Supporting Information

Alloying nickel and cobalt with iron on ZSM-5 for tuning competitive hydrogenation reactions for selective one-pot conversion of furfural to gamma-valerolactone

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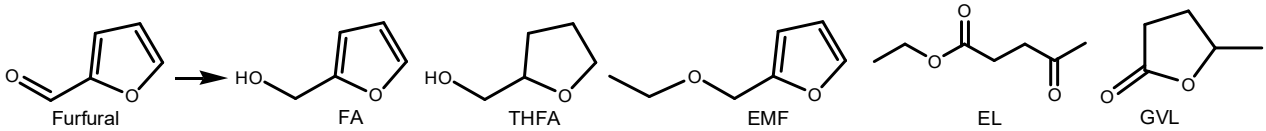
Number of Tables: 6

Number of Scheme: 1

Number of Figures: 2

Number of Pages: 11

Table S1 Distribution of the products in hydrogenation of furfural versus catalyst loading[a]



Entry	Catalysts	Catalyst loading (mg)	Con. (%)	Yield (%)				
				FA	THFA	EMF	EL	GVL
1	Ni/ZSM-5	40	100.0	0.0	36.6	0.0	25.8	28.5
2	Co/ZSM-5	40	100.0	0.0	0.0	0.0	21.0	60.7
3	Fe/ZSM-5	40	36.7	0.0	0.0	0.6	17.5	2.5
4	Ni-Fe/ZSM-5	40	100.0	0.0	0.0	18.4	38.9	39.0
5	Co-Fe/ZSM-5	40	100.0	0.0	0.9	20.0	41.2	36.3
6	Ni-Co/ZSM-5	40	100.0	0.0	68.7	0.0	5.4	18.5
7	Ni-Co-Fe/ZSM-5	40	100.0	0.0	1.8	5.5	9.7	75.0
8	Ni/ZSM-5	80	100.0	0.0	40.1	0.0	17.7	28.1
9	Co/ZSM-5	80	100.0	0.0	0.0	0.0	7.9	63.2
10	Fe/ZSM-5	80	56.1	0.0	0.0	0.0	24.2	5.4
11	Ni-Fe/ZSM-5	80	100.0	0.0	2.1	2.1	41.4	46.3
12	Co-Fe/ZSM-5	80	100.0	0.0	0.0	1.0	38.3	42.5
13	Ni-Co/ZSM-5	80	100.0	0.0	71.8	0.0	2.6	24.0
14	Ni-Co-Fe/ZSM-5	80	100.0	0.0	2.9	0.0	2.7	73.9
15	Ni/ZSM-5	100	100.0	0.0	46.6	0.0	15.8	25.8
16	Co/ZSM-5	100	100.0	0.0	0.0	0.0	5.5	54.5
17	Fe/ZSM-5	100	60.4	0.0	0.0	0.0	29.1	8.1
18	Ni-Fe/ZSM-5	100	100.0	0.0	4.9	0.0	41.6	54.7
19	Co-Fe/ZSM-5	100	100.0	0.0	0.0	0.0	40.1	52.0
20	Ni-Co/ZSM-5	100	100.0	0.0	67.8	0.0	1.4	18.4
21	Ni-Co-Fe/ZSM-5	100	100.0	0.0	2.6	0.0	2.0	73.7

[a]Reaction conditions: T = 150 °C; t = 10 h; P_{H2} = 4 MPa (at room temperature); stirring speed = 600 rpm; reactant: 0.4 mmol; ethanol: 5 mL.

Table S2 Distribution of the products in hydrogenation of furfural versus reaction medium[a]

Entry	Catalysts	Solvents	Con. (%)	Yield (%)						
				FA	THFA	AMF	AL	GVL	CPO	CPL
1	Ni/ZSM-5	Isopropanol	100.0	0.0	89.3	0.0[b]	0.0[c]	9.1	–	–
2	Co/ZSM-5	Isopropanol	100.0	0.0	2.9	79.1[b]	0.0[c]	5.9	–	–
3	Fe/ZSM-5	Isopropanol	63.2	0.0	0.0	11.7[b]	12.8[c]	5.4	–	–
4	Ni-Fe/ZSM-5	Isopropanol	100.0	57.9	3.9	36.2[b]	0.0[c]	0.0	–	–
5	Co-Fe/ZSM-5	Isopropanol	100.0	21.4	2.9	59.5[b]	3.2[c]	10.3	–	–
6	Ni-Co/ZSM-5	Isopropanol	100.0	0.0	89.1	1.7[b]	0.0[c]	0.0	–	–
7	Ni-Co-Fe/ZSM-5	Isopropanol	100.0	0.0	3.0	61.4[b]	0.3[c]	5.6	–	–
8	Ni/ZSM-5	Methanol	100.0	0.0	17.6	0.0	50.3[d]	17.9	–	–
9	Co/ZSM-5	Methanol	100.0	0.0	0.0	0.0	5.0[d]	55.5	–	–
10	Fe/ZSM-5	Methanol	22.6	0.0	0.0	0.0	12.5[d]	0.0	–	–
11	Ni-Fe/ZSM-5	Methanol	100.0	0.0	0.7	0.0	78.7[d]	17.3	–	–
12	Co-Fe/ZSM-5	Methanol	100.0	0.0	0.0	0.0	65.5[d]	21.4	–	–
13	Ni-Co/ZSM-5	Methanol	100.0	0.0	27.9	0.0	13.8[d]	35.6	–	–
14	Ni-Co-Fe/ZSM-5	Methanol	100.0	0.0	1.3	0.0	3.7[d]	56.0	–	–
15	Ni/ZSM-5	H_2O	100.0	0.0	12.1	–	6.4[e]	4.4	3.1	5.2
16	Co/ZSM-5	H_2O	100.0	0.0	12.9	–	4.0[e]	12.0	2.0	27.1
17	Fe/ZSM-5	H_2O	63.1	0.0	0.0	–	0.0[e]	0.0	0.0	0.0
18	Ni-Fe/ZSM-5	H_2O	100.0	0.0	11.1	–	7.5[e]	7.6	3.7	30.5
19	Co-Fe/ZSM-5	H_2O	100.0	0.0	1.2	–	4.2[e]	11.7	2.1	37.5
20	Ni-Co/ZSM-5	H_2O	100.0	0.0	33.9	–	3.1[e]	9.6	1.5	5.2
21	Ni-Co-Fe/ZSM-5	H_2O	100.0	0.0	22.6	–	3.9[e]	8.2	1.9	20.2

[a]Reaction conditions: T = 150 °C; t = 10 h; P_{H2} = 4 MPa (at room temperature); stirring speed = 600 rpm; catalyst: 60 mg; reactant: 0.4 mmol; solvent: 5 mL. AMF represents 2-alkoxymethyl-furan; AL represents alkyl levulinate.

[b]2-Isopropoxymethyl-furan was formed in isopropanol. [c]Isopropyl levulinate was formed in isopropanol. [d]Methyl levulinate was formed in methanol.

[e]1,4-Pentanediol was formed in water.

Table S3 Distribution of the products in hydrogenation of various reactants[a]

Entry	Catalysts	Reactants	Con. (%)	Yield (%)				
				FA	THFA	EMF	EL	GVL
1	Ni/ZSM-5	FA	100.0	–	46.5	0.0	17.9	22.5
2	Co/ZSM-5	FA	100.0	–	0.0	0.0	10.3	61.9
3	Fe/ZSM-5	FA	100.0	–	0.0	0.0	72.3	13.7
4	Ni-Fe/ZSM-5	FA	100.0	–	1.7	0.0	46.8	35.7
5	Co-Fe/ZSM-5	FA	100.0	–	0.0	0.7	42.0	45.2
6	Ni-Co/ZSM-5	FA	100.0	–	62.6	0.0	3.8	17.7
7	Ni-Co-Fe/ZSM-5	FA	100.0	–	0.0	0.0	3.9	66.6
8	Ni/ZSM-5	EL	41.1	–	–	–	–	38.3
9	Co/ZSM-5	EL	96.1	–	–	–	–	75.2
10	Fe/ZSM-5	EL	14.0	–	–	–	–	13.2
11	Ni-Fe/ZSM-5	EL	40.1	–	–	–	–	39.0
12	Co-Fe/ZSM-5	EL	35.7	–	–	–	–	33.5
13	Ni-Co/ZSM-5	EL	93.7	–	–	–	–	71.1
14	Ni-Co-Fe/ZSM-5	EL	95.1	–	–	–	–	84.7

[a]Reaction conditions: T = 150 °C; t = 10 h; P_{H2} = 4 MPa (at room temperature); stirring speed = 600 rpm; catalyst: 60 mg; reactant: 0.4 mmol; ethanol: 5 mL.

Table S4 Distribution of the products in hydrogenation of furfural via transfer hydrogenation[a]

Entry	Catalysts	Con. (%)	Yield (%)				
			FA	THFA	EMF	EL	GVL
1	Ni/ZSM-5	76.7	0.0	0.0	1.2	41.2	16.2
2	Co/ZSM-5	99.3	0.0	0.0	13.2	49.2	19.0
3	Fe/ZSM-5	43.3	0.0	0.0	0.7	26.6	3.9
4	Ni-Fe/ZSM-5	66.2	0.0	0.0	9.8	34.6	11.8
5	Co-Fe/ZSM-5	70.9	0.0	0.0	9.5	40.8	6.8
6	Ni-Co/ZSM-5	83.8	0.0	0.0	32.4	25.7	13.0
7	Ni-Co-Fe/ZSM-5	98.7	0.0	0.0	33.5	41.9	23.9

[a]Reaction conditions: T = 150 ºC; t = 14 h; P_{N2} = 4 MPa (at room temperature); stirring speed = 600 rpm; catalyst: 60 mg; reactant: 0.4 mmol; ethanol: 5 mL.

Table S5 Kinetic study for the conversion of various reactants over Ni-Co-Fe/ZSM-5 catalyst[a]

Entry	T (°C)	Reaction rate for furfural ($mmol \cdot g_{cat}^{-1} \cdot h^{-1}$)	T (°C)	Reaction rate for FA ($mmol \cdot g_{cat}^{-1} \cdot h^{-1}$)	T (°C)	Reaction rate for EL ($mmol \cdot g_{cat}^{-1} \cdot h^{-1}$)
1	120	23.1	120	5.7	140	1.7
2	140	43.3	140	16.1	160	4.9
3	160	78.5	160	27.9	180	9.7

[a]Reaction conditions: P_{H2} = 4 MPa, stirring speed = 800 rpm, catalyst: 20 mg, reactant: 6 mmol; ethanol: 20 g.

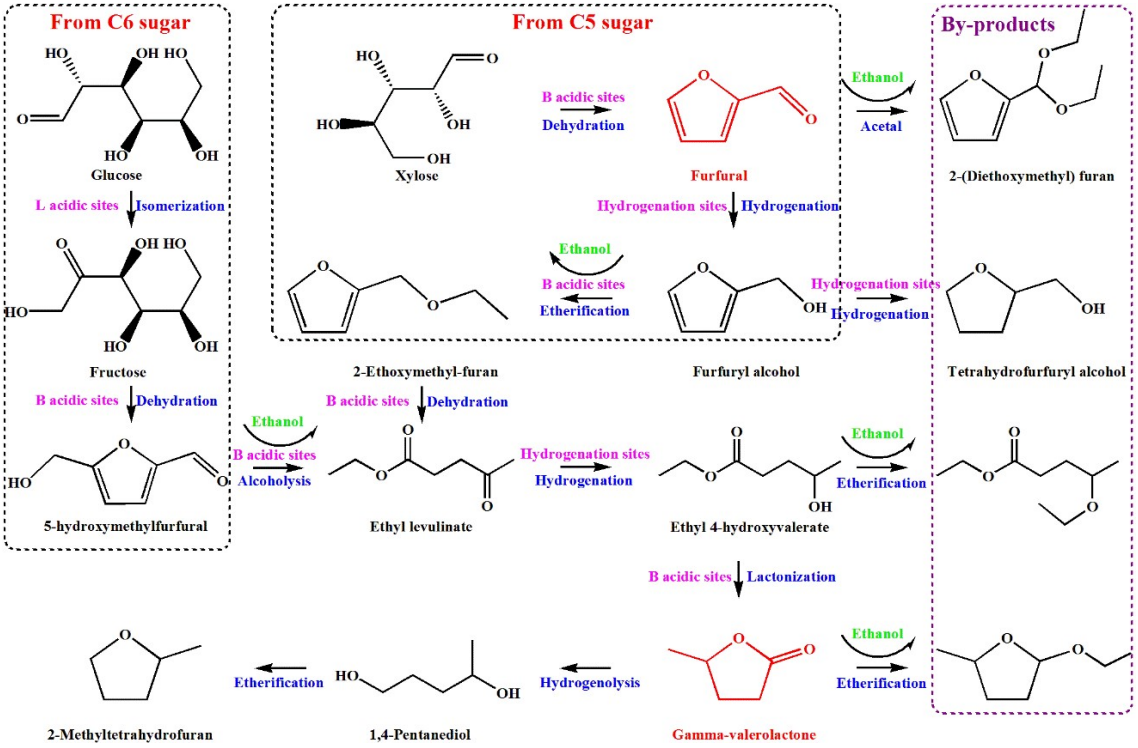
Table S6 The abundance of various functionalities recorded over Ni/ZSM-5, Ni-Co/ZSM-5 and Ni-Co-Fe/ZSM-5 catalysts[a]

Entry	Catalysts	Functional groups	Wavenumber (cm^{-1})	Abundance (a.u.)	Ratio of other functional groups to C-O-C
1	Ni/ZSM-5	C=O	1673	2.2293	3.55
2		C=C	1568	1.4910	2.38
3		C-O	1156	0.6273	1.00
4		C-O-C	1020	1.1358	1.81
5		$-(CH_2)_n-$	755	1.2385	1.97
6	Ni-Co/ZSM-5	C=O	1673	2.0551	4.04
7		C=C	1568	1.1597	2.28
8		C-O	1157	0.5088	1.00
9		C-O-C	1020	0.9949	1.96
10		$-(CH_2)_n-$	755	1.2008	2.36
11	Ni-Co-Fe/ZSM-5	C=O	1673	2.1466	3.53
12		C=C	1567	1.0979	1.81
13		C-O	1157	0.6076	1.00
14		C-O-C	1020	1.2038	1.98
15		$-(CH_2)_n-$	755	1.6765	2.76

[a]The functional groups were obtained from in-situ FT-IR spectra at 150 °C in Fig. 5 (d). The abundance of functional groups was measured based on the absorbance of peaks.

Table S6 Distribution of the products for the hydrogenation of various reactants to GVL over various catalysts

Entry	Catalysts	Reaction conditions	Con. (%)	Yield (%)	Ref.
1	Zr-Beta and Al-MFI nanosheets	T = 120 °C; t = 48 h; furfural	100.0	78.0	38
2	PDVB-IL polymer and Co/TiO_2	One step: T = 150 °C, t = 12 h; two step: T = 130 °C, t = 6 h; furfuryl alcohol	100.0	69.0	39
3	Au/ZrO_2 catalyst combined with ZSM-5	T = 120 °C; t = 24 h; hemicellulose	100.0	61.5	40
4	Sn-Al-Beta	T = 180 °C; t = 24 h; furfural	100.0	60.5	41
5	Heteropolyacid supported on Zr-Beta zeolite	T = 160 °C; t = 24 h; furfural	100.0	70.0	42
6	DUT-67(Hf)	T = 180 °C; t = 24 h; furfural	100.0	87.1	43
7	Zr-Al-beta	T = 190 °C; t = 48 h; furfural	100.0	35.0	44
8	Ni-Co-Fe/ZSM-5	T = 150 °C; t = 14 h; furfural	100.0	85.7	In this study



Scheme S1 Proposed reaction pathways for conversion of the sugars-derived furans.

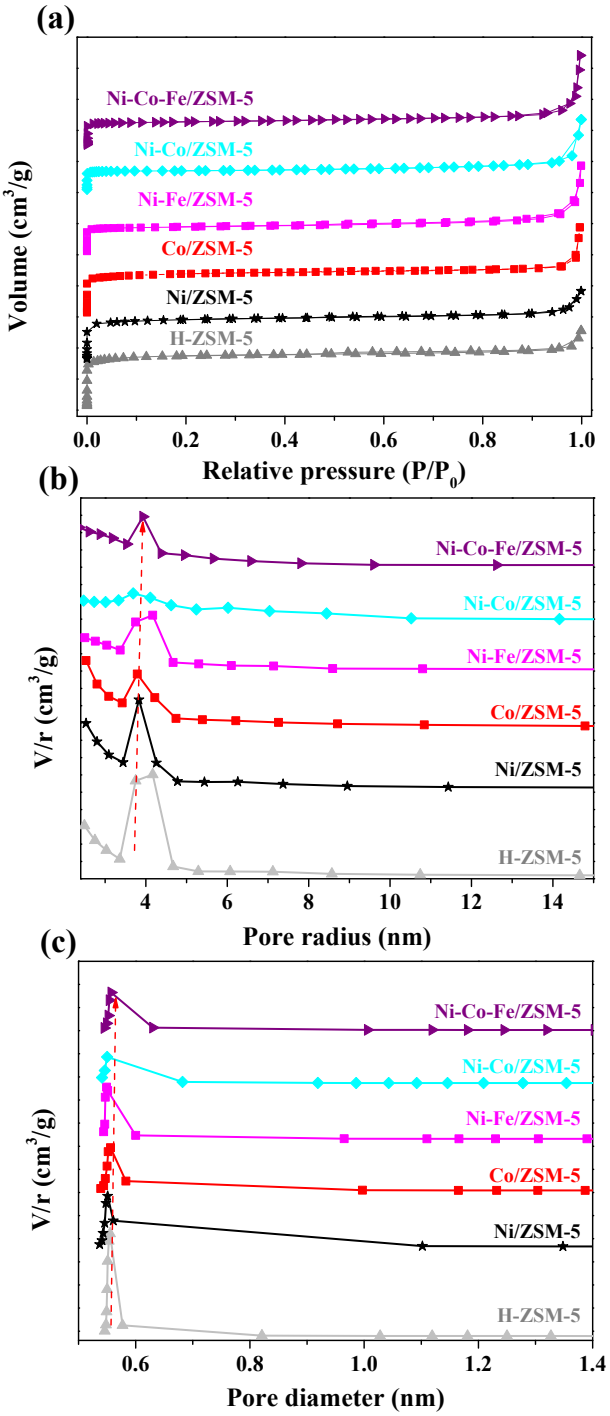


Fig. S1 (a) N_2 adsorption/desorption isotherms; (b) and (c) pore size distribution curves of Ni, Co and Fe supported on ZSM-5 catalysts.

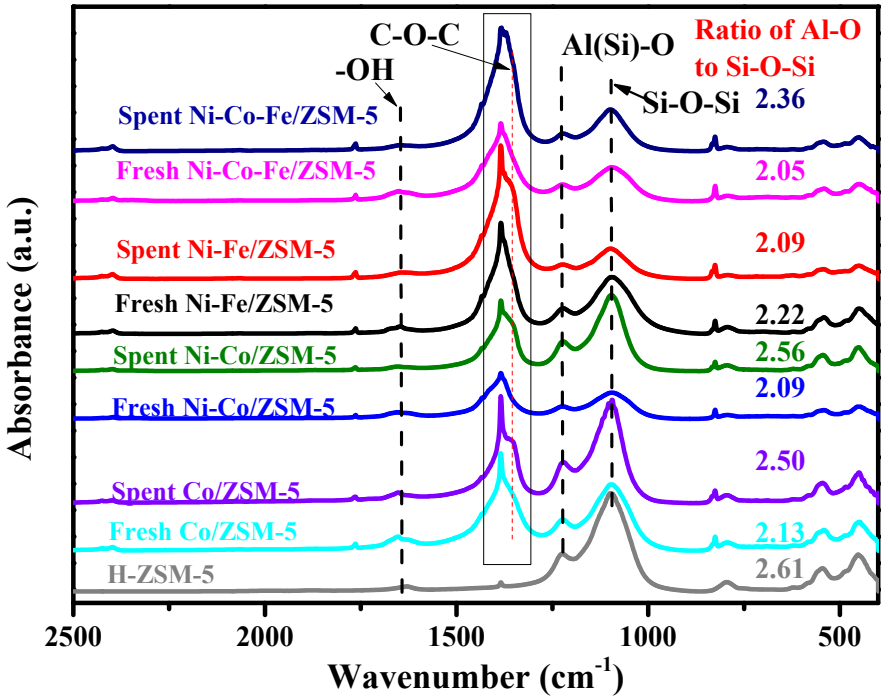


Fig. S2 FT-IR spectra of the used and the fresh metal supported on H-ZSM-5 catalysts.