Electronic Supplementary Material (ESI) for RSC Advances.

Experimental Section

Materials: D-fructose (99%), inulin (from dahlia tubers), 5-hydroxymethylfurfural (5-HMF, 99%), $MnCl_2•4H_2O$ (99%), $NiCl_2•6H_2O$ (99%), $LaCl_3•7H_2O$ (99%), $CoCl_2•6H_2O$ (99%), $ZnCl_2$ (99%), $AlCl_3•6H_2O$ (98%) and $InCl_3•4H_2O$ (99%) were purchased from Aladdin (China). $CrCl_3•6H_2O$ (98%) was purchased from Sigma-Aldrich (China). $YCl_3•6H_2O$ (99%) was purchased from Energy Chemical (China). $SnCl_4•5H_2O$ (99%), P_2O_5 (98%), $Ni(NO_3)_2•6H_2O$ (98%), $NiSO_4•6H_2O$ (98%), $Cr(NO_3)_3•9H_2O$ (99%), $Cr_2(SO_4)_3•6H_2O$ (99%), NaCl (99%), H_3PO_4 (85 wt%), Na_3PO_4 (98%), Na_2HPO_4 (99%), $NaH_2PO_4•2H_2O$ (99%), dimethyl sulfoxide (DMSO, 99%) and glycerol (99%) were purchased from Sinopharm (China). Sulfuric acid (H_2SO_4, 98 wt%) was provided by a local supplier. All of the commercial chemicals were used as received. Purified water (H_2O) with a resistivity of 18.2 MΩ-cm was produced by an ultra-pure water system (Taoshi Brand, China).

Reaction procedure: Typically, fructose (60 mg), catalyst (10 mol% to fructose) and DMSO (1 mL) were added into a reaction vial with a magnetic stir bar. The vial was sealed and inserted into a heating block. The reaction mixture was stirred at the reaction temperature. After a specified time, the reaction was quenched by immersing the reaction vial in an ice-water bath. The mixture was diluted by water and a certain amount of glycerol (internal standard) was added. A small amount of reaction mixture was taken out, further diluted with water and filtered for analysis.

Analysis method: The samples were analyzed by high performance liquid chromatography (HPLC). HPLC was performed on a Shimadzu LC-16 system equiped with a Shimadzu RID-20 refractive index detector and an Agilent Hi-Plex ligand exchange column (H-form, 300×7.7 mm). A 0.005 M aqueous solution of H_2SO_4 was used as the mobile phase. The flow rate was set to be 0.65 mL/min. The column and detector temperatures were 65 ^oC and 50 ^oC, respectively. Glycerol was added as the internal standard for quantitative calculations. Fructose conversion, 5-HMF yield and selectivity were calculated by mole.

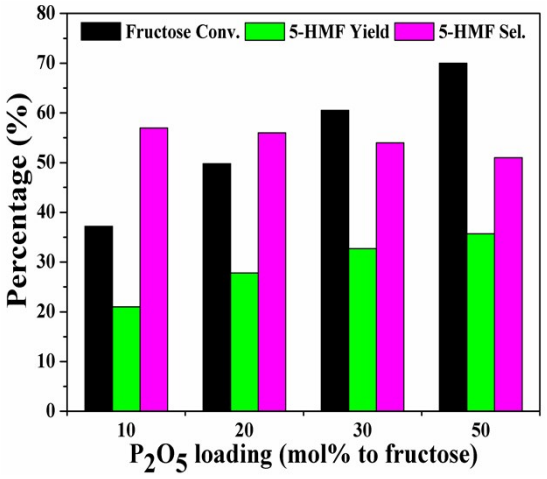

Fig. S1 The conversion of fructose into 5-HMF with different amounts of P_2O_5 (reaction conditions: fructose 60 mg; DMSO 1mL; 80 °C; 30 min).

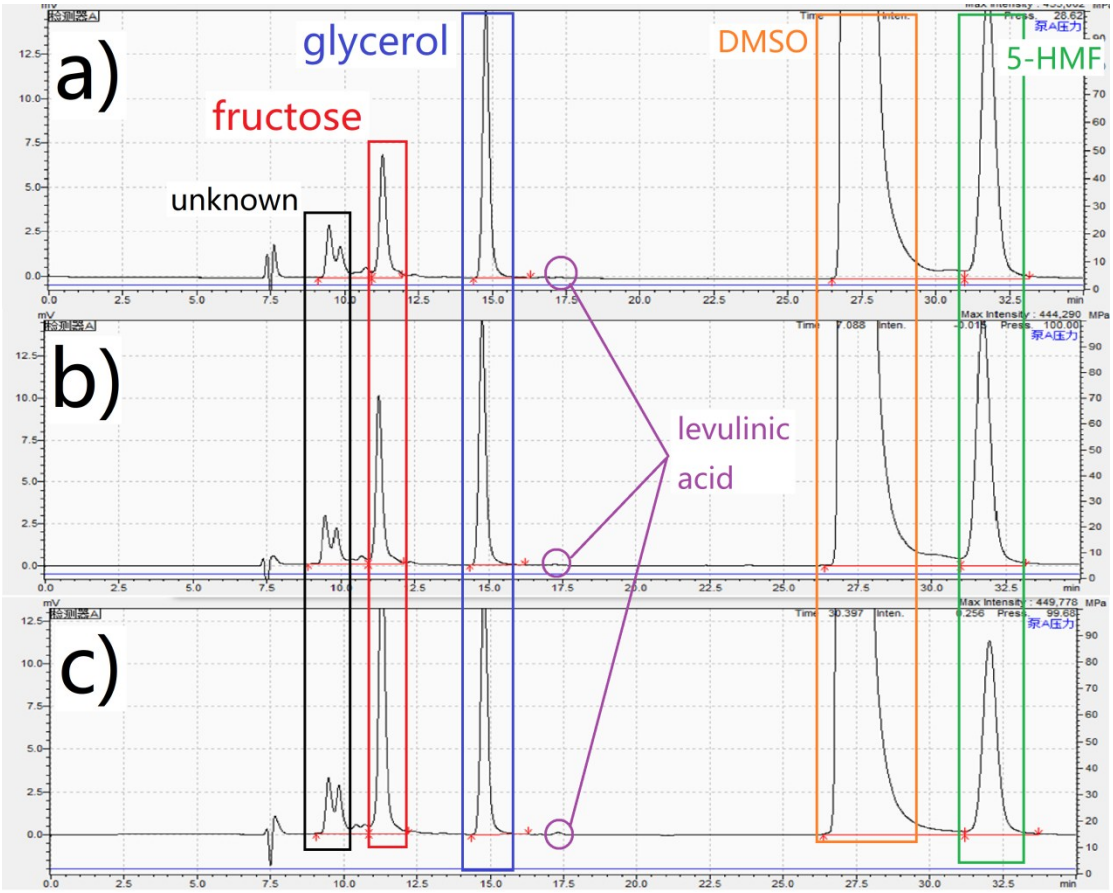

Fig. S2 The HPLC chromatograms for the reactions with a) P_2O_5 and $NiCl_2 \cdot 6H_2O$, b) P_2O_5 and $CrCl_3 \cdot 6H_2O$, c) P_2O_5 and NaCl (reaction conditions: fructose 60 mg; P_2O_5 10 mol% to fructose; metal chloride 10 mol% to fructose; DMSO 1mL; 80 °C; 30 min).

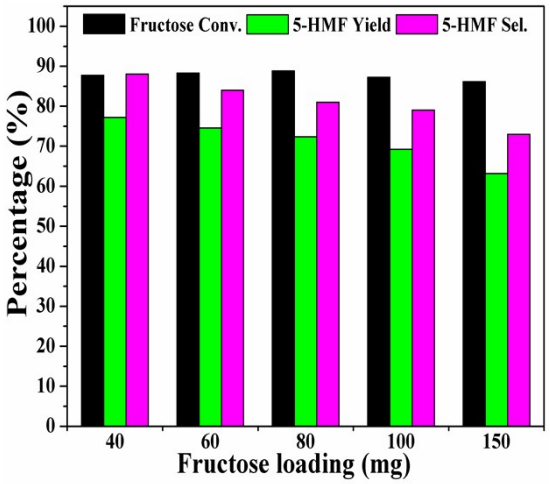

Fig. S3 Effect of different substrate loadings on the conversion of fructose (reaction conditions: P_2O_5 10 mol% to fructose; $NiCl_2$•$6H_2O$ 10 mol% to fructose; DMSO 1mL; 80 °C; 30 min).

Table S1 Results on the conversion of fructose over P_2O_5 and different chromium salts.[a]

Entry	Catalyst	Fructose Conv. (%)	5-HMF Yield (%)	5-HMF Sel. (%)
1	P_2O_5	37	21	57
2	P_2O_5+$CrCl_3 \cdot 6H_2O$	81	67	83
3	P_2O_5+$Cr(NO_3)_3 \cdot 9H_2O$	75	49	65
4	P_2O_5+$Cr_2(SO_4)_3 \cdot 6H_2O$	40	26	65

[a] Reaction conditions: fructose 60 mg; P_2O_5 10 mol% to fructose; Cr fraction 10 mol% to fructose; DMSO 1mL; 80 °C; 30 min.

Table S2 Results on the conversion of inulin into 5-HMF in the studied system.[a]

Entry	Temperature (°C)	Time (min)	5-HMF Yield (%)
1	80	8	22
2	80	15	36
3	80	30	42
4	80	60	45
5	90	8	35
6	90	15	43
7	90	30	45
8	100	8	39
9	100	15	44

[a] Reaction conditions: inulin 60 mg; P_2O_5 10 mol% to fructose unit in inulin; $NiCl_2$•$6H_2O$ 10 mol% to fructose unit in inulin; DMSO 1mL.

Table S3 Results on the conversion of glucose in the studied system.[a]

Entry	Catalyst	Time (min)	Glucose Conv. (%)	5-HMF Yield (%)
1	P_2O_5	30	10	
2	$NiCl_2 \cdot 6H_2O$	30	6	
3	$CrCl_3 \cdot 6H_2O$	30	11	
4	P_2O_5+$NiCl_2 \cdot 6H_2O$	30	11	
5	P_2O_5+$CrCl_3 \cdot 6H_2O$	30	23	
6	P_2O_5+$NiCl_2 \cdot 6H_2O$	60	23	
7	P_2O_5+$CrCl_3 \cdot 6H_2O$	60	31	0.2
8	P_2O_5+$AlCl_3 \cdot 6H_2O$	60	44	0.2

[a] Reaction conditions: glucose 60 mg; P_2O_5 10 mol% to glucose; metal chloride 10 mol% to glucose; DMSO 1mL; 100 ^oC.