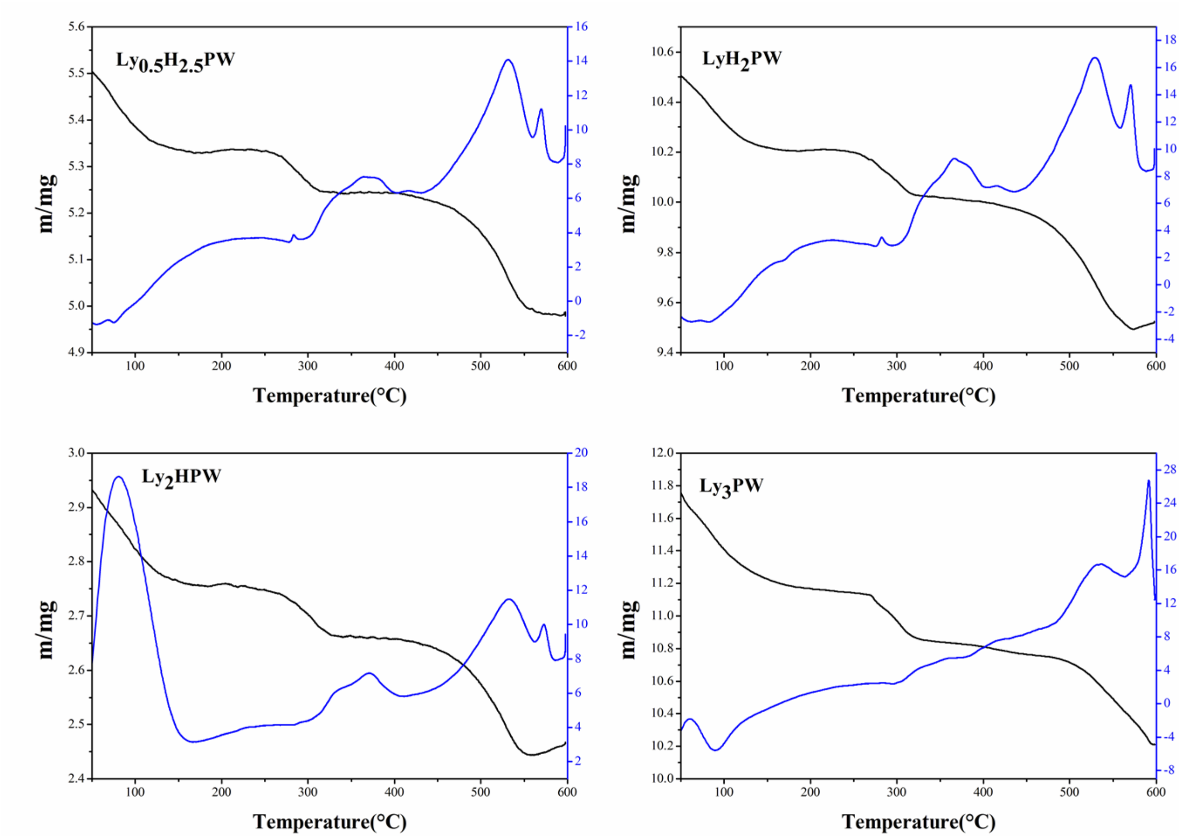
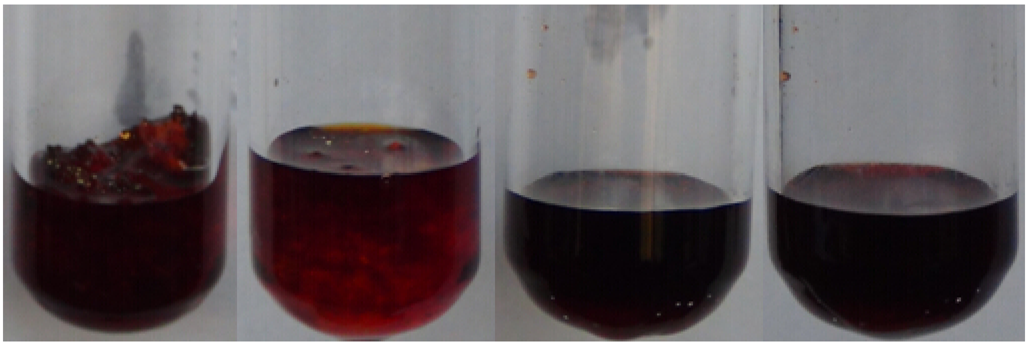


Fig. S4 The thermal analysis (TG/DTA) curves of $Ly_{3-x}H_xPW$.



a b c d

Fig. S5 The different fructose/ChCl weight ratio of fructose conversion. Reaction conditions: 110 ºC in 1 min. a. fructose/ChCl weight ratio is 2:6; b. fructose/ChCl weight ratio is 3:6; c. fructose/ChCl weight ratio is 4:6; d. fructose/ChCl weight ratio is 5:6.

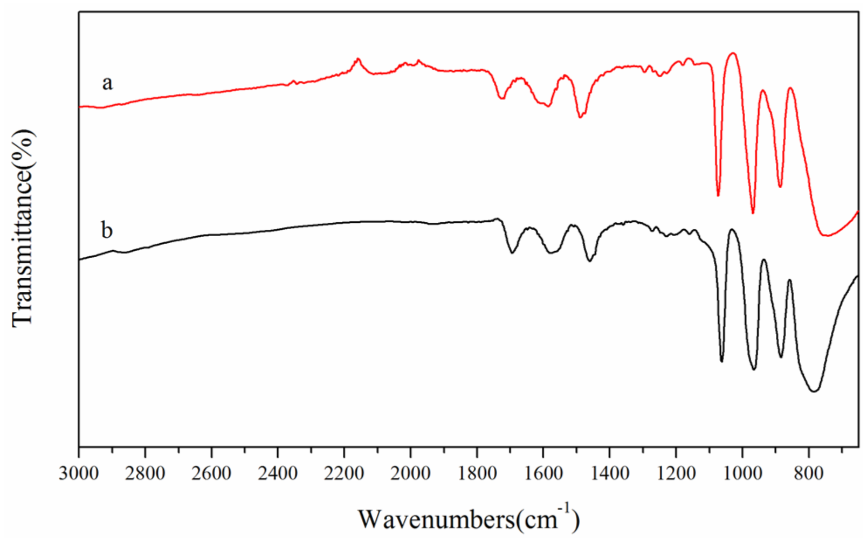


Fig. S6 The IR spectra of Ly_2HPW (a) and reused Ly_2HPW (b).

Table S1 HMF formation from fructose in low melting mixtures. Ly_2HPW (0.016 mmol) was used as catalyst in all cases; the reaction temperature was 110 ºC in 1 min.

	Choline chloride	Imidazole	Malonic acid	urea	Guanidineacetic acid
HMF	92.3%	62.5%	39.9%	25.7%	<5%

Table S2 The comparison between different catalysts on dehydration of fructose

Catalysts	System	Concentration	T(ºC)	time	Yield(%)	Con.(%)	Ref
[MBClm]SO_3Cl	acetonitrile/ water	33wt%	80	3h	81		[1]
Al-SBA_{15}	water: MIBK	10wt%	165	1h		59	[2]
$CuHPO_4 \cdot H_2O$	water	10wt%	200	5min	14.3	92.3	[3]
H_3PO_4	water	10wt%	200	5min	29.1	93.5	
4-styrenesulfonic-acid-grafted	water	6.6wt%	120	6h	27	80	[4]
formic acid	n-butanol/ water	6.6wt%	170	60min	69.2	98.3	[5]
NbPO-pH2	water	8wt%	130	30min	45	57.6	[6]
Ambersty-15	water	8wt%	130	30min	31.3	61.6	
BHC	ChCl/MIBK/ water	10wt%	110	60min	84		[7]
$FeCl_3/Et_4NBr$	water /NMP=1:1	10wt%	90	120min	70		[8]
$Ag_3PW_{12}O_{40}$	water /MIBK	30wt%	120	60min	77.7	82.8	[9]
TESAS-SBA-15	water /MIBK/2-butanol	30wt%	130	141min		84	[10]
pSO_3H-SBA-15	water /MIBK/2-butanol	30wt%	130	140min		79	
SSA-SBA-15	water /MIBK/2-butanol	30wt%	130	140min		81	
Amberlyst 70	water /MIBK/2-butanol	30wt%	130	225min		85	
Glu-TsOH	water	8wt%	130	1.5h	8	67	[11]
H_3PO_4	water	10wt%	200	5min	28.2		[12]
CaP_2O_6	water	10wt%	200	5min	34.1		
a-$Sr(PO_3)_2$	water	10wt%	200	5min	39.3		
$ZnCl_2$/HCl	water	15wt%	120	40min	53.3	97.3	[13]
$B(OH)_3/MgCl_2$	MIBK/ water	30wt%	150	45min	52	81	[14]
$AlCl_3$	water /MIBK/microwave	5wt%	130	5min	61.6		[15]
$AlCl_3$	water / microwave	5wt%	120	5min	54.8		
$AlCl_3$	water / microwave	30wt%	120	5min	52.1		
Nb_2O_5	DMSO	2wt%	120	2h	86.2	100	[16]
Amberlyst-15	DMF	13wt%	120	1h	64		[17]
Amberlyst-15	DMSO	13wt%	120	1h	83		
PS-NHC-Al	DMSO	8.2wt%	100	3h	70	93	[18]
PS-NHC-Sn	DMSO	8.2wt%	100	3h	71	89	
PS-NHC-Cr	DMSO	8.2wt%	100	3h	64	83	
PS-NHC-Fe	DMSO	8.2wt%	100	3h	73	97	
Amberlyst 15	DMSO	8.2wt%	100	3h	65	79	
NBS	NMP	8wt%	90	1h	56.1		[19]
NBS	DMSO	8wt%	100	2h	47.5		
$SnCl_4$+NBS	NMP	8wt%	100	2h	82.3		
[AMIM]Cl	DMF	7.2wt%	100	45min	84.9	99	[20]
--	DMSO/microwave	15wt%	150	10min	71	100	[21]
$InCl_3$	water	5wt%	180	10min	76	100	[22]
([tetraEG(mim)(triethylamo)]	--	10wt%	70	40min	92	100	[23]

$[HSO_4]_2)$							
$[C_6(mpy)_2][NiCl_4]^{2-}$	DMSO	7wt%	110	60min	95.5	95.6	[24]
HCCP	DMSO	5wt%	90	2h	91	98.9	[25]
HCl	water/butanol	54.6wt%	170	20min	81.7	92	[26]
STZ-05	DMSO	10wt%	120	2.5h	76		[27]
Si–OH	H3PO4/ DMSO/H2O	0.25%	80	5h	97		[28]
$FeCl_3$	[Bmim]Cl	3.6%	100	4h	90.8		[29]
K-10 clay-$CrCl_3$	DMSO	4.5%	120	2h	95.8		[30]
K-10 clay-$CrCl_3$	[BMIM]Cl	4.5%	120	1h	95.4		

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