Supporting Information

Production of 2,5-hexanedione and 3-methyl-2-cyclopenten-1-one from 5-hydroxymethylfurfural

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Calculation of the hydrogen pressure

The hydrogen pressure was generated by *in-situ* hydrogen by oxidation of metal Zn in water. For instance, 5 mmol Zn can be generated 5 mmol H_2,so the hydrogen pressure at room temperature can be calculated by the state of equation of ideal gas (PV=nRT).

$$P = \frac{nRT}{V} = \frac{5\ (mmol) \times 10^{-3} \times 8.31\ (Pa*m^3*mol^{-1}*K^{-1}) \times (273+25)\ (K)}{(30-7.5)\ mL \times 10^{-6}} \times 10^{-6} = 0.55\ (MPa)$$

Table SI-1. Effect of active metals in HMF conversion.[a]

Entry	Metals	Conv (%)	Yield (%)				
			HDN	3-MCO	MF	MFM	MCPE
1	Zn	100	21.3	19.7	4.3	0	1.0
2	Mn	100	0	0	0	0	0
3	Fe	100	0	0	0	0	0
4	Al	100	0	0	0	0	0
5	Mg	100	0	0	0	0	0

[a]Reaction condition: 0.20 mmol HMF, 25 mmol metal, 7.5 mL H_2O, 250 ^oC, 60 min.

Table SI-2. Conversion of HMF in presence of catalysts.[a]

Entry	Catalyst	Conv. (%)	Yield (%)				
			HDN	3-MCO	MF	MFM	MCPE
1	Ni/γ-Al_2O_3 (6 mg)	100	20.5	12.1	2.1	0	0
2	Porous Ni (50 mg)	100	2.7	0	0	0	0
3	Ni powder (293 mg)	100	12.2	5.0	1.2	0	6.5
4	Pd/C (100 mg)	100	0	0	0	0	0
5	Ag/SiO_2 (20 mg)	100	24.6	5.9	1.1	0	0
6	Cu (317 mg)	100	8.0	10.0	0	0	8.0
7	Cu_2O (715 mg)	100	2.5	2.5	1.1	0	1.3
8	CuO (398 mg)	100	0	0	0	0	0

9	ZrO_2 (616 mg)	100	0	0	0	0	0
10	HCOOH (0.35 M) [b]	100	23.6	3.2	0	0	0
11	NaOH (0.01 M) [b]	100	1.0	11.1	0	0	1.2

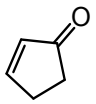
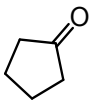
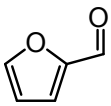
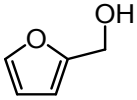
[a]Reaction condition: 0.20 mmol HMF,25 mmol Zn, 7.5 mL H_2O, 250 °C, 60 min.[b] 140 min.

Table SI-3. Effect of gaseous H_2 and role of formed ZnO in HMF conversion.[a, b]

Entry	ZnO	Conv. (%)	Yield (%)				
			HDN	3-MCO	MF	MFM	MCPE
1	ZnO[c]	58.0	0	0	1.3	0	0
2	ZnO[d]	59.1	0	0	2.7	0	0
3	None	67.8	0	0	0	0	0

[a] Reaction condition: 0.20 mmol HMF,25 mmol Zn, 7.5 mL H_2O, 250 °C, 60 min. [b] The amount of HMF, ZnO and H_2O were scaled down according to the ratio between the volume of SUS316 tube and Teflon lined, 3 MPa H_2. [c] ZnO obtained. [d] commercial ZnO.

Table SI-4. Conversion of furfural and furfuryl alcohol.[a]

Entry	Feedstock	Conv (%)	Yield (%)	
				
			cyclopentenone	cyclopentanone
1	 furfural	100	23.1	3.1
2	 furfuryl alcohol	100	66.1	9.4

[a] Reaction condition: 0.24 mmol Furfural /0.23 mmol furfuryl alcohol, 25 mmol Zn, 7.5 mL H_2O, 250 °C, 140 min.

Table SI-5. The theoretical value of p*Kw* (0.1 MPa or saturated pressure)

Temperature (°C)	25	100	150	200	250	300
p*Kw*	13.99	12.25	11.64	11.31	11.20	11.34

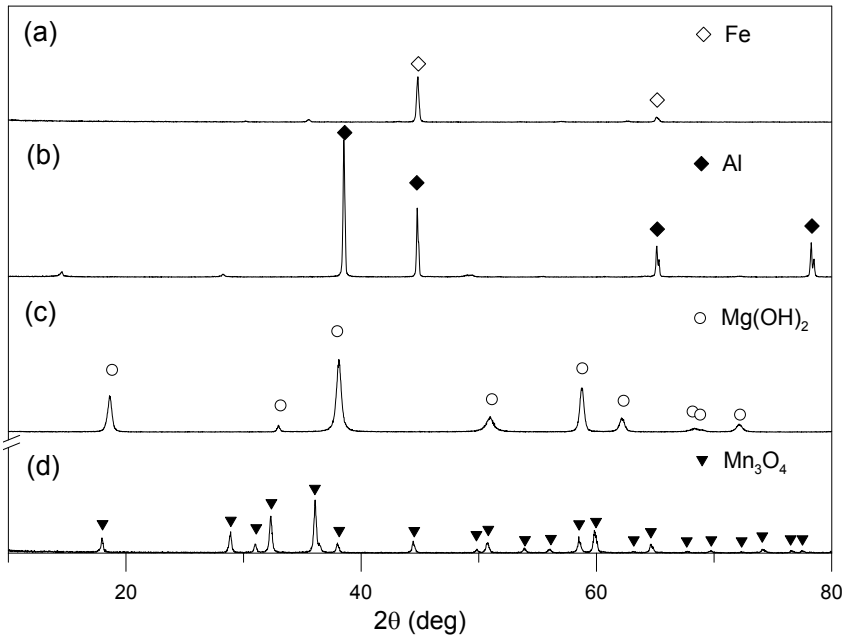


Figure SI-1. XRD patterns for the oxidation of Fe, Al, Mn, Mg in water (25 mmol metal, 7.5 mL H_2O, 250 ^oC, 140 min).

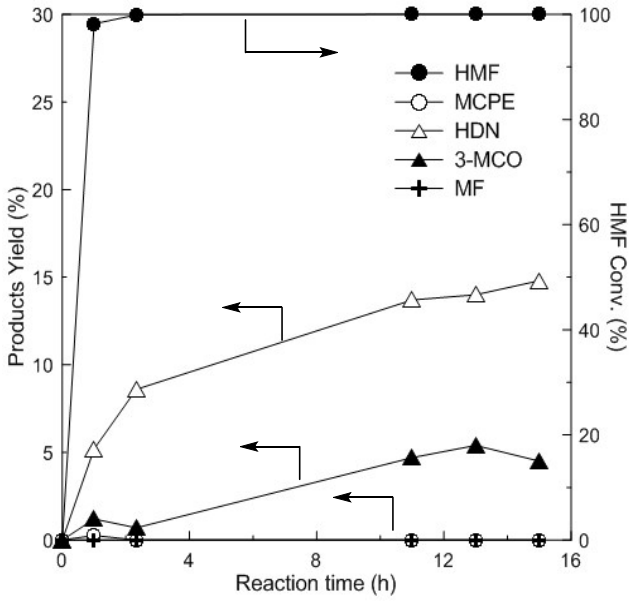
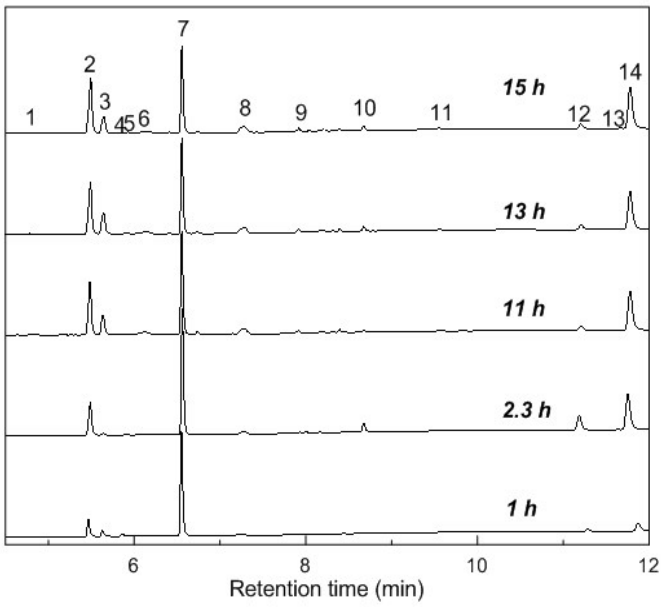


Figure SI-2. Time profile for the conversion of HMF (0.20 mmol HMF,25 mmol Zn, 7.5 mL H_2O, 100 ^oC).



Peak	Name
1.	2-MCO
2.	HDN
3.	3-MCO
4.	MF
5.	Unknown
6.	Unknown
7.	MFM
8-14.	Unknown

Figure SI-3.Gas chromatogram for HMF conversion at different time (0.20 mmol HMF,25 mmol Zn, 7.5 mL H_2O, 100 ^oC).

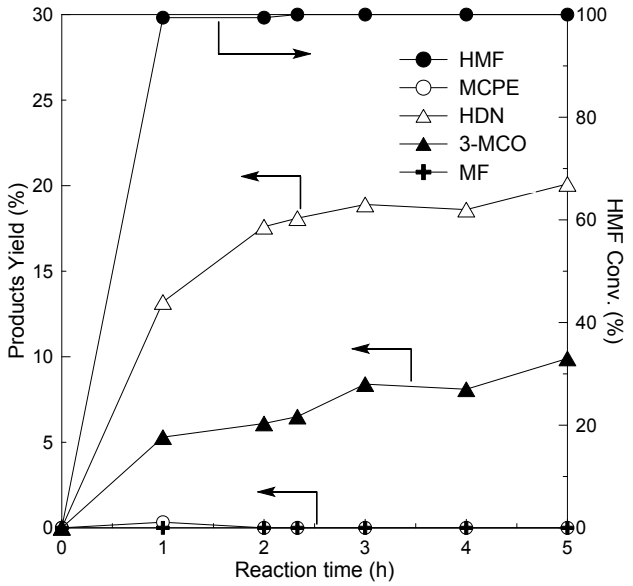
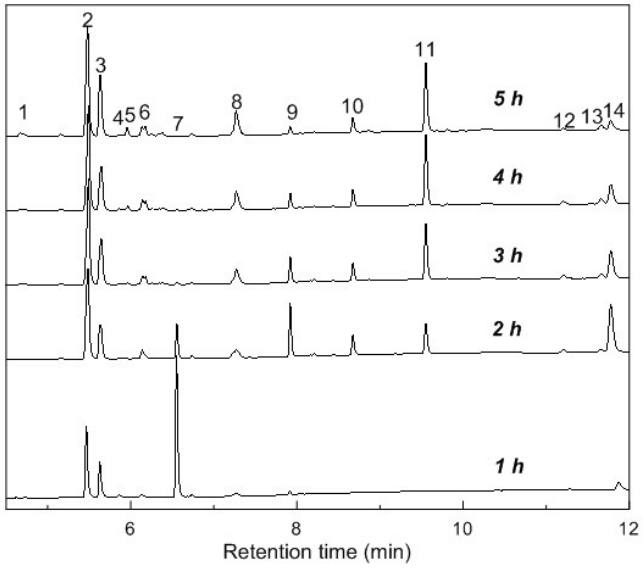


Figure SI-4. Time profile for the conversion of HMF (0.20 mmol HMF,25 mmol Zn, 7.5 mL H_2O, 150 ^oC).



Peak	Name
1.	2-MCO
2.	HDN
3.	3-MCO
4.	MF
5.	Unknown
6.	Unknown
7.	MFM
8-14.	Unknown

Figure SI-5. Gas chromatogram for HMFconversion at different time (0.20 mmol HMF,25 mmol Zn, 7.5 mL H_2O, 150 ^oC).

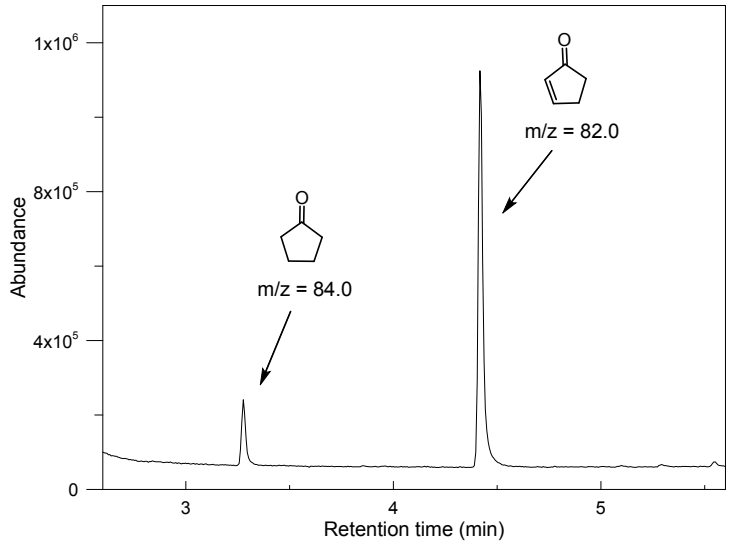
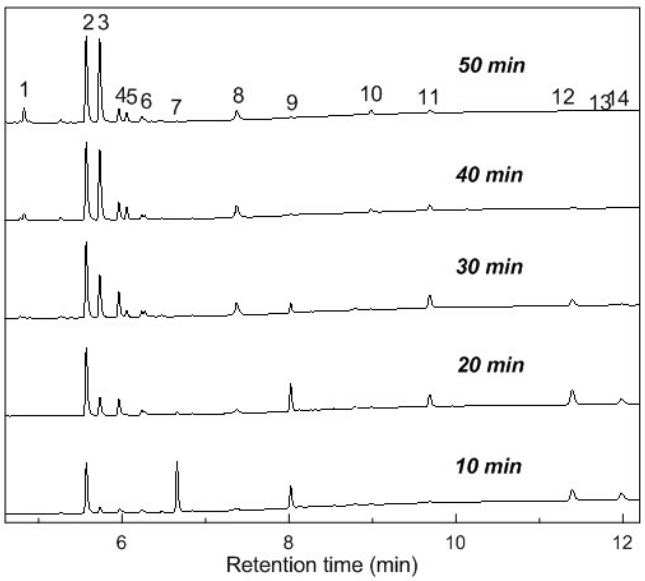


Figure SI-6. GC-MS chromatogram of main products after the furfuryl alcohol conversion. (0.23 mmol Furfuryl alcohol, 25 mmol Zn, 7.5 mL H_2O, 250 ^oC, 140 min.



Peak	Name
1.	2-MCO
2.	HDN
3.	3-MCO
4.	MF
5.	Unknown
6.	Unknown
7.	MFM
8-14.	Unknown

Figure SI-7. Gas chromatogramfor the change of HMF conversion at different time (0.20 mmol HMF,25 mmol Zn,7.5 mL H_2O, 250 ^oC).