

**Fabrication of micellar heteropolyacid with Lewis-Brønsted acid sites and application for
the production of 5-hydroxymethylfurfural from saccharides in water**

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Supporting information

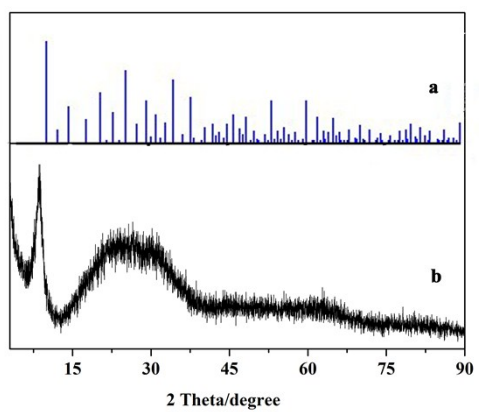


Fig. S1. XRD patterns of (a) $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and (b) $(\text{C}_{16}\text{TA})\text{H}_4\text{PW}_{11}\text{Ti}$

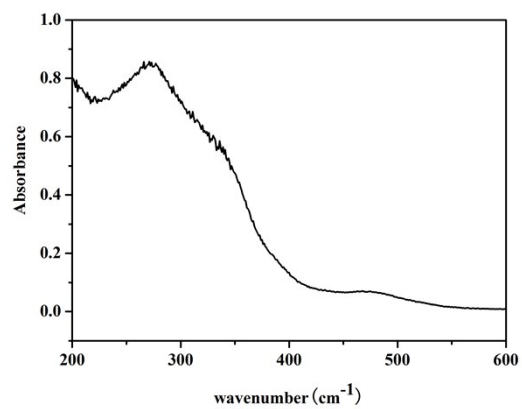


Fig. S2. The UV-vis pattern of $(C_{16}TA)H_4PW_{11}Ti$

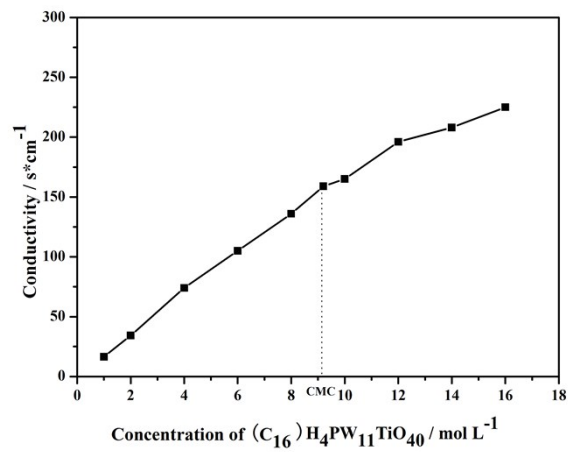


Fig. S3. The conductivity of $(\text{C}_{16})\text{H}_4\text{PW}_{11}\text{Ti}$ at the room temperature.

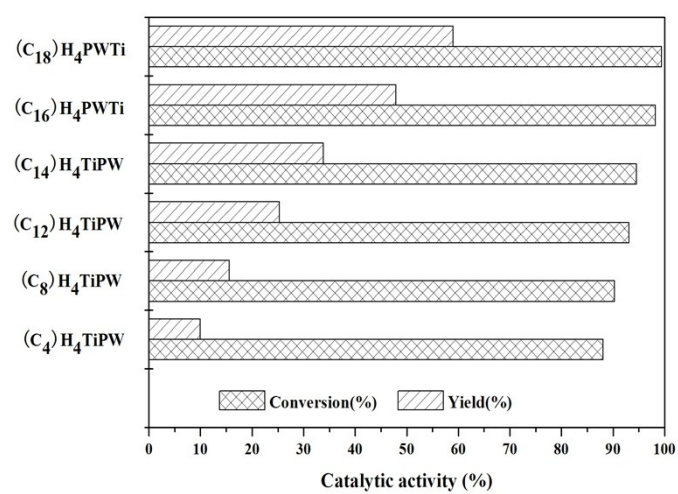


Fig. S4. The influence of the carbon chain length on the conversion of fructose into HMF.
Reaction conditions: 0.6 g of fructose, 0.01 mmol of catalyst, 2 mL of water, 130 °C for 90 min.

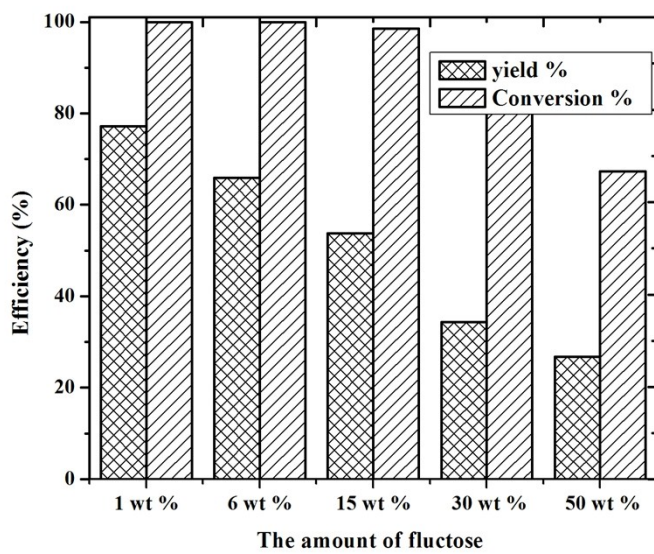


Fig. S5. The influence of the amount of fructose on the conversion. Reaction conditions: 0.01 mmol of catalyst, 2 mL of water, 130 °C for 30 min.

Table S1 The comparison between different catalysts on dehydration of glucose to HMF

Catalysts	System	Concentration (wt%)	T(°C)	time	Yield(%)	Con.(%)	Ref
NbPO-pH 2	water	5	140°C	60min	14.1	24.4	1
NbPO-pH 7	water	5	140°C	60min	33.6	68.1	1
HCl	C ₁₂ MI.Cl	10	120°C	8min	30	79	2
HCl	C ₁₂ MI.Cl	10	120°C	12min	34	75	2
InCl ₃	water	5	180°C	5min	52.0	81.9	3
InCl ₃	water	5	180°C	10min	59.8	91.4	3
InCl ₃	NaCl-H ₂ O/THF	4.5	200°C	2h	50.9	99	4
CrCl ₃ ·6H ₂ O	water	5	110°C	30min	10.5	12.0	5
Hβ-zeolite	[BMIM]Cl	10	150°C	50min	50.3	80.6	6
InCl ₃	water	5	180°C	10min	59.8	91.4	7

SO ₄ /ZrO ₂	water	-	100 °C	6h	1.0	20.9	8
Beta-ST600	Water/DMSO	3	180°C	3h	43	78	9
Sn-MCM-41(50)	[EMIM]Br	10	110°C	4h	70	99	10
SO ₄ ²⁻ /ZrO ₂ -TiO ₂	n-butanol/water	6	170°C	2h	26.0	96.5	11
phosphate/TiO ₂	Water/THF	10	120 °C	2h	81.2	98	12
IL-5	Water/MIBK	30	120 °C	6h	78.4	99.8	13
TiHP	water- NaCl/THF	25	140 °C	3h	17	29	14
Zr-MCM-550	Water/MIBK	10	175 °C	2.5h	23	82	15
CrCl ₂ -Im-SBA-15	Water/DMSO	10	100 °C	3h	35	51	16
Mesoporous tantalum phosphate	Water/MIBK	10	170 °C	1h	32.8	56.3	17
Mesoporous tantalum oxide	Water/MIBK	10	175 °C	90min	23	69	18
ZrP	Water/diglyme	10	180 °C	3h	63		19
TiO ₂	Water	2	140 °C	6h	30	80	20
CrCl ₃	Et-DBUBS	10	100 °C	3h	78.6	93	21
ZrSil /Amberlyst-15	THF/H ₂ O	5	180 °C	1.5h	39	87	22
K-10 clay-CrCl ₃	[BMIM]Cl	4.5	120 °C	2h	56.3		23
AlCl ₃ /NaI	DMAC	4.5	130 °C	15min	62	86	24
H ₃ PO ₄ / NaH ₂ PO ₄	Water	10	160 °C	90min	39.5	83.2	25
Amberlyst-70 resin	DMSO	7.6	140 °C	24h	32.0	98.1	26
[C ₃ SO ₃ HMIM][HSO ₄]/ CoCl ₂	[AMIM]Cl	9	120 °C	2h	62.2	95.5	27
H ₃ BO ₃ /SiO ₂	[bmim]HSO ₄	10	120 °C	3h	81		28
H ₃ PO ₄ /Nb ₂ O ₅ ·nH ₂ O	Water	1	120 °C	3h	47.9	92	29
P-VI-0/P-SO ₃ H-154	THF/DMSO	2	100 °C	10h	95.4		30

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