Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

Importance of the synergistic effects between cobalt sulfate and tetrahydrofuran for selective production of 5-hydroxymethylfurfural from carbohydrates

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Table S1 Yields of HMF from fructose with different loading in THF with $CoSO_4 \cdot 7H_2O$[a]

Entry	Fructose (g)	$CoSO_4 \cdot 7H_2O$ (g)	Yield (%)	
			LA	HMF
1	0.02	0.62	0	56.9
2	0.04	0.62	0	88.0
3	0.1	0.62	0	76.8
4	0.2	0.62	6.5	75.3
5	0.4	0.62	8.2	64.6
6	0.6	0.62	9.6	54.7
7	0.4	0	8.4	3.7

[a]Reaction conditions: THF: 3.6 g, T = 170°C, reaction time: 2 h, N_2: 3 MPa. All the conversions were 100%.

Table S2 Conversion of fructose or glucose over $CoSO_4 \cdot 7H_2O$ in H_2O/THF[a]

Entry	Sugar	Catalyst[b]	H_2O (wt%)[c]	Yield (%)	
				LA	HMF
1	Glucose	-	0	0	0
2	Glucose	$CoSO_4$	0	0	4.6
3	Glucose	$CoSO_4 \cdot 7H_2O$	10	0	7.7
4	Glucose	$CoSO_4 \cdot 7H_2O$	20	0	15.3
5	Glucose	$CoSO_4 \cdot 7H_2O$	30	0	27.2
6	Glucose	$CoSO_4 \cdot 7H_2O$	50	0	34.8
7	Glucose	$CoSO_4 \cdot 7H_2O$	70	8.7	11.7
8	Fructose	-	0	0	3.1
9	Fructose	$CoSO_4$	0	0	25.7
10	Fructose	$CoSO_4 \cdot 7H_2O$	10	0	44.1
11	Fructose	$CoSO_4 \cdot 7H_2O$	20	0	41.2
12	Fructose	$CoSO_4 \cdot 7H_2O$	30	0	29.6
13	Fructose	$CoSO_4 \cdot 7H_2O$	50	0	25.4
14	Fructose	$CoSO_4 \cdot 7H_2O$	70	0	9.2

[a]Reaction conditions: sugar: 0.04 g, solvents (THF-H_2O): 3.60 g, T = 170°C, reaction time: 2 h, N_2: 3 MPa. All the conversions were 100%.

[b]The mole number of catalysts was 1.5 times that of the sugar.

[c]The mass fraction of water in THF-H_2O

Table S3 The conversion of inulin with $CoSO_4 \cdot 7H_2O$ in THF[a]

Entry	Reaction temperature (°C)	The amount of $CoSO_4 \cdot 7H_2O$ (g)	Yield of HMF (%)
1	170	0	2.7
2	170	0.01	4.0
3	170	0.02	2.3
4	170	0.05	11.9
5	170	0.1	7.2
6	170	0.2	26.9
7	170	0.5	28.4
8	200	0	5.6
9	200	0.01	17.1
10	200	0.02	13.1
11	200	0.05	10.8
12	200	0.1	31.5
13	200	0.2	34.1
14	200	0.5	40.1
15	220	0	13.6
16	220	0.01	8.9
17	220	0.02	15.1
18	220	0.05	15.1
19	220	0.1	4.6
20	220	0.2	18.1
21	220	0.5	16.4

[a]Reaction conditions: inulin: 0.05 g, THF: 5 g, reaction time = 6 h, N_2 = 3 MPa. All the conversions were 100%.

Table S4 The conversion of cellulose with $CoSO_4 \cdot 7H_2O$ in THF[a]

Entry	Reaction temperature (°C)	The amount of $CoSO_4 \cdot 7H_2O$ (g)	Yield of HMF (%)
1	200	0	0
2	200	0.01	2.9
3	200	0.02	7.1
4	200	0.05	15.4
5	200	0.1	22.1
6	200	0.2	25.0
7	200	0.5	28.1
8	200	1	32.5
9	220	0	0
10	220	0.01	15.0
11	220	0.02	7.6
12	220	0.05	18.4
13	220	0.1	19.7
14	220	0.2	26.7
15	220	0.5	27.4
16	220	1	35.3
17	240	0	0
18	240	0.01	3.8
19	240	0.02	9.9
20	240	0.05	20.5
21	240	0.1	15.0
22	240	0.2	19.7
23	240	0.5	21.0
24	240	1	20.8

[a]Reaction conditions: cellulose: 0.05 g, THF: 5 g, reaction time = 6 h, N_2 = 3 MPa. All the conversions were 100%.

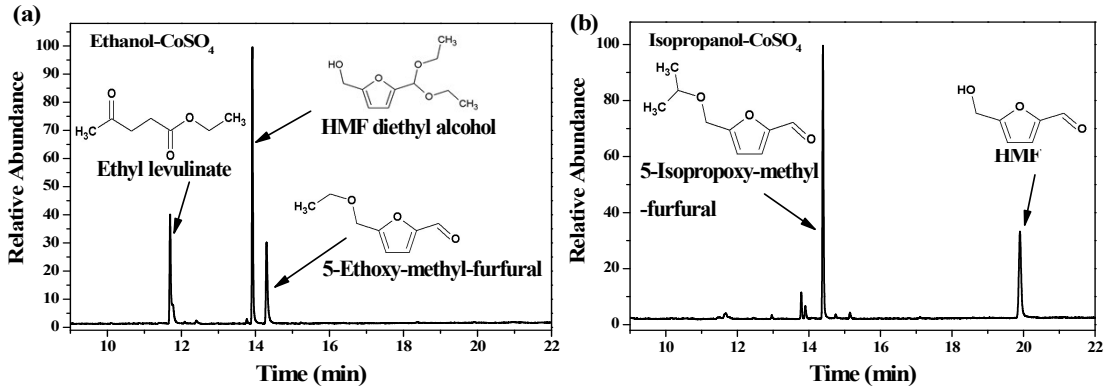

Figure S1 The chromatogram of the products from the conversion of HMF with $CoSO_4 \cdot H_2O$ in (a) ethanol and (b) isopropanol. The products were identified with a standard library (NIST MS Search 2014).

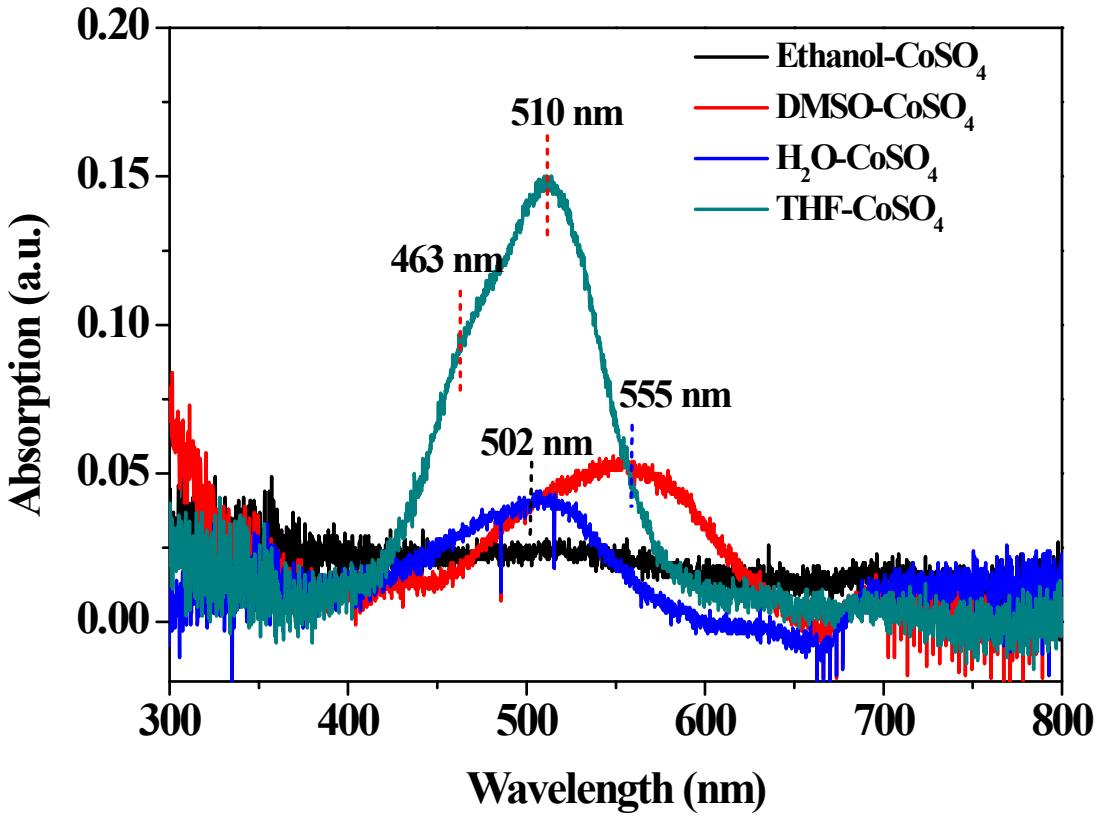

Figure S2 UV-Vis spectra of H_2O, DMSO and THF dissolved $CoSO_4 \cdot 7H_2O$. Test condition: $CoSO_4 \cdot 7H_2O$ was dissolved in water or DMSO to form a homogeneous solution with a concentration of 20 ppm, respectively. $CoSO_4 \cdot 7H_2O$ and 3-5 drops of water seriously weighed was well mixed to make sure the appearance of a uniform solution which was diluted to 20 ppm. The prepared solution was tested by UV-Vis spectrophotometer at once.

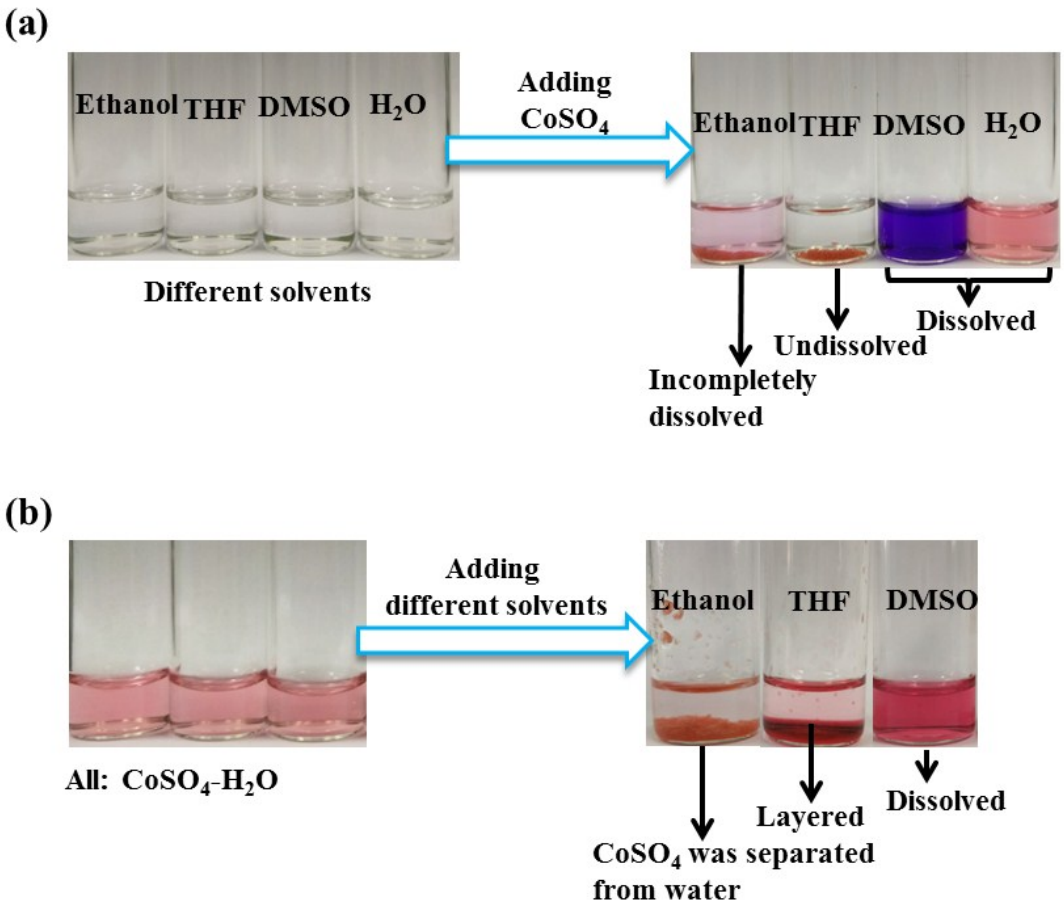

Figure S3 The solubility test about $CoSO_4 \cdot 7H_2O$ in ethanol, DMSO, H_2O or THF. The process of test: (a) $CoSO_4$ was added into ethanol, DMSO, H_2O or THF; (b) 3 set of $CoSO_4$ aqueous solution with the same concentration of 0.015 g/mL was added 0.5 mL of ethanol, DMSO and THF, respectively. The change of solution was observed with eyes.