Supplementary materials

CO_2 hydrogenation to formic acid over heterogenized ruthenium catalysts using a fixed bed reactor with separation units

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Contents

1. Preparation method for synthesis of bpyTN-mixed CTFs

Table S1. Molar ratio of bpy and TN for the synthesis of bpyTN-mixed CTFs , and furnace temperature program

Sample	DCBPY	TN	Heating rate	T	Holding Time	Cooling rate
	[g]	[g]	[^{o}C h^{-1}]	[^{o}C]	[h]	[^{o}C h^{-1}]
bpyTN-1-CTF@250	1.23	0.767	60	250	72	10
bpyTN-5-CTF@250	0.487	1.51	60	250	72	10
bpyTN-10-CTF@250	0.277	1.72	60	250	72	10
bpyTN-30-CTF@250	0.102	1.90	60	250	72	10
bpyTN-1-CTF	1.23	0.767	60	400	48	10
bpyTN-5-CTF	0.487	1.51	60	400	48	10
bpyTN-10-CTF	0.277	1.72	60	400	48	10
bpyTN-30-CTF	0.102	1.90	60	400	48	10

*furnace was turned off at 200 ^{o}C in a cooling step.

2. Nitrogen sorption isotherm measurements

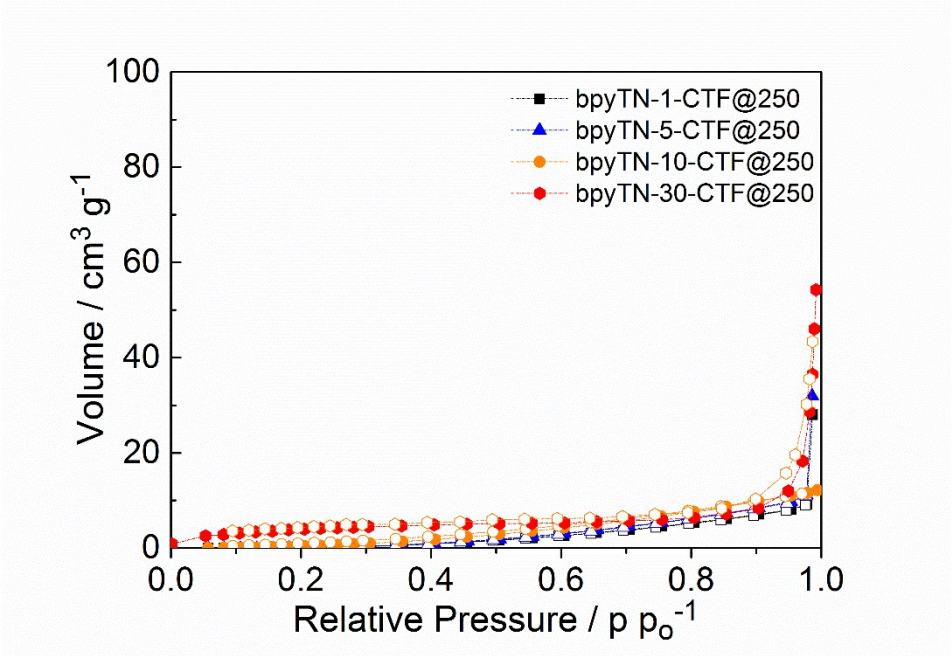

Figure S1. Nitrogen sorption isotherms of bpyTN-mixed CTFs@250 at 77 K

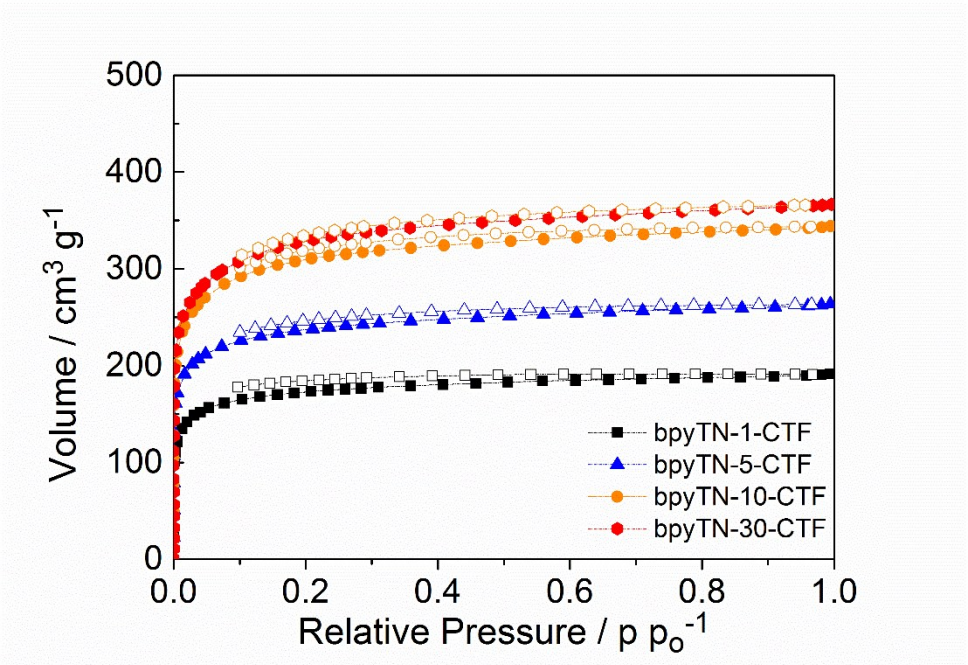

Figure S2. Nitrogen sorption isotherms of bpyTN-mixed CTFs at 77 K

Table S2. Pore parameters of bpyTN-mixed CTFs

Sample name	$a_{s,BET}$ [$m^2\ g^{-1}$]	$V_{pore,\ tot}$ [$cm^3\ g^{-1}$]	V_{mean} [nm]
bpyTN-1-CTF	652	0.30	1.81
bpyTN-5-CTF	914	0.41	1.78
bpyTN-10-CTF	1178	0.53	1.81
bpyTN-30-CTF	1251	0.57	1.81

3. Preliminary catalytic screening of Ru/bpyTN-CTF with batch reactor

Table S3. preliminary catalytic activity tests for CO_2 hydrogenation to formate with batch reactor.

Sample name	$[HCOO^-]$* [M]
Ru/bpyTN-1-CTF	0.20
Ru/bpyTN-5-CTF	0.23
Ru/bpyTN-10-CTF	0.26
Ru/bpyTN-30-CTF	0.31

*batch reactions were performed in 300 ml of batch reactor with 40 mg of catalysts (Ru loading amount, 3 wt%) under 80 MPa (CO_2/H_2=1:1, pressurized at room temperature), at 120 ^{o}C, for 2 h in 80 ml of 1M TEA aqueous solution.

4. Nitrogen sorption isotherm measurements for Ru/bpyTN-30-CTF (fresh)

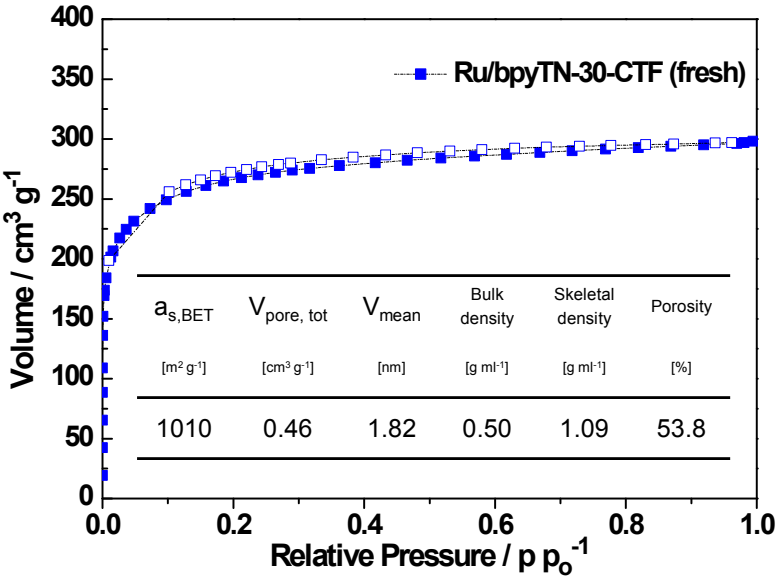

Figure S3. Nitrogen sorption isotherms at 77 K, porosity parameter, and mercury porosimetry of Ru/bpyTN-30-CTF

5. ICP-MS measurements

Table S4. ICP-MS analysis results for and the Ru/bpyTN-30-CTFs and filtrate

Sample	Ru amount / Wt %
Ru/bpyTN-30-CTF (Fresh)	3.03
Filtrate with methanol washing	NA
Ru/bpyTN-30-CTF (Spent)	2.67
Produced liquid products	NA

6. SEM and EDS measurements

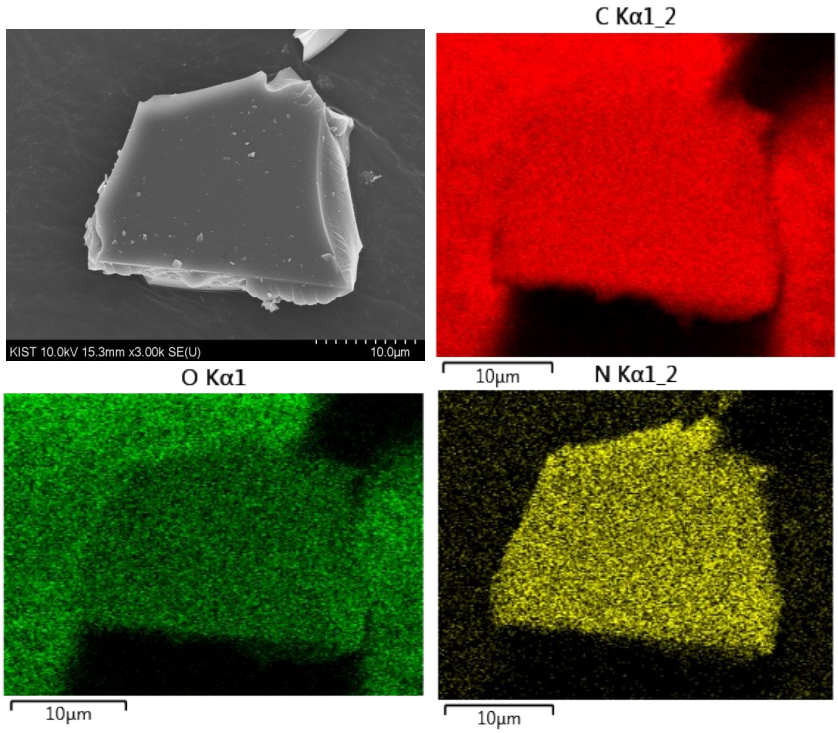

Figure S4. SEM & EDS mapping of bpyTN-30-CTF

Element	Line Type	Wt%	Atomic %
C	K series	78.39	82.41
N	K series	10.82	9.75
O	K series	10.79	7.83
Total:		100.00	100.00

Table S5. Atomic composition of bpy-TN30-CTF determined by EDS

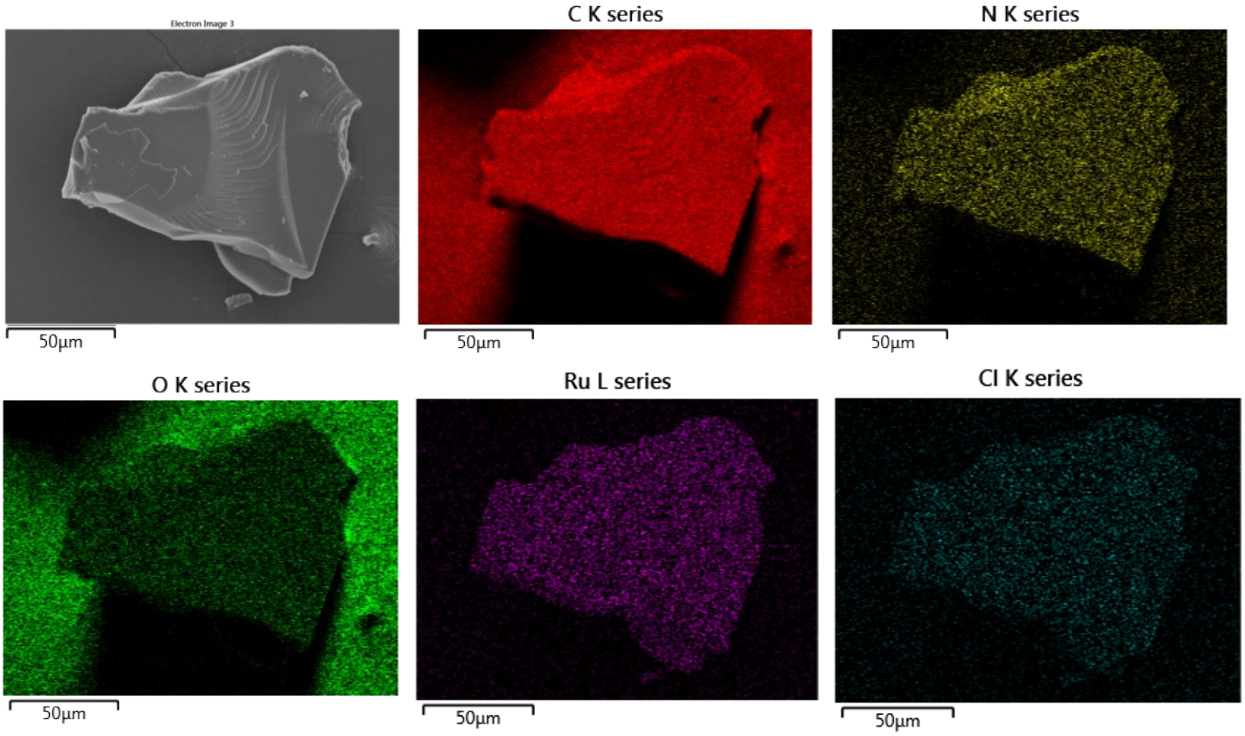

Figure S5. SEM & EDS mapping of Ru/bpyTN-30-CTF (fresh)

Table S6. Atomic composition of Ru/bpy-TN-30-CTF (fresh) determined by EDS

Element	Line Type	Wt%	Atomic %
C	K series	71.38	78.16
N	K series	9.66	9.07
O	K series	14.19	11.55
Cl	K series	2.51	0.93
Ru	L series	2.27	0.29
Total:		100.00	100.00

7. TGA measurements

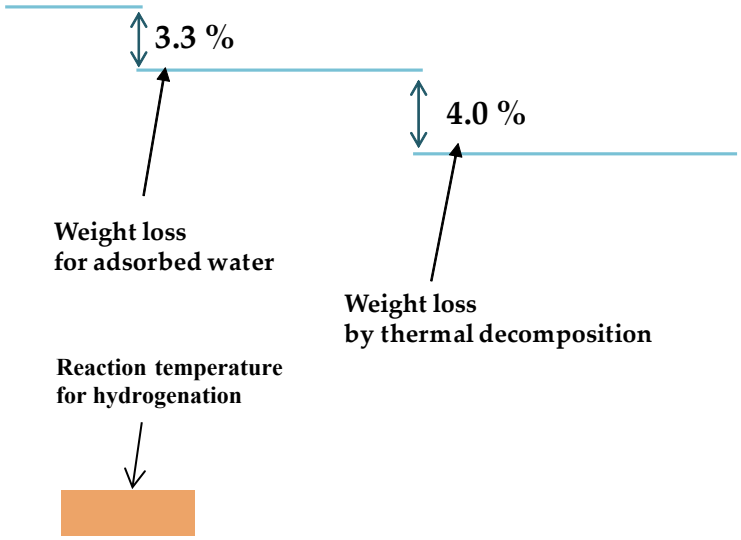

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Figure S6. TGA measurements of Ru/bpyTN-30-CTF

8. XPS analysis

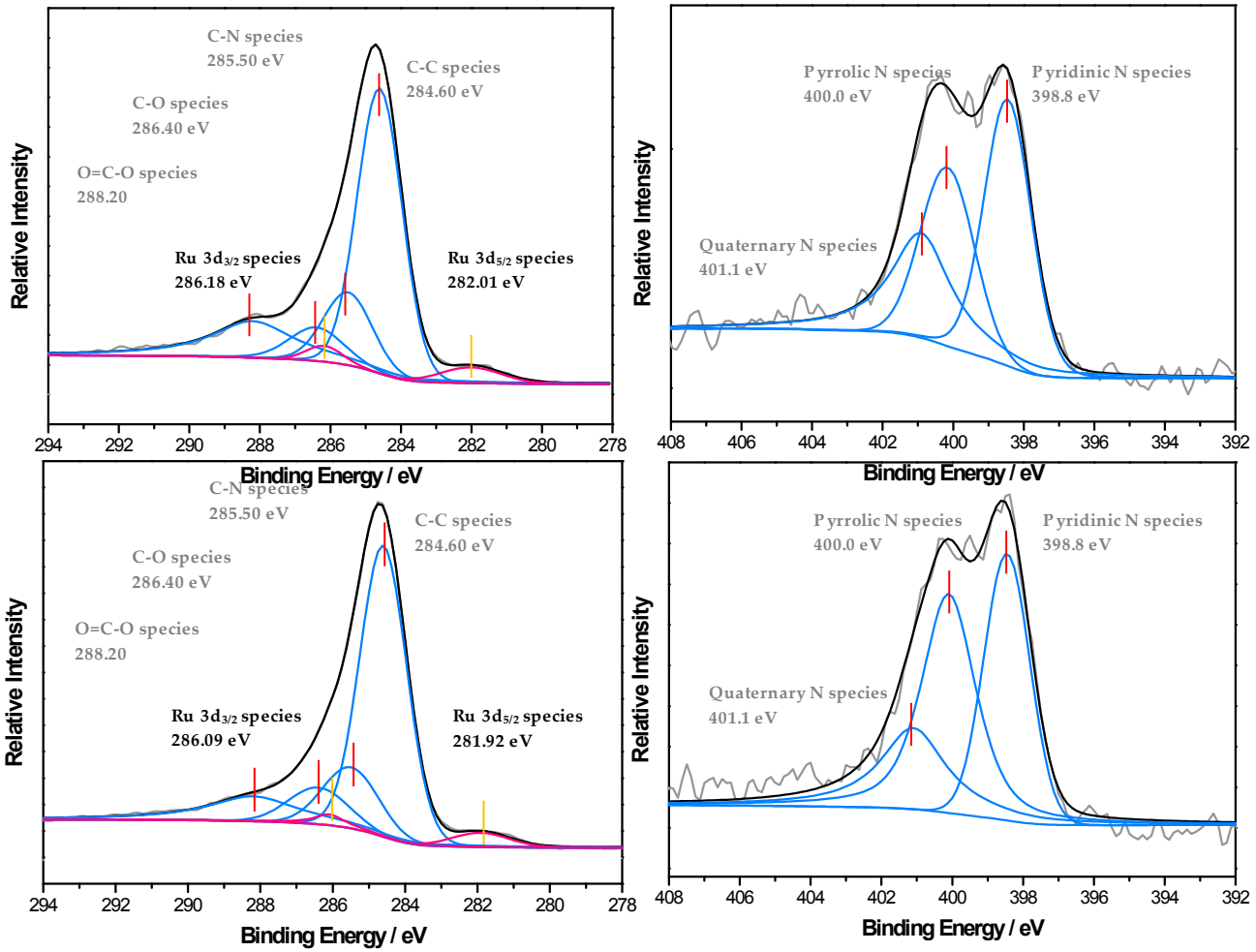


Figure S7. Deconvoluted C 1s and Ru 3d (top left), N 1s (top right) spectrum of Ru/bpyTN-30-CTF (fresh) and C 1s and Ru 3d (bottom left), N 1s (bottom right) spectrum of Ru/bpyTN-30-CTF (spent)

Table S7. Atomic composition determined by XPS of fresh and spent Ru/bpy-TN-30-CTF

Sample	C1s	N1s	O1s	Cl2p	Ru3p3
Ru/bpyTN-CTF (Fresh)	81.14	8.52	9.04	1.04	0.27
Ru/bpyTN-CTF (Spent)	81.59	9.25	8.60	0.36	0.21

Table S8. Deconvolution parameters of XPS analysis for fresh and spent Ru/bpy-TN-30-CTF

	Peak	BE	FWHM	Area	Doublet separation
		[eV]	[eV]		[eV]
Ru/bpyTN-30-CTF (fresh)	C1s, C-C	284.60	1.49	7692	
	C1s, C-N	285.50	1.62	2176	
	C1s, C-O	286.40	1.81	1163	
	C1s, O=C-O	288.20	2.79	2693	
	$Ru3d_{5/2}$	282.01	2.04	571	4.17
	$Ru3d_{3/2}$	286.18	1.21	342	
	N1s, pyridinic N	398.50	1.57	960	
	N1s, pyrrolic N	400.20	1.79	712	
	N1s, quaternary N	401.00	2.01	693	
Ru/bpyTN-30-CTF (spent)	C1s, C-C	284.60	1.52	9052	
	C1s, C-N	285.50	1.82	2235	
	C1s, C-O	286.40	1.93	1427	
	C1s, O=C-O	288.20	2.97	2198	
	$Ru3d_{5/2}$	281.92	1.88	530	4.17
	$Ru3d_{3/2}$	286.09	0.99	318	
	N1s, pyridinic N	398.50	1.53	1068	
	N1s, pyrrolic N	400.20	1.80	1301	
	N1s, quaternary N	401.00	2.20	691	

9. Feed flow reagents conditions for continuous CO_2 hydrogenation process

Table S9. Feed flow reagents conditions for continuous CO_2 hydrogenation process with trickle-bed reactor system.

Entry	T	P	H_2O[a]	TEA[a]	$[Et_3N]$	H_2[b]	CO_2[b]	u_l[c]	u_g[d]	AAR	Productivity	CO_2 Conv.
	[°C]	[bar]	[mol h^{-1}]		[M]	[mol h^{-1}]		[cm s^{-1}]	[cm s^{-1}]	[M]	[g_{form} g_{cat}^{-1} d^{-1}]	[%]
1	60	100	13.60	0.68	2	0.68	0.68	0.25	24	0.05	25.9	5.2
2	80	100	13.60	0.68	2	0.68	0.68	0.25	24	0.10	51.7	10.4
3	100	100	13.60	0.68	2	0.68	0.68	0.25	24	0.28	142.5	28.6
4	120	100	13.60	0.68	2	0.68	0.68	0.25	24	0.51	265.7	53.3
5	140	100	13.60	0.68	2	0.68	0.68	0.25	24	0.67	355.1	71.3
6	120	60	13.60	0.68	2	0.68	0.68	0.25	24	0.42	219.9	44.2
7	120	80	13.60	0.68	2	0.68	0.68	0.25	24	0.50	259.2	52.0
8	120	120	13.60	0.68	2	0.68	0.68	0.25	24	0.60	317.5	63.8
9	120	140	13.60	0.68	2	0.68	0.68	0.25	24	0.63	333.2	66.9
10	120	120	32.74	0.68	1	0.68	0.68	0.49	24	0.40	204.9	41.1
11	120	120	7.33	0.68	3	0.68	0.68	0.16	24	0.61	307.2	65.6
12	120	120	13.0	0.68	5	0.68	0.68	0.24	24	0.51	166.0	33.3
13	120	120	2.30	0.68	6	0.68	0.68	0.10	24	0.38	66.2	13.3
14	120	120	0	0.68	neat	0.68	0.68	0.07	24	-	-	-
15	120	120	10.99	1.02	3	1.02	1.02	0.25	36	0.54	435.6	58.3
16	120	120	14.65	1.36	3	1.36	1.36	0.33	48	0.51	542.8	54.5
17	120	120	21.98	2.04	3	2.04	2.04	0.49	72	0.42	669.0	44.8
18	120	120	5.49	0.51	3	0.68	0.68	0.12	24	0.70	283.5	56.9
19	120	120	8.24	0.77	3	1.02	1.02	0.18	36	0.67	407.5	54.6
20	120	120	10.99	1.02	3	1.36	1.36	0.25	48	0.62	499.5	50.1
21	120	120	16.48	1.53	3	2.04	2.04	0.37	72	0.54	650.8	43.6
22	120	120	3.66	0.34	3	0.68	0.68	0.08	24	0.86	239.0	48.0
23	120	120	5.49	0.51	3	1.02	1.02	0.12	36	0.82	341.2	45.7
24	120	120	7.33	0.68	3	1.36	1.36	0.16	48	0.78	427.6	42.9
25	120	120	10.82	1.02	3	2.04	2.04	0.24	72	0.68	549.4	36.8
26-54	120	120	3.66	0.34	3	0.68	0.68	0.08	24	0.86	238.7	47.9

[a]liquid flow rate were controlled by high-pressure liquid pump, [b]gas flow rate were controlled by mass flow controller, [c]superficial liquid velocity, and [d]superficial gas velocity

10. Side products analysis

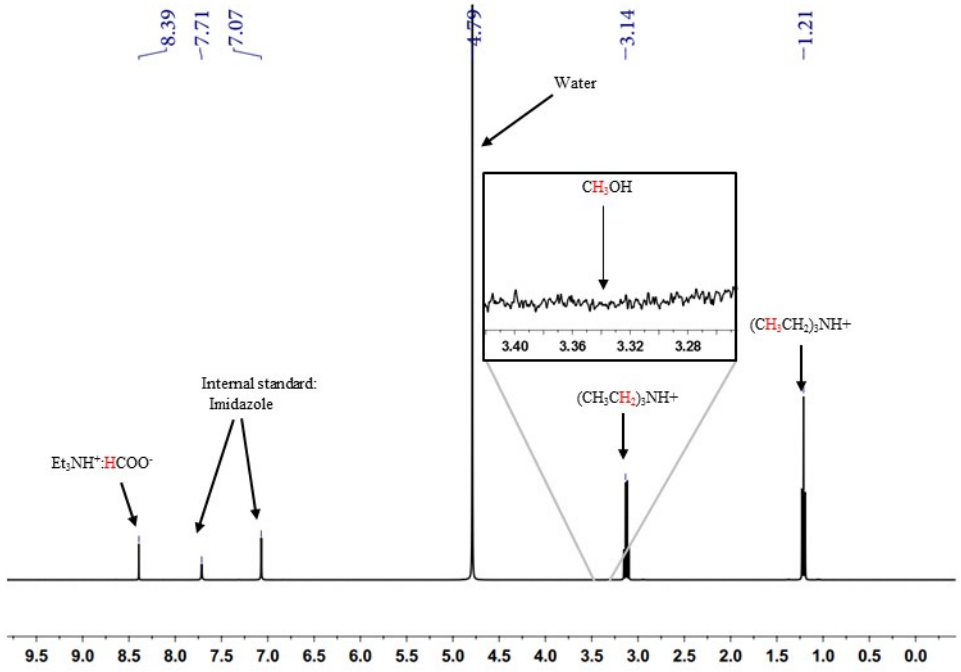


Figure S8. ^{1}H NMR spectrum of the liquid product collected from the hydrogenation process

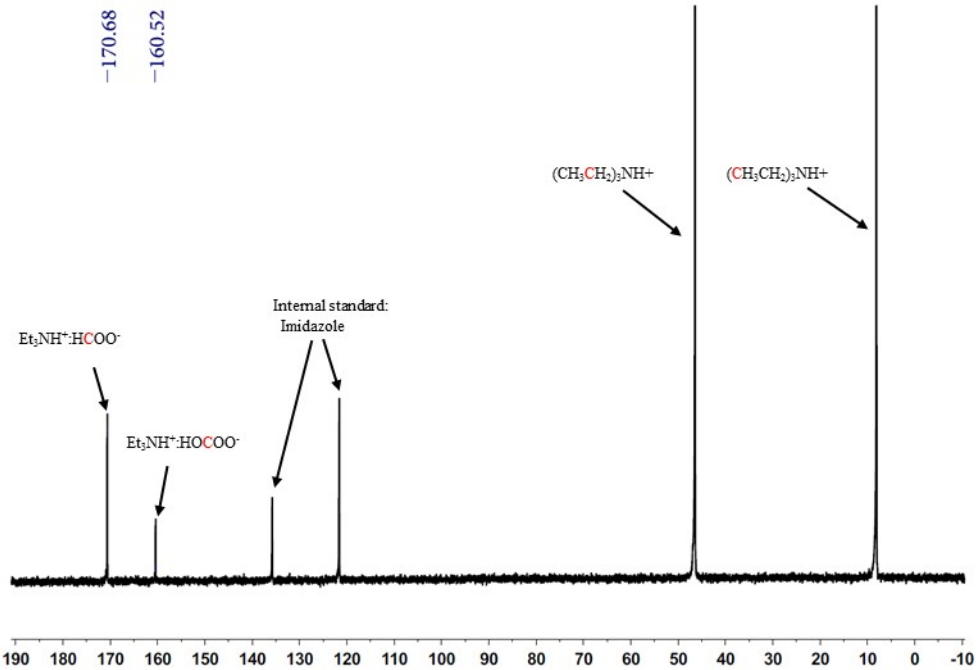
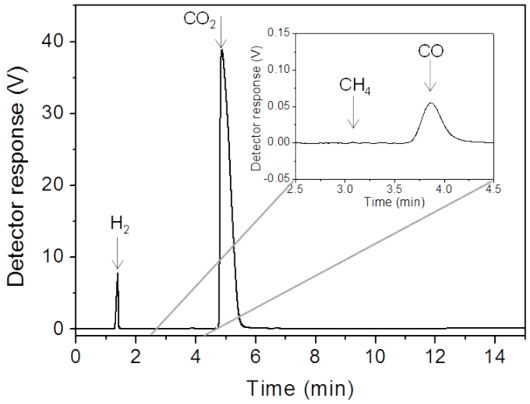


Figure S9. ^{13}C NMR spectrum of the liquid product collected from the hydrogenation process



Gas	Retention time (min)
H_2	1.40
CH_4	3.20
CO	3.86
CO_2	4.86

Figure S10. Gas chromatograph result for discharged gaseous feed from the continuous hydrogenation reaction

11. SEM & EDS for spent catalyst

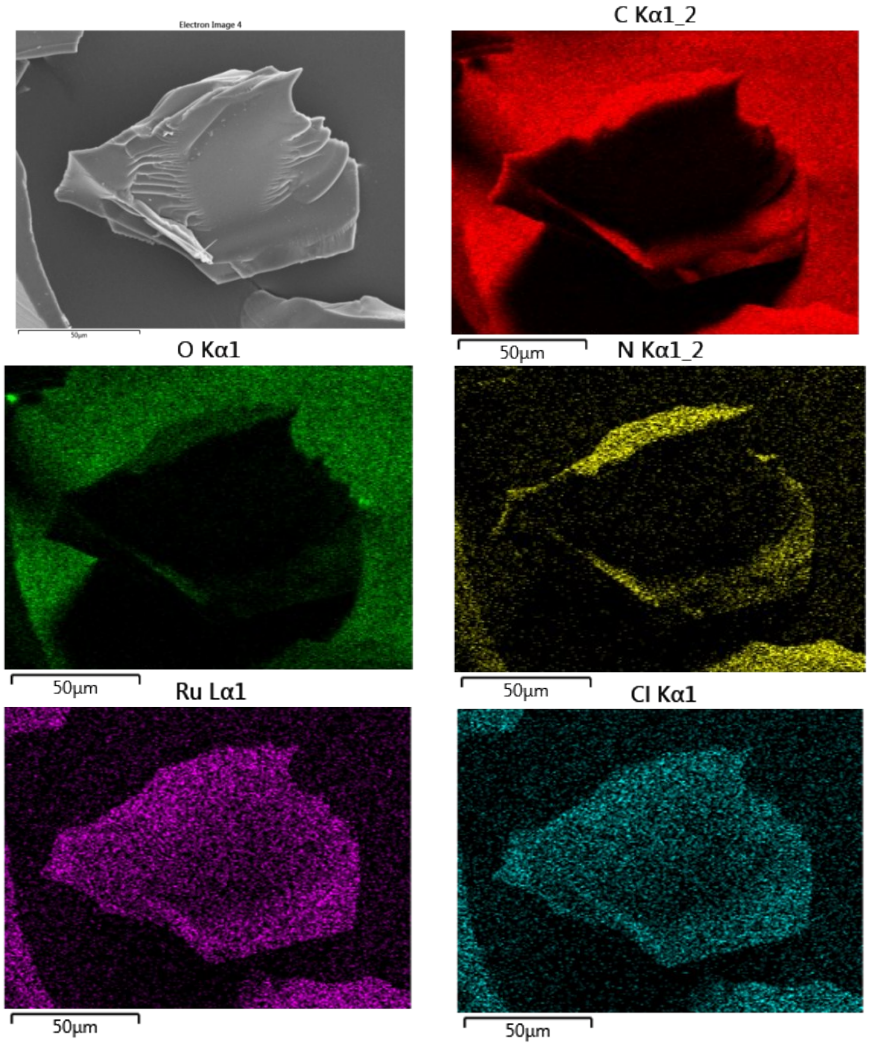


Figure S11. SEM & EDS mapping of Ru/bpyTN-30-CTF (spent)

Table S11. Atomic composition of Ru/bpy-TN-30-CTF (spent) determined by EDS

Element	Line Type	Wt%	Atomic %
C	K series	72.47	79.08
N	K series	5.58	5.22
O	K series	18.17	14.88
Cl	K series	1.37	0.51
Ru	L series	2.41	0.31
Total:		100.00	100.00

12. Ternary phase equilibria in the system of Et_3N, H_2O and CO_2

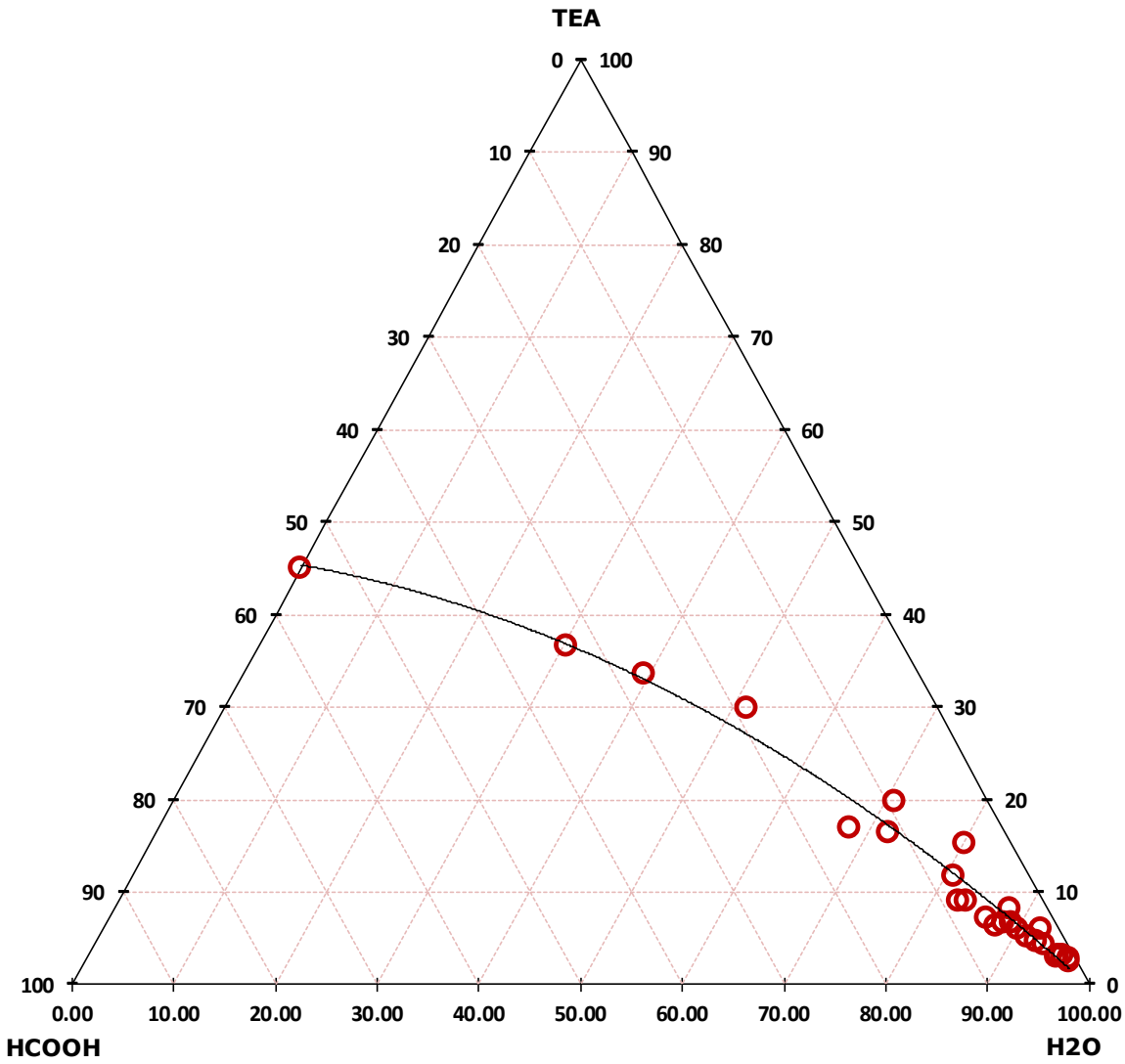


Figure S12. Ternary phase diagram of triethyl amine (Et_3N)-formic acid (HCOOH)-water (H_2O)

13. Vapour-liquid equilibrium measurement

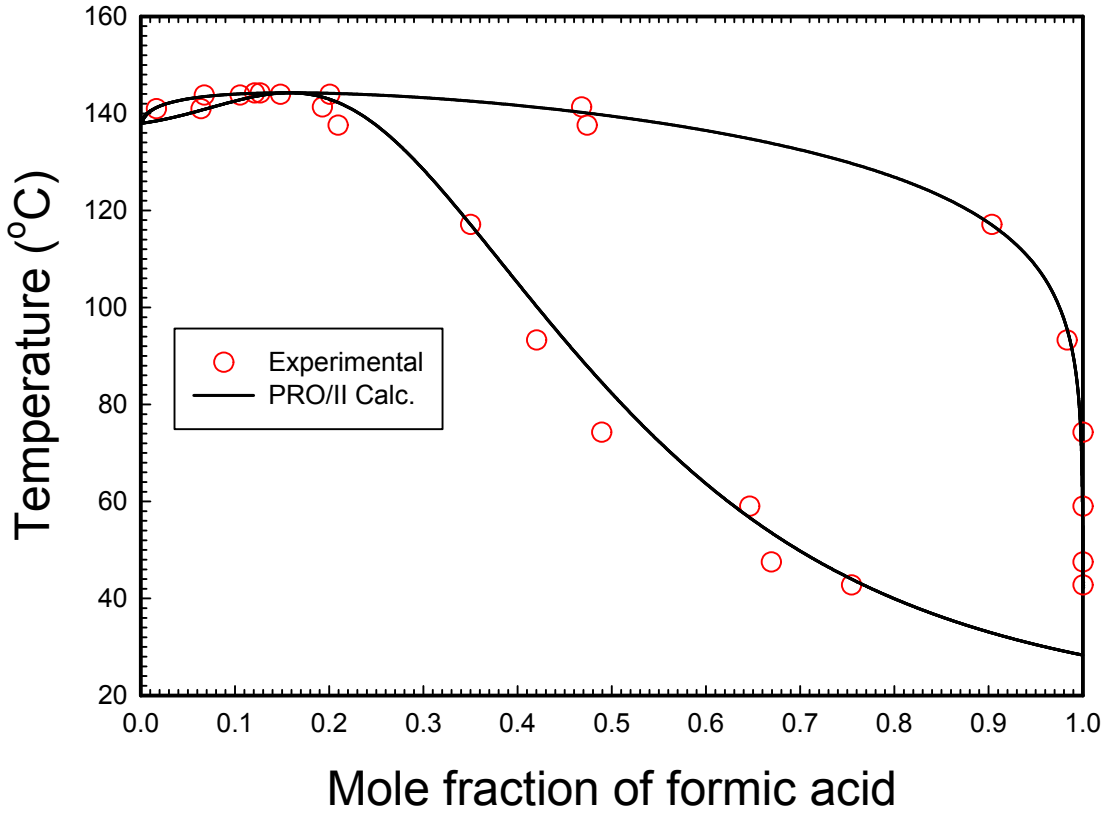


Figure S13. Vapor-Liquid Equilibrium at 50 mmHg