Supporting Information

Acidic sites-assisted catalytic oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid with Ru-Mn supported on modified ZSM-5 under aqueous conditions

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Table S1. Catalytic oxidation of HMF to FDCA with previously reported catalytic systems.

Entry	Catalyst	Solvent/Base	Temp. (°C) / time (h) / oxidant	Product yield (%)	HMF conv. (%)	Yield (%)	Ref.
1	MnO_X-CeO_2	Water/$KHCO_3$ base	110/12/O_2	FDCA	98	91.0	10
2	$MnFe_2O_4$	Acetonitrile/ no base	100/50/TBHP	FDCA	>99	85.0	11
3	Cu/MnO_2	tert-butyl alcohol/no base	80/12/TBHP	FDCA	99.4	95.7	12
4	Cu-MnO_2 @PDVTA-3	tertbutyl alcohol (TBA)/no base	80/12/TBHP	FDCA	>99	96.8	13
5	$CuMn_2O_4$	Acetonitrile/no base	80/12/TBHP	FDCA	100	96.4	14
6	Ru(4%)/Mn Co_2O_4	Water/no base	120/10/Air	FDCA	100	99.1	15
7	Ru/Mn_6Ce_1 O_y	Water/no base	150/15/O_2	FDCA	100	99.0	16
8	3wt% Ru-NaY	Water solvent/ No base	120/ 8/ O_2	FDCA/FFCA	100	94/6	18
9	Pt-Ca-Hie-ZSM5	Water/ No base	110/ 24/ O_2	FDCA	100	80.1	19
10	2Au/Mg-Beta-Ps	Water/ Na_2CO_3	130/ 4/ O_2	FDCA	95	93.3	20
11	1%Au/MgSi -ZSM-12	Water/No base	90/24/O_2 ballon	HMFCA/FDCA	>99	9.2/87	21
12	Au/HY	Water/ NaOH	60/ 6/ O_2	FDCA	>99	>99	22
13	Au-clicked@ZSM-5	Water/ NaOH	60/ 6/ O_2	FDCA	100	99	23
14	Au/Sn-Beta	Water/Na_2CO_3	140/1/O_2	FDCA	100	98	24
15	$RuZS_{90}$	Water/ no base	140/ 5/ O_2	FFCA/FDCA	99.0	10.8/66.9	25
16	Nb-ZSM 5(25)	Acetonitrile/ No base	140/ 24/ t-BuOOH-	FDCA	96.7	59.2	26
17	Cr-Mn/USY	DMSO-Water/ $KHCO_3$ base	180/ 0.5	FDCA	100	98	27
18	RuMn/ZS	Water/ no base	140/ 7/ Air	FFCA/FDCA	99.0	5.2/76.7	This work

Table S2. Catalytic efficiency of Ru and Mn catalysts supported on modified zeolite for the HMF oxidation.

Entry	Catalyst	Con (%)	DFF yield (%)	FFCA yield (%)	FDCA yield (%)
1	$Ru_{1.5}$ $Mn_{0.83}ZS$	99.4	3.0	31.9	41.8
2	$Ru_{1.5}$ $Mn_{1.66}ZS$	99.9	0.8	15.0	63.0
3	$Ru_{1.5}$ $Mn_{2.49}ZS$	99.8	0.8	18.8	59.4

Reaction conditions: 0.5 mmol HMF, 50 mg Catalyst, 20 ml Water, 140 °C temperature, 3h time, 30 bar O_2.

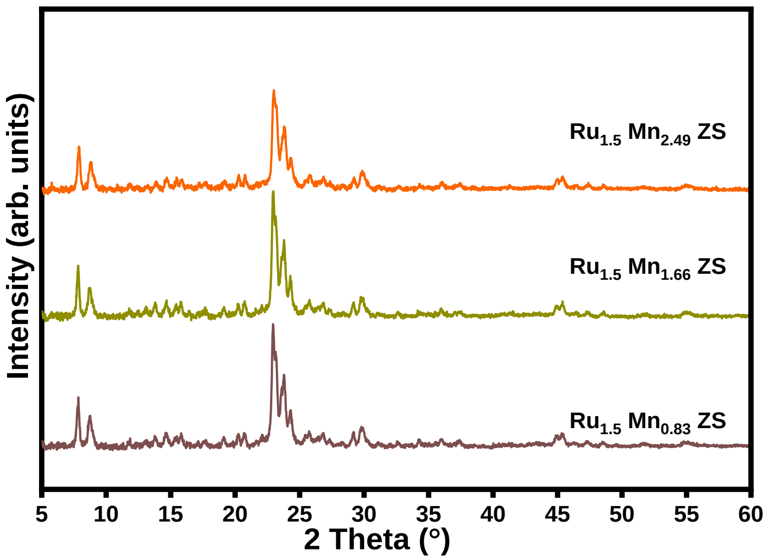


Figure S1. X-ray diffractograms of the modified HZ catalysts with varied Mn wt%.

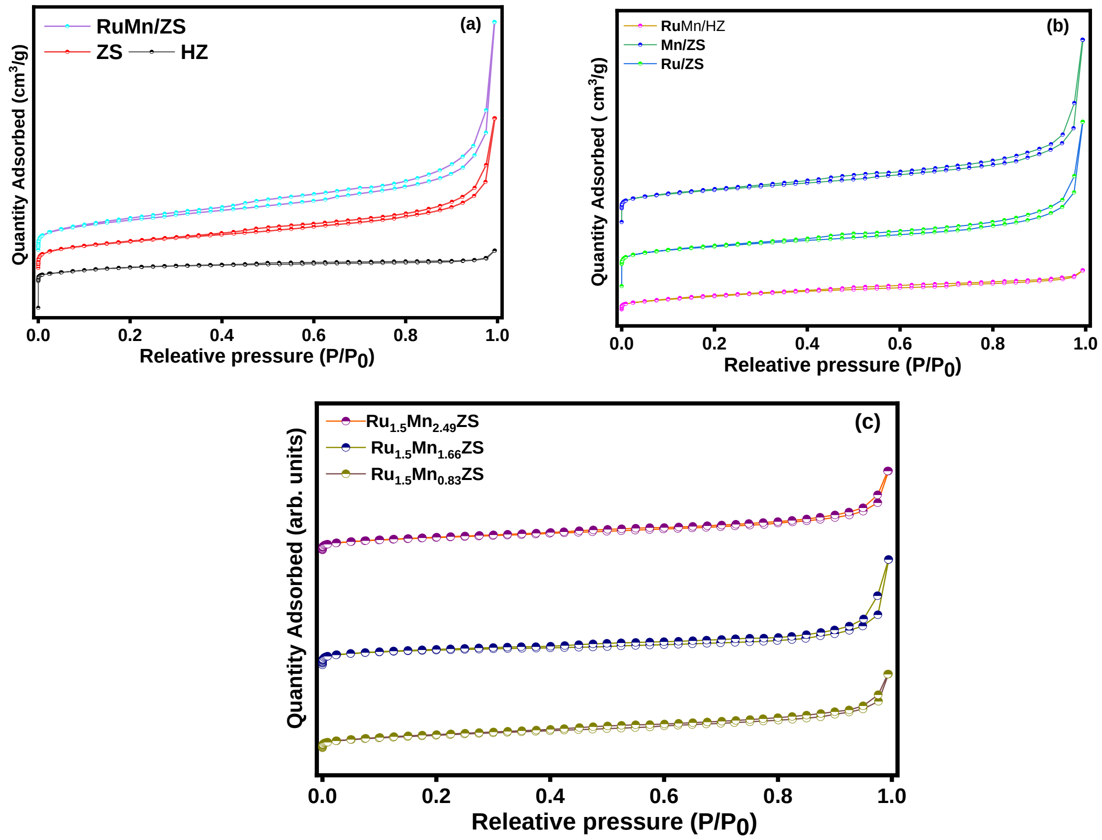


Figure S2. N_2-sorption isotherms of a) parent and b) modified HZ catalysts, and c) modified HZ catalysts with varied Mn wt%.

Table S3. Physicochemical properties of the parent and modified HZ zeolites.

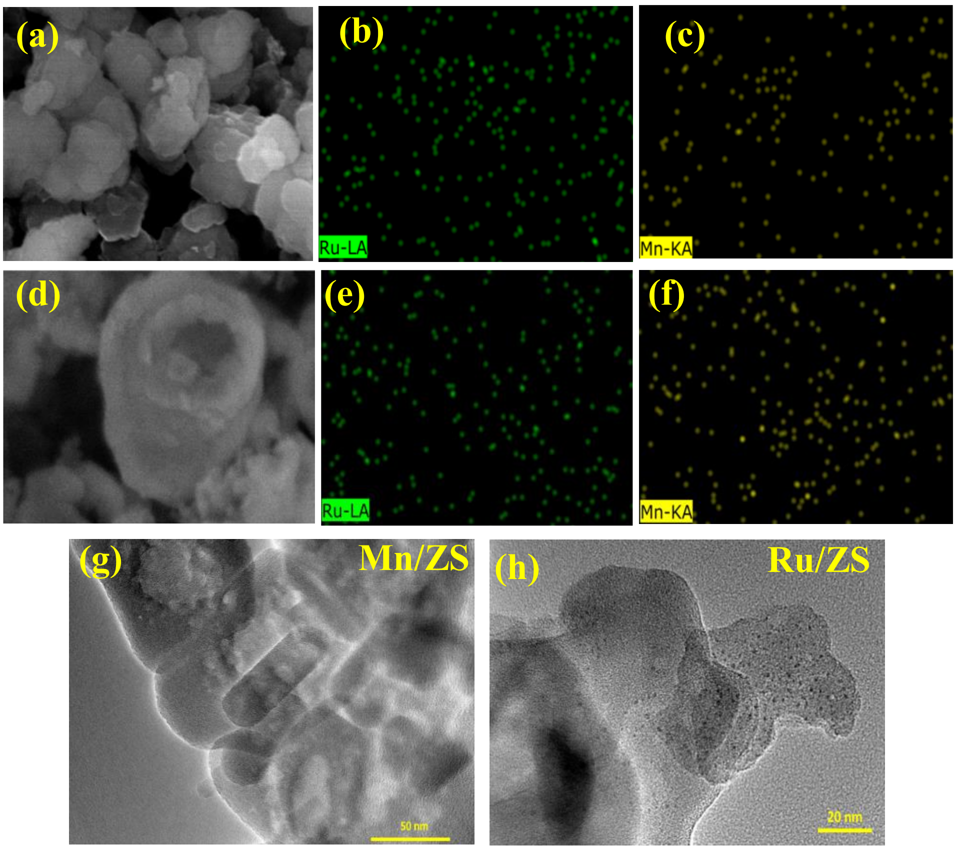
Entry	Catalyst	$^aS_{BET}$ (m^2/g)	^{b}Micropore area (m^2/g)	^{c}Mesopore/macropore surface area (m^2/g)	$^bV_{micro}$ (cm^3/g)	$^cV_{meso/macro}$ (cm^3/g)
1	Ru/ZS	433	225	142	0.106	0.651
2	Mn/ZS	327	80	169	0.051	0.784
3	$Ru_{1.5}Mn_{0.83}ZS$	385	141	154	0.076	0.509
4	$Ru_{1.5}Mn_{1.66}ZS$	408	124	125	0.095	0.735
5	$Ru_{1.5}Mn_{2.49}ZS$	413	195	146	0.085	0.553

^{a,b,c}determined by the BET, t-plot and BJH method, respectively.

Table S4. Acidic and basic properties of the parent and modified HZ zeolites.

Entry	Catalyst	Acidic sites (μmol/g)[a]			Basic sites (μmol/g)[b]			Total Acidic/ Total Basic sites ratio
		Type I	Type II	Total	Type I	Type II	Total	
1	Ru/ZS	785	456	1241	234	0	234	5.3
2	Mn/ZS	1027	239	1266	241	43	284	4.5
3	$Ru_{1.5}$ $Mn_{0.83}$ZS	838	399	1237	237	0	237	5.2
4	$Ru_{1.5}$ $Mn_{1.66}$ZS	924	345	1269	324	0	324	3.9
5	$Ru_{1.5}$ $Mn_{2.49}$ZS	928	389	1317	391	0	391	3.4

[a,b]determined by NH_3- and CO_2-TPD, respectively.



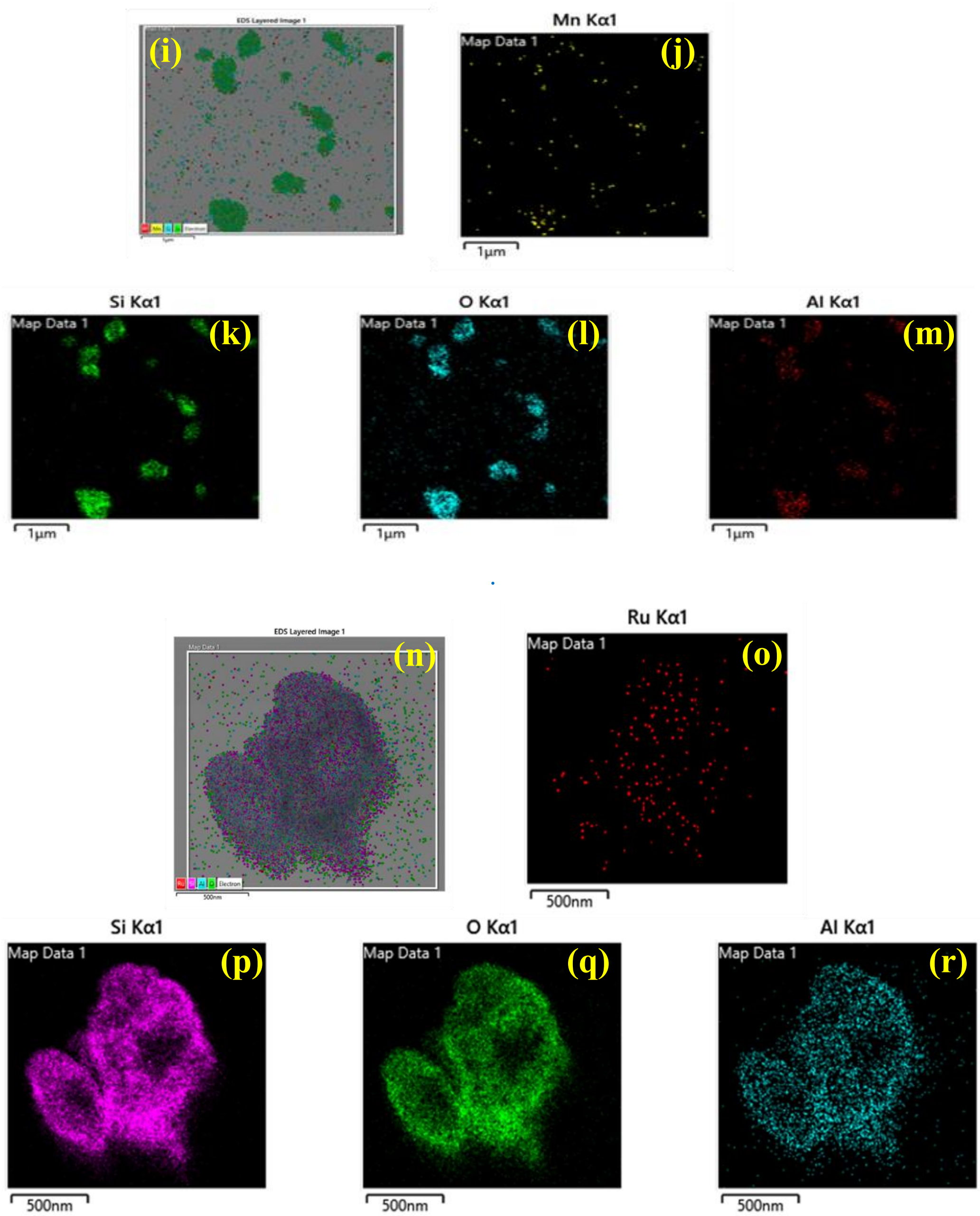


Figure S3. FESEM-EDX mapping of RuMn/HZ (a-c), RuMn/ZS (d-f), HRTEM image of Mn/ZS and Ru/ZS catalyst (g and h), and HRTEM-EDX mapping of Mn/ZS (i-m) and Ru/ZS (n-r) Ru/ZS catalyst.

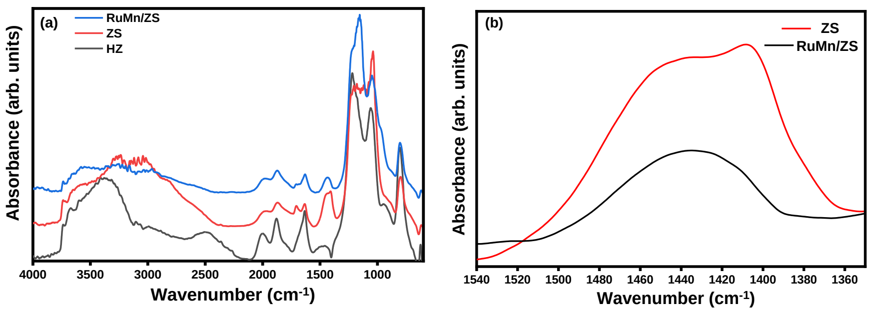


Figure S4. FTIR spectra of the a) parent and modified HZ catalysts and b) zoomed-in spectra of Figure S4a in the wavenumber range of 1350 to 1540 cm^{-1}.

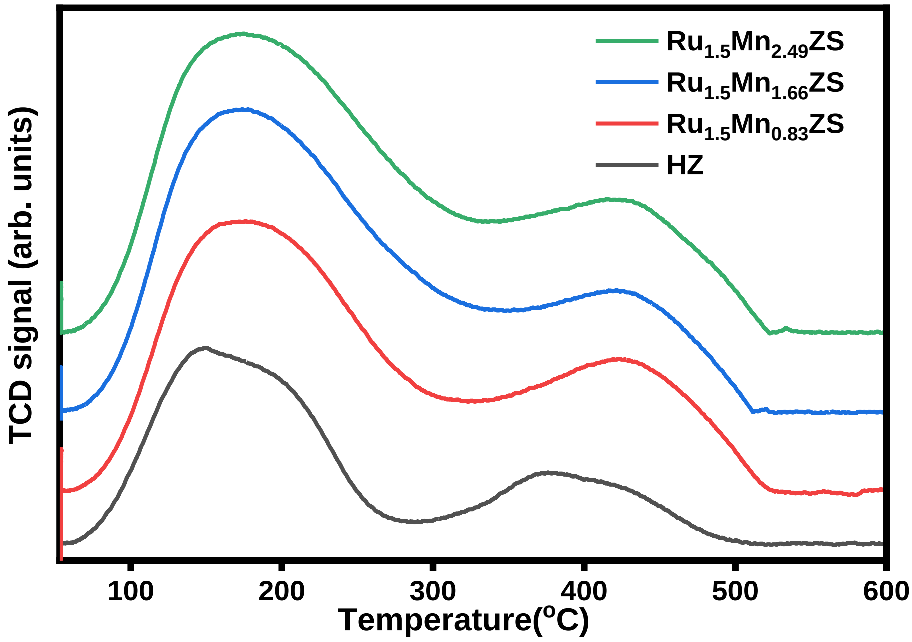


Figure S5. NH_3-TPD of profiles of parent and modified HZ catalysts with varied Mn wt%.

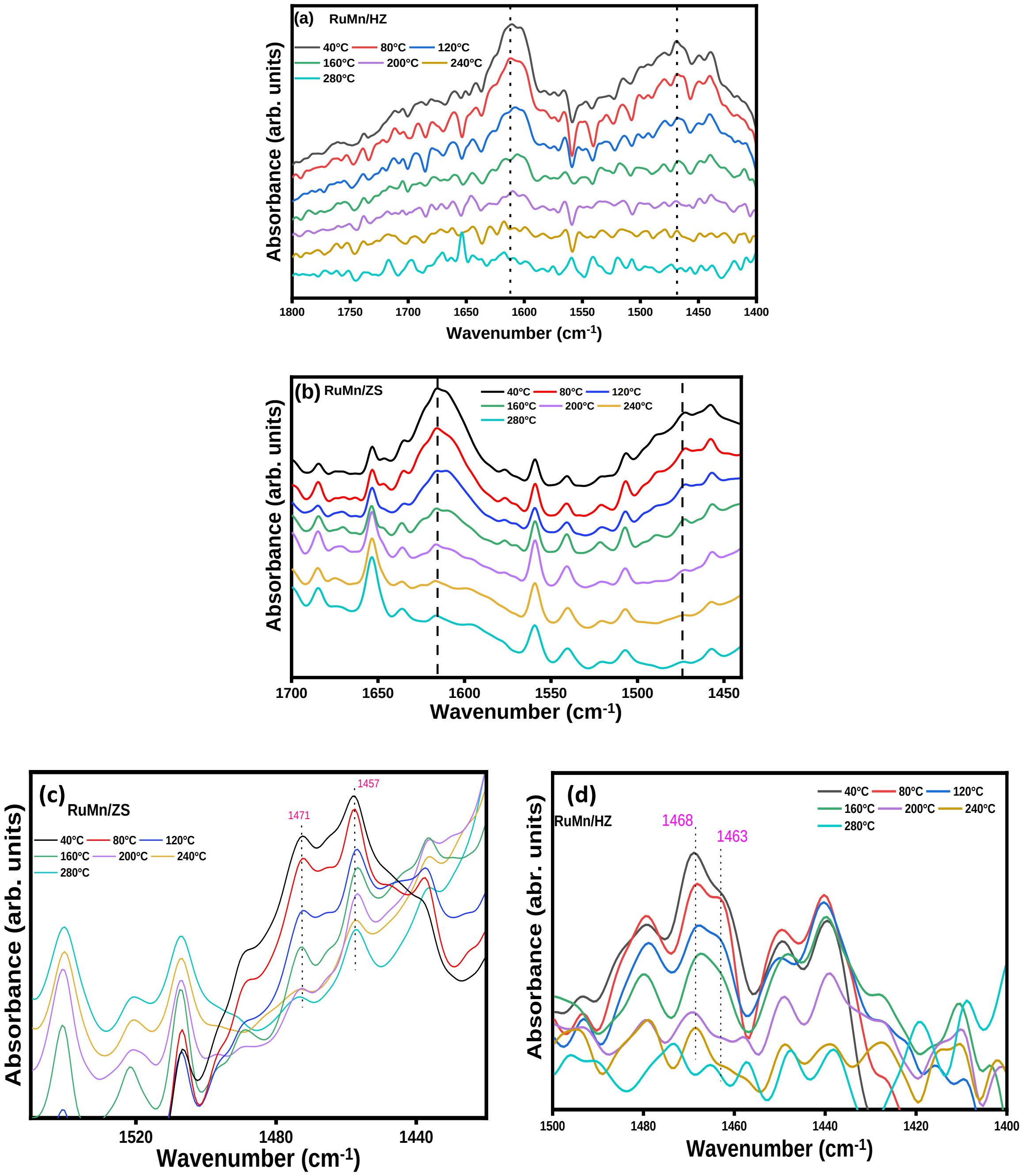


Figure S6. NH_3-DRIFT spectra of (a and b) RuMn/HZ and RuMn/ZS catalysts, (c and d) Brønsted acidic sites of RuMn/ZS and RuMn/HZ at various desorption temperatures.

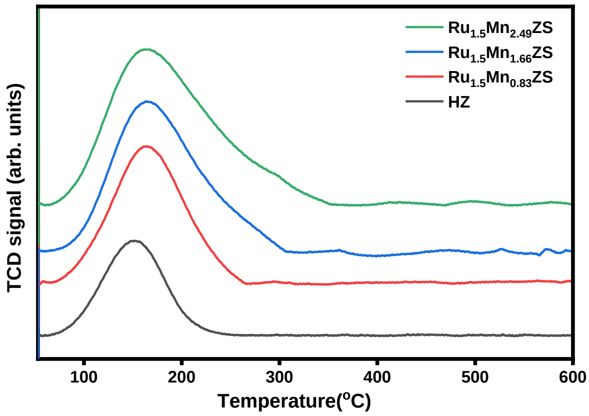
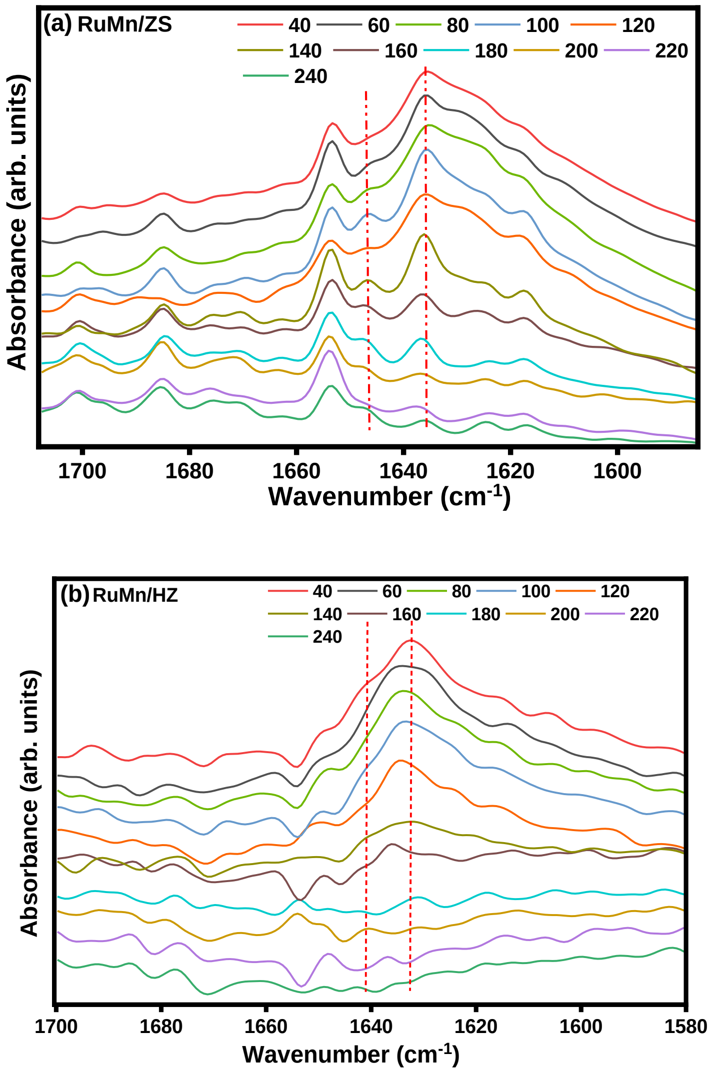


Figure S7. CO_2-TPD profile of parent and modified HZ catalysts with varied Mn wt%.



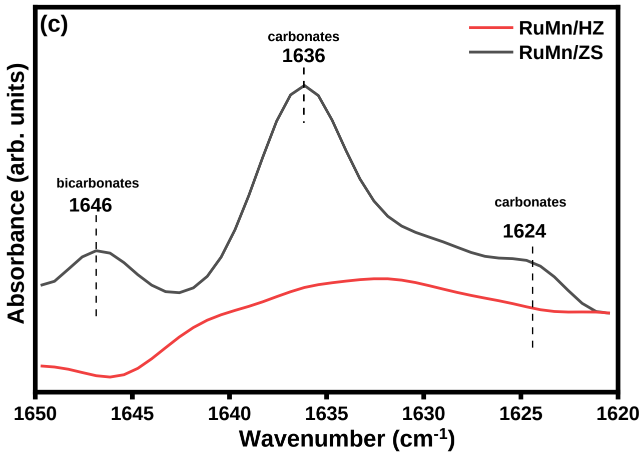


Figure S8. CO_2-DRIFT spectra of a) RuMn/ZS, b) RuMn/HZ catalysts at various temperatures, and c) at 140 °C.

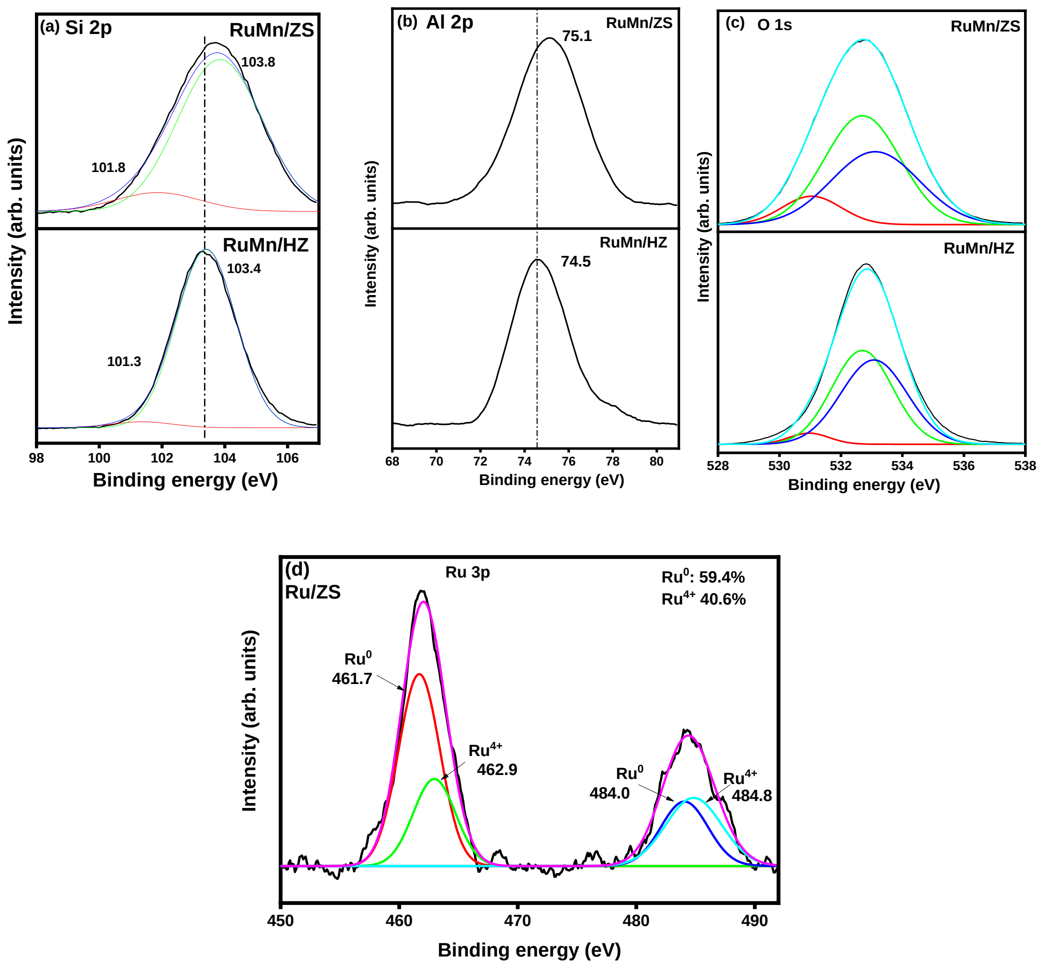


Figure S9. XPS spectra of parent and modified HZ catalysts a) Si 2p, b) Ap 2p and c) O1s. and d) Ru 3p spectra of Ru/ZS catalyst.

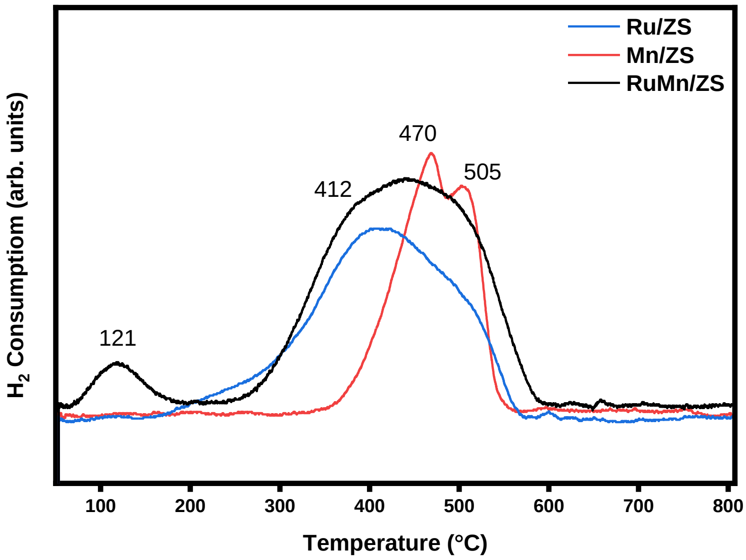


Figure S10. H_2-TPR profiles of RuMn/ZS, Ru/ZS, and Mn/ZS catalysts.

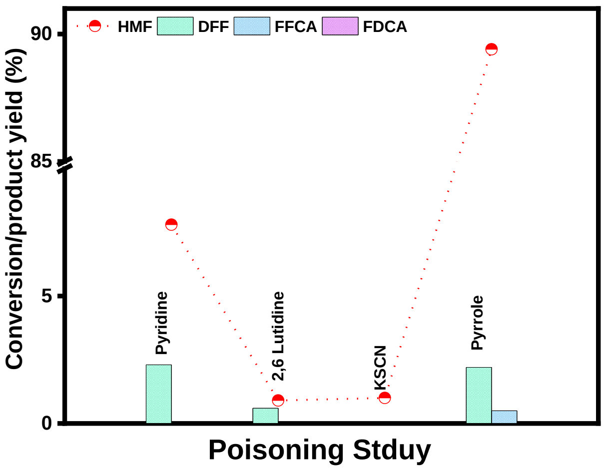


Figure S11. Poisoning study with additives without a catalyst (Reaction conditions: 0.25 mmol HMF, 20 ml water, 140 °C, 0.5 h, 30 bar O_2, 0.8 mmol additive).

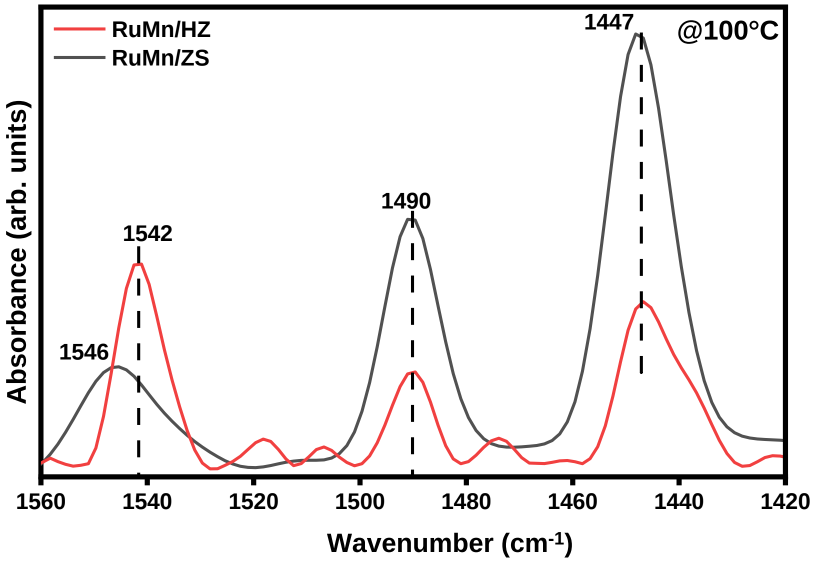


Figure S12. Pyridine-DRIFT spectra of RuMn on parent HZ and modified ZS at 100 °C.

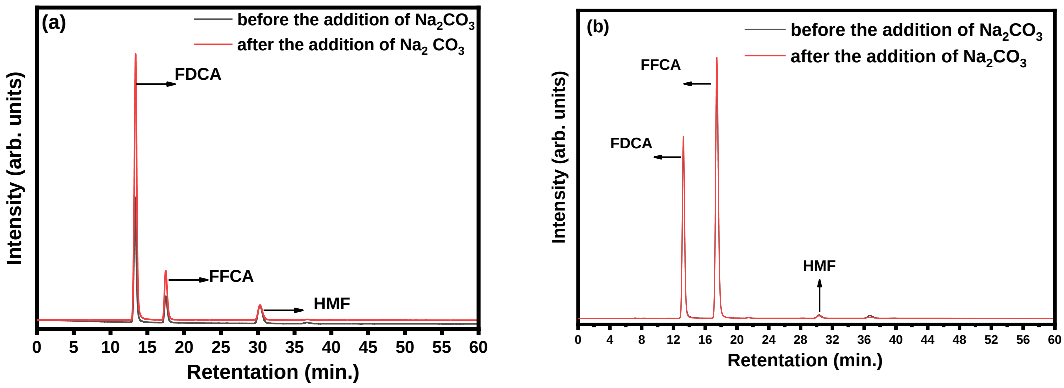


Figure S13. a and b) HPLC chromatograms of the reaction mixture of high and low concentrations of HMF oxidation to FDCA before and after the addition of Na_2CO_3 (Reaction conditions: step i): 0.25 (or 0.91) mmol HMF, 50 (180) mg RuMn/ZS, 20 ml water, 140 °C, 5 h, 30 bar air. Step ii) 0.25 (0.91) mmol of Na_2CO_3 was added after the reaction.

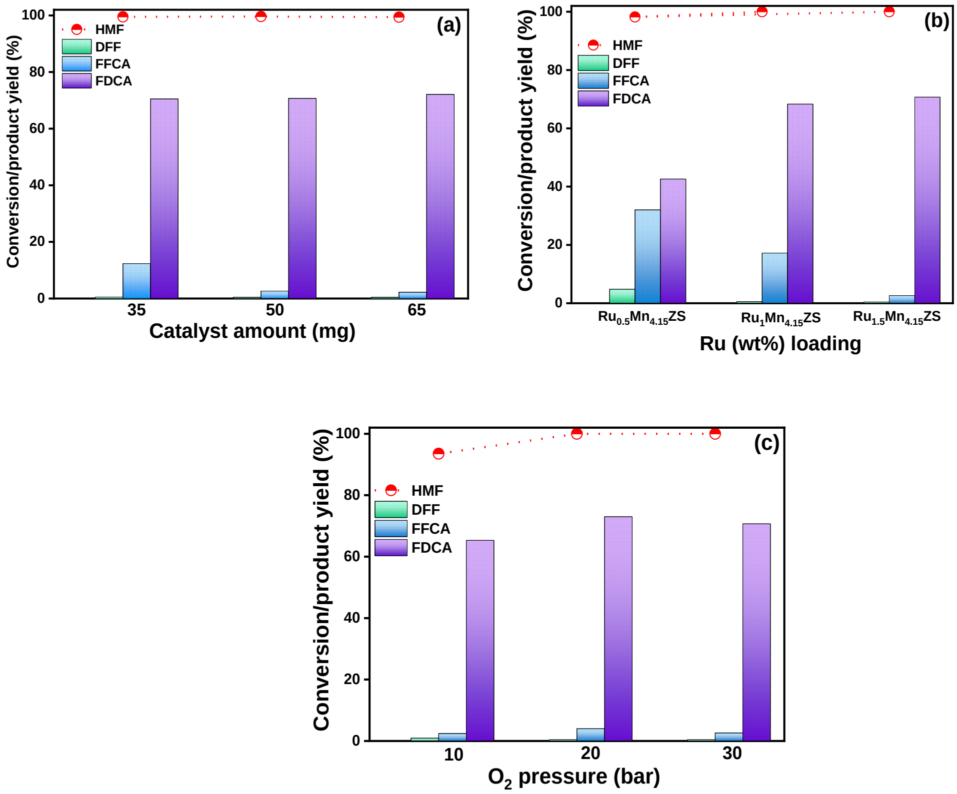


Figure S14. Influence of a) catalyst loading, b) Ru wt% and c) oxygen pressure (Reaction conditions: a) 0.25 mmol HMF, RuMn/ZS, 20 ml water, 140 °C, 5 h, 30 bar O_2 b) 0.25 mmol HMF, 50 mg RuMn/ZS, 20 ml water, 140 °C, 5 h, 30 bar O_2 and c) 0.25 mmol HMF, 50 mg RuMn/ZS, 20 ml water, 140 °C, 5 h).

Table S5. A time-course study of HMF oxidation at a low temperature.

Entry	Time (h)	HMF Conv. (%)	DFF yield (%)	FFCA yield (%)	FDCA yield (%)
1	0.5	15.4	2.2	0.2	0
2	1	15.6	4.4	1.4	0
3	3	21.3	7.2	3.9	0

Reaction condition: 0.25 mmol HMF, 20 ml water, 50 mg RuMn/ZS, 30 bar O_2, 60 °C

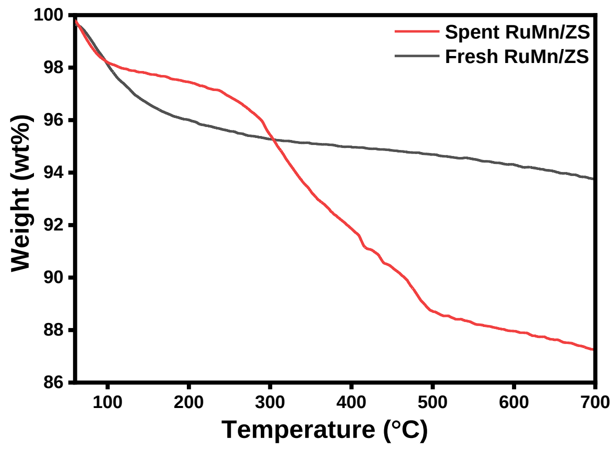


Figure S15. TGA thermographs of fresh and spent RuMn/ZS catalyst.

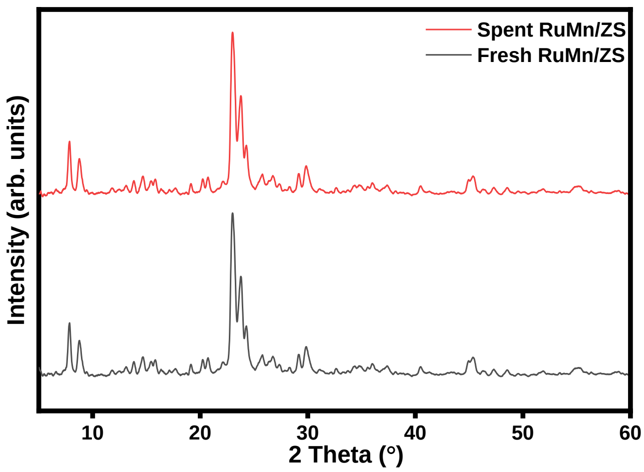


Figure S16. X-ray diffractograms of fresh and spent RuMn/ZS catalyst.