Electronic Supplementary Information

Selectivity controlled synthesis of furan-ring nitrogenous compounds from 5-hydroxymethylfurfural, ammonia and hydrogen peroxide

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Contents

1. The quantitative formulae for the HMF ammoxidation

The formula for calculating HMF conversion, HMFO conversion, as well as HMFO, HMFC and HMFA yields are provided as follows:

$$HMF\ conversion = 1 - \frac{moles\ of\ HMF\ remained}{moles\ of\ HMF\ in\ the\ feed} \times 100\% \tag{1}$$

$$HMFO\ yield = \frac{moles\ of\ HMFO\ produced}{moles\ of\ HMF\ in\ the\ feed} \times 100\% \tag{2}$$

$$HMFO\ conversion = 1 - \frac{moles\ of\ HMFO\ remained}{moles\ of\ HMFO\ in\ the\ feed} \times 100\% \tag{3}$$

$$HMFC\ yield = \frac{moles\ of\ HMFC\ produced}{moles\ of\ HMFO\ in\ the\ feed} \times 100\% \tag{4}$$

$$HMFA\ yield = \frac{moles\ of\ HMFA\ produced}{moles\ of\ HMFO\ in\ the\ feed} \times 100\% \tag{5}$$

2. GC-MS spectra of products

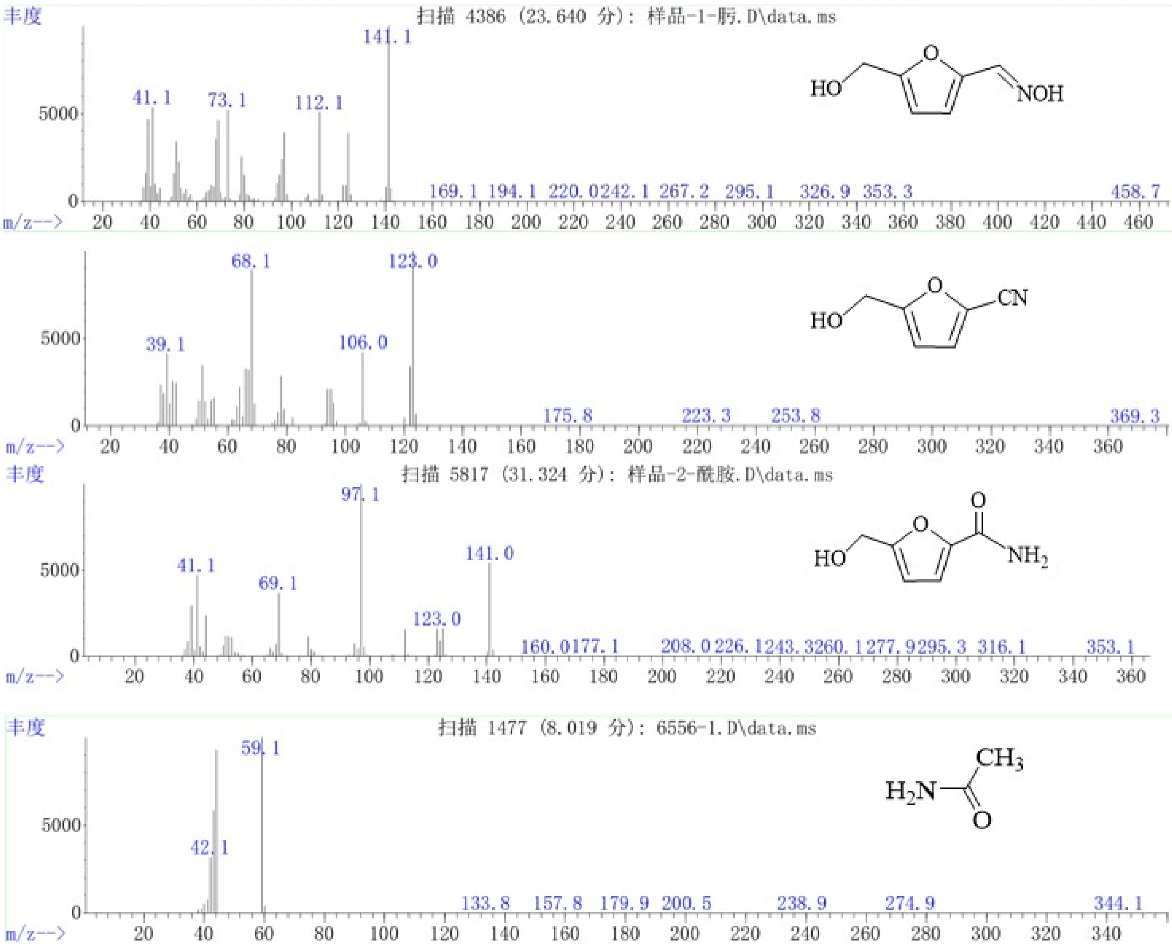

Fig. S1 GC-MS spectra of products.

3. GC spectra of products

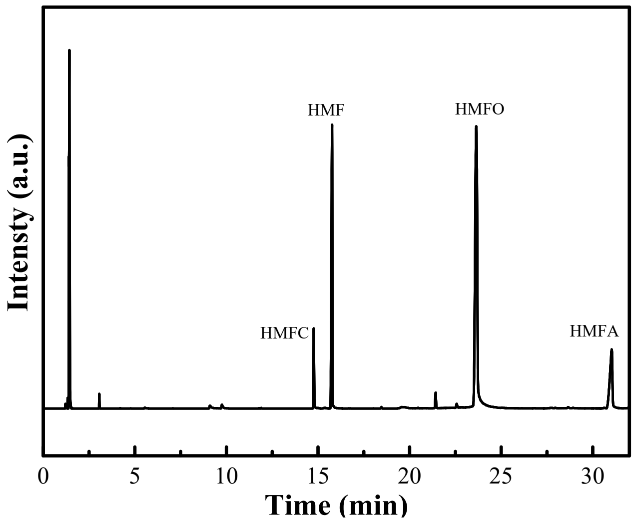

Fig. S2 GC spectra of products.

4. FT-IR spectra of products

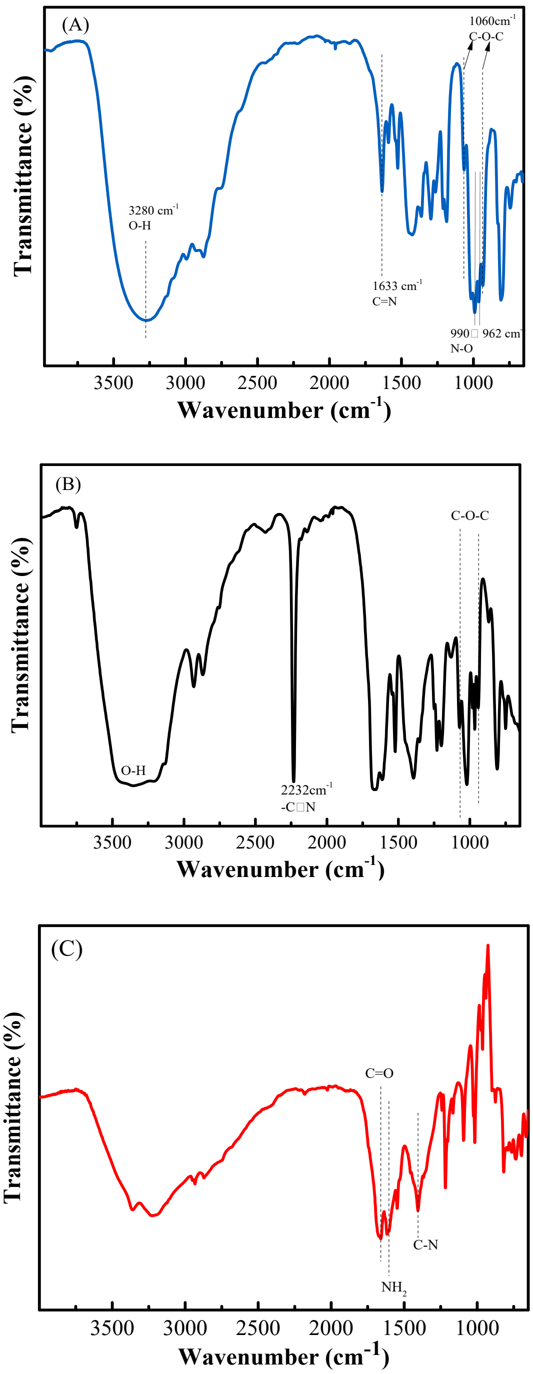

Fig. S3 FT-IR spectra of products: (A)HMFO; (B)HMFC; (C)HMFA.

5. NMR spectra of products

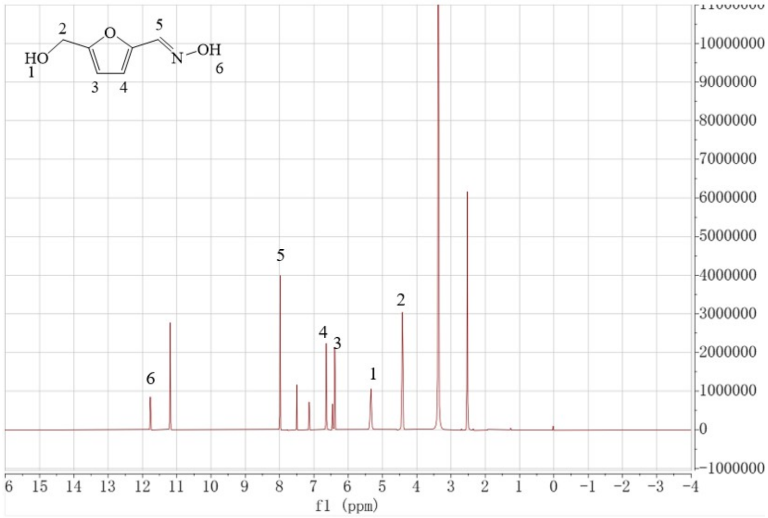

Fig. S4 ^{1}H NMR of HMFO.

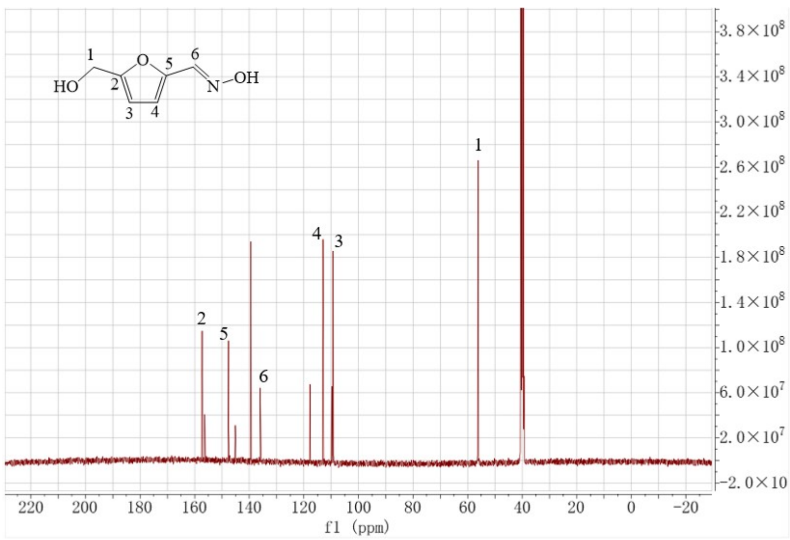

Fig. S5 ^{13}C NMR of HMFO.

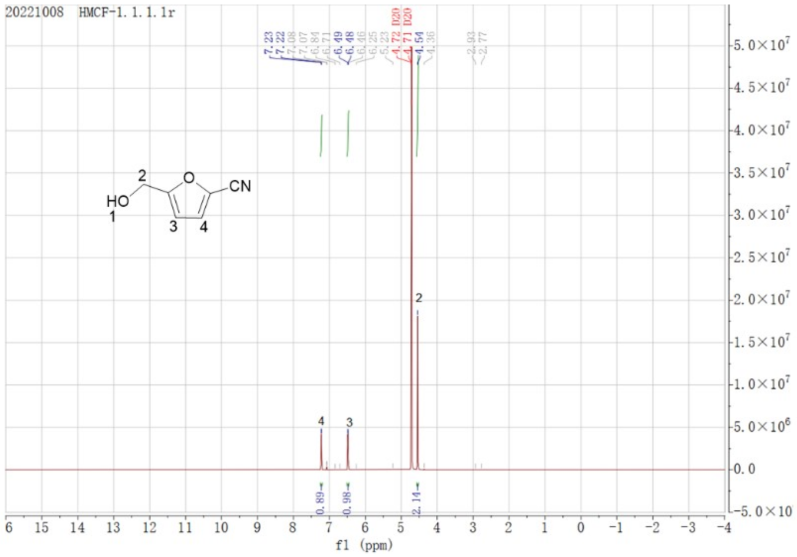

Fig. S6 ^{1}H NMR of HMFC.

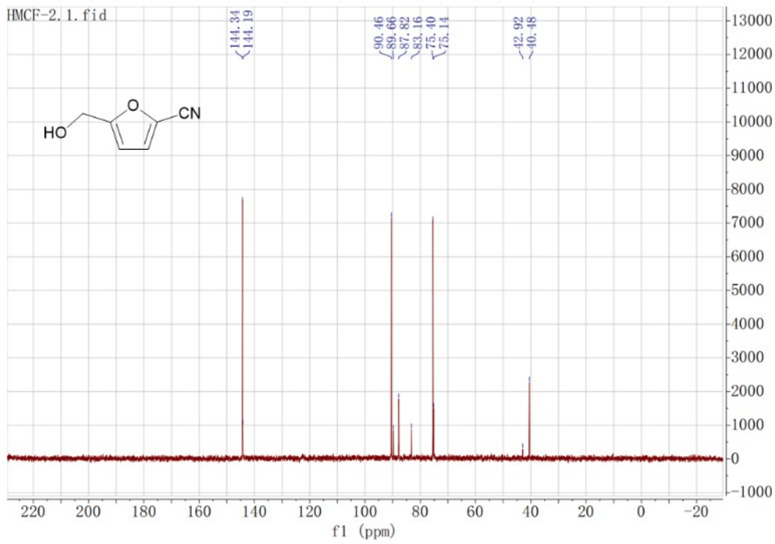

Fig. S7 ^{13}C NMR of HMFC.

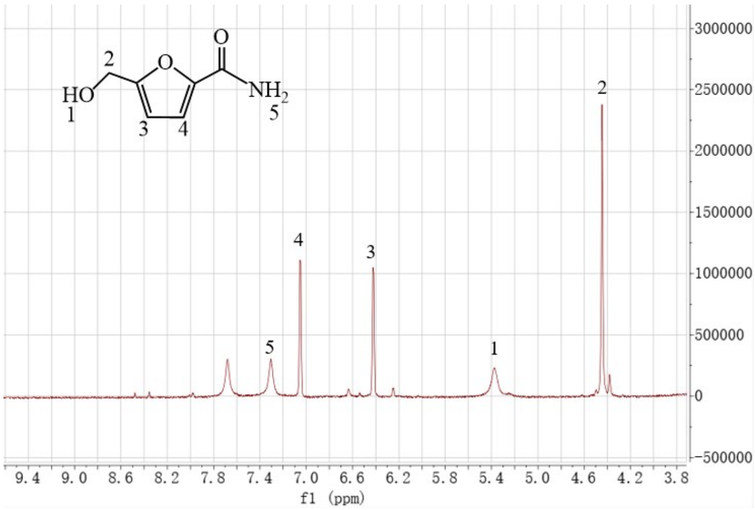

Fig. S8 [1]H NMR of HMFA.

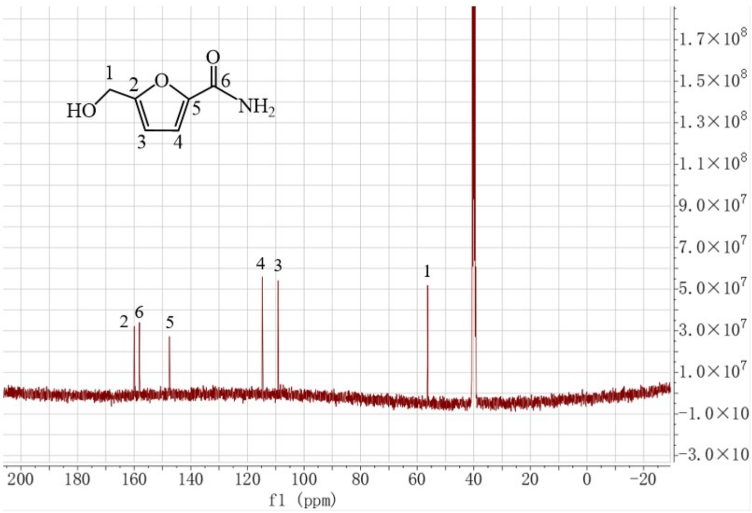

Fig. S9 [13]C NMR of HMFA.

6. XRD patterns of catalysts

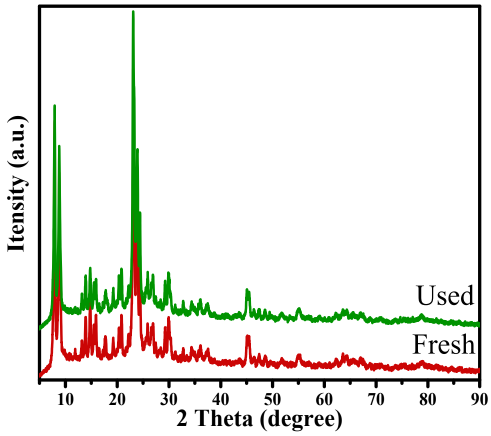

Fig. S10 XRD patterns of the fresh and used $Cu(OAc)_2$/TS-1.

7. FT-TR spectra of the fresh and used $Cu(OAc)_2$/TS-1

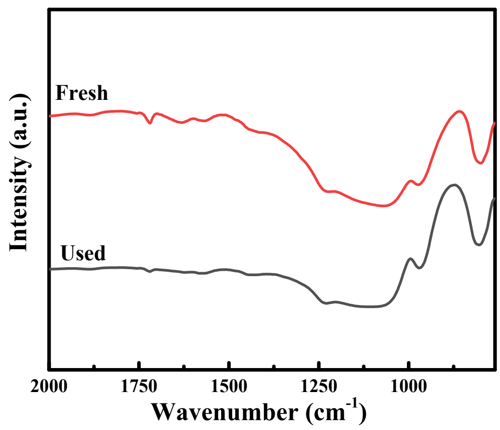

Fig. S11 FT-TR spectra of the fresh and used $Cu(OAc)_2$/TS-1.

8. Pore size distribution of $Cu(OAc)_2$/TS-1 and TS-1

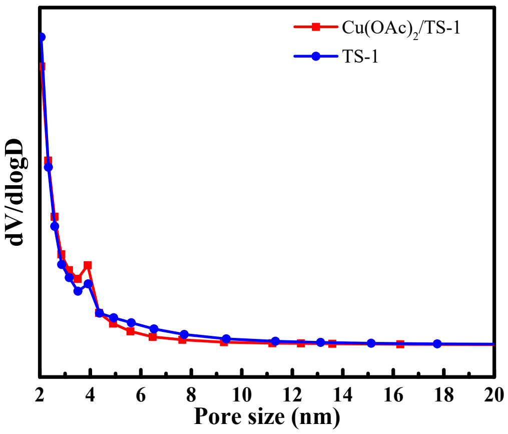

Fig. S12 Pore size distribution of $Cu(OAc)_2$/TS-1 and TS-1.

9. Catalytic performance for the synthesis of HMFA from HMFO over 10%$Cu(OAc)_2$/TS-1

Table S1 Catalytic performance for the synthesis of HMFA from HMFO over 10%$Cu(OAc)_2$/TS-1

Entry	Conditions	X_{HMFO} / %	Y_{HMFA} / %	Y_{HMFC} / %
1	Isopropanol (10 mL)，2 h	12.5	0	12.5
2	Isopropanol (10 mL)+ acetonitrile (0.1 mmol)，1 h	84.9	62.6	21.7

Reaction conditions：HMFO 1 mmol, 10%$Cu(OAc)_2$/TS-1 0.25 mmol, 95 ℃.

10. The physicochemical property of $Cu(OAc)_2$/TS-1 and TS-1

Table S2 The physicochemical property of $Cu(OAc)_2$/TS-1 and TS-1.

Sample	S_{BET} (m^2g^{-1})	V pore (cm^3g^{-1})	D pore (nm)
TS-1	475.1113	0.173274	6.8356
$Cu(OAc)_2$/TS-1	359.4973	0.149491	6.2599

11. ICP results and catalytic activity of 10%$Cu(OAc)_2$/TS-1

Table S3 ICP results and catalytic activity of 10%$Cu(OAc)_2$/TS-1.

Catalyst	ICP Cu content (%)	$Cu(OAc)_2$ content (%)	X_{HMFO} / %	Y_{HMFC} / %
Fresh	3.11	9.77	100	92.8

12. Reaction performance comparison of different methods for the synthesis of HMFC

Table S4 Reaction performance comparison of different methods for the synthesis of HMFC.

No.	Catalyst	Conditions	Conversion (%)	HMFC Yield (%)	Ref.
1	β-MnO_2	NH_3 aq. (10 equiv), 0.5 MPa O_2, DMF, 100 °C, 1 h	76	25	[11]
2	Hac-modified MnO_x	120 μL NH_3 aq., 0.3 MPa O_2, CH_3CN, 60 °C, 3 h	95	87.4	[12]
3	Fe-OMS-2	0.7 mmol $(NH_4)_2C_2O_4$, 0.4 MPa O_2, Benzonitrile, 105 °C, 12 h	100	98	[13]
4	$ZnCl_2$	NH_2OH (1.5 equiv), Methanol, 55 °C, 30 min	100	65.6	[18]
5	$ZnCl_2$	$ZnCl_2 \cdot 2NH_2OH$ (0.75 equiv), Methanol, 100 °C, 20 min	100	100	[18]
6	$Cu(OAc)_2$/TS-1	CH_3CN, 60 °C, 3 h	100	92.8	This work