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Supporting Information

Synergetic Effect of Brønsted/Lewis Acid Sites and Water on the Catalytic Dehydration of Glucose to 5-Hydroxymethylfurfural by Heteropolyacid-Based Ionic Hybrids

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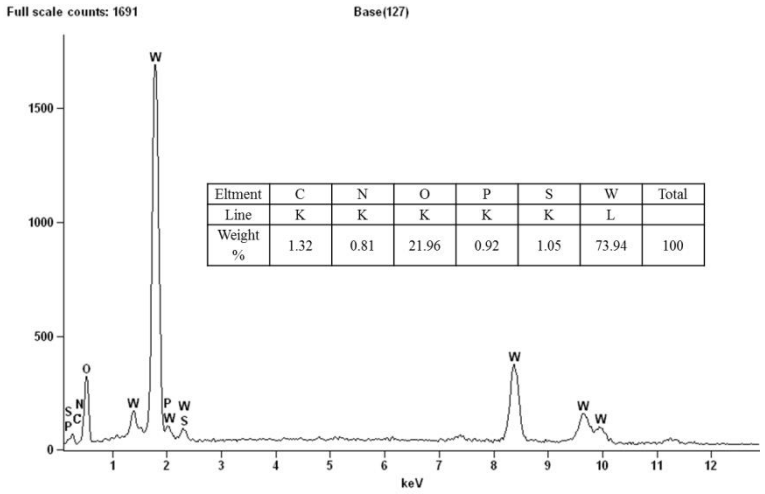
Supporting Information



Eltment	C	N	O	P	S	W	Total
Line	K	K	K	K	K	L	
Weight %	1.32	0.81	21.96	0.92	1.05	73.94	100

Figure S1 SEM-EDX analysis of [PzS]H_2PW.

Theoretical calculation of Brønsted and Lewis acid sites on [PzS]$_x$H$_y$PW catalysts.

First the acid strength of [PzS]H_2PW cannot be measured by NH_3-TPD technique due to the high temperature instability of the organic moiety. Furthermore, we have tried to determine the number of acidic sites by pyridine adsorption infrared spectroscopy. However, the viscosity of [PzS]H_2PW is too high to be detected by the method of tabletting. Therefore, we only gave the theoretical number of acid sites according to the chemical formula.

For each mol of [PzS]xHyPW formula, we assumed a possible maximum of 3 mol Brønsted acid sites and 1 mol Lewis acid sites for $H_3PW_{12}O_{40}$ (3 H protons and 1 PW anion);

2 mol Lewis acid sites for Pz (2 N that can accept H protons);

1 mol Brønsted acid sites and 1 mol Lewis acid sites for [PzS]Cl (1 SO_3H and 1 N),

2 mol Brønsted acid sites for [PzS-H]Cl_2 (1 SO_3H and 1 NH);

3 mol Brønsted acid sites and 2 mol Lewis acid sites for [PzS]H_2PW (1 SO_3H, 2 H_2PW and 1 N, 1 PW anion);

3 mol Brønsted acid sites and 1 mol Lewis acid sites for [PzS-H]HPW (1 SO_3H, 1 NH, 1 HPW and 1 PW anion)

3 mol Brønsted acid sites and 3 mol Lewis acid sites for $[PzS]_2HPW$ (2 SO_3H, 1 HPW and 2 N, 1 PW anion)

3 mol Brønsted acid sites and 4 mol Lewis acid sites for $[PzS]_3PW$ (3 SO_3H, and 3 N, 1 PW anion)

The basic characterization data for synthesized compounds

(1) [PzS]Cl: Elemental analysis Calcd: C, 24.41 wt%; N, 14.24 wt%; H, 2.54 wt%. Found: C, 24.58 wt%; N, 13.97 wt%; H, 2.56 wt%. ^{1}H NMR (300 MHz, D^6-DMSO, TMS) δ 9.75 (d, 2H), 9.57 (m, 2H), 8.50 (s, 1H).

(2) [PzS-H]Cl_2: Elemental analysis Calcd: C, 12.87 wt%; N, 3.75 wt%; H, 2.02 wt%. Found: C, 12.73 wt%; N, 3.71 wt%; H, 1.98 wt%. ^{1}H NMR (300 MHz, D^6-DMSO, TMS) δ 13.38 (s, 1H), 9.46 (d, 2H), 9.12 (m, 2H), 8.40 (s, 1H).

(3) [PzS]H_2PW: Elemental analysis Calcd: C, 1.58 wt%; N, 0.92 wt%; H, 0.23 wt%. Found: C, 1.61 wt%; N, 0.98 wt%; H, 0.23 wt%. ^{1}H NMR(300 MHz, D^6-DMSO, TMS) δ 9.56 (d, 2H), 9.69 (m, 2H), 8.62 (s, 1H).

(4) [PzS-H]HPW: Elemental analysis Calcd: C, 12.87 wt%; N, 3.75 wt%; H, 2.02 wt%. Found: C, 12.73 wt%; N, 3.71 wt%; H, 1.98 wt%. ^{1}H NMR(300 MHz, D^6-DMSO, TMS) δ 13.32 (s, 1H), 9.39 (d, 2H), 9.21 (m, 2H), 8.85 (s, 1H).

(5) $[PzS]_2HPW$: Elemental analysis Calcd: C, 2.99 wt%; N, 1.75 wt%; H, 0.37 wt%. Found: C, 2.54 wt%; N, 1.68 wt%; H, 0.25 wt%.

(6) $[PzS]_3PW$: Elemental analysis Calcd: C, 4.28 wt%; N, 2.50 wt%; H, 0.45 wt%. Found: C, 3.73 wt%; N, 2.25 wt%; H, 0.34 wt%.

(7) [MimPS]H_2PW: Elemental analysis Calcd: C, 2.72 wt%; N, 0.91 wt%; H, 0.49 wt%. Found: C, 2.87 wt%; N, 0.96 wt%; H, 0.62 wt%. ^{1}H NMR (300 MHz, D^6-DMSO, TMS) δ 2.24 (m, 2H), 2.83 (t, 2H), 3.81 (s, 3H), 4.28 (t, 2H), 4.65 (s, 1H), 7.37 (d, 1H), 7.44 (d, 1H), 8.67 (s, 2H).

Recycling test

To examine the durability of $[PzS]_2HPW$, the recycling tests of water phase in reaction mixture for glucose dehydration to HMF were preformed, as shown in Figure S2. It can be seen that the decline in the HMF yield is unnoticeable, suggesting that $[PzS]_2HPW$ is a reusable catalyst in water-NaCl/THF for glucose dehydration to

HMF.

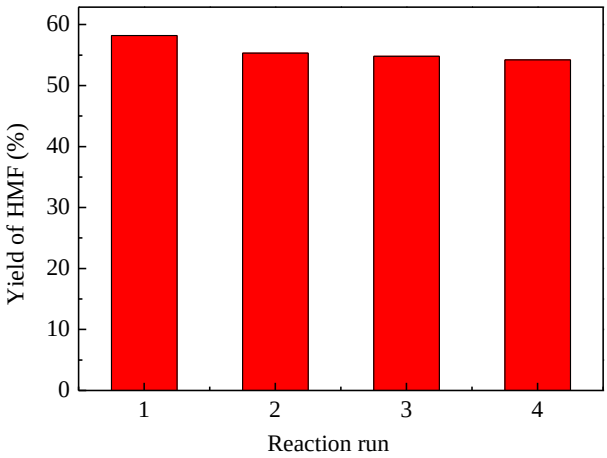


Figure S2 Catalytic recycling of $[PzS]_2HPW$ for glucose dehydration to HMF.