Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

The Solvent-free Continuous Flow Hydrogenation of N-Methyl Pyrrolidone to N-methylpyrrolidine catalyzed with bimetallic Pt/V on HAP

Pengxiang Gao,[a] Song Liu,[a] Jitao Yang,[a] Dishun Zhao,[b] Qingbin Liu,[*a]

[a] Hebei Key Laboratory of Organic Functional Molecules, College of Chemistry and Materials Science, Hebei Normal University, Shijiazhuang, 050024, China, E-mail: Liuqingbin@hebtu.edu.cn

[b] College of Chemical Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang, 050018, China

Contents

S1. General information and methods

$Pt(acac)_2$, $VO(acac)_2$, Hydroxyapatite(HAP) were all purchased from Innochem Co. Ltd., and used without any further purification. N-methylpyrrolidone was purchased from Damao Chemical Reagent Factory and used as received. The Pt/V/HAP catalyst was prepared refer to S1.

S2. Reactor equipment specifications

The reactor was usd for solid catalytic reactions under continuous flow conditions, and the reactor was purchased from Yanzheng Shanghai Experimental Instrument Co., LTD., and the H_2 used in the reactor was fed in to the system from a steel cylinder.

S3. The results of the yields of N-methylpyrrolidine under specified conditions each hour

S3.1 Pt/V/HAP (Pt/V molar ratio = 1:5)

Table S1 The yields of N-methylpyrrolidine every hour [a]

Time (h)	Yield (%)	Conversion (%)
1	52.71	52.71
2	50.57	50.57
3	33.51	33.51
4	25.40	25.40
5	20.57	20.57
6	18.84	18.84
7	22.41	22.41
Average	32.00	32.00

[a] Pt/V molar ratio = 1:5, temperature = 220 ºC, pressure of H_2 = 20 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

S3.2 Pt/V/HAP (Pt/V molar ratio=1:1)

Table S2 The yields of N-methylpyrrolidine every hour[a]

Time (h)	Yield (%)	Conversion (%)
1	71.19	73.17
2	70.25	72.06
3	69.00	69.03
4	66.53	67.50
5	65.55	66.92
6	66.37	66.39
7	64.70	65.70
Average	67.66	68.68

[a] Pt/V molar ratio = 1:1, temperature = 220 ºC, pressure of H_2 = 20 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

S3.3 Pt/V/HAP (Pt/V molar ratio=1:0.5)

Table S3 The yields of N-methylpyrrolidine every hour[a]

Time (h)	Yield (%)	Conversion (%)
1	88.50	95.21
2	86.19	92.06
3	86.64	92.58
4	85.45	92.13
5	83.34	93.78
6	86.88	86.88
7	78.49	83.75
Average	85.07	90.91

[a] Pt/V molar ratio = 1:0.5, temperature = 220 ºC, pressure of H_2 = 20 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

Table S4 The yields of N-methylpyrrolidine every hour at 210 ºC and the same as entry 13 in Table 2[a]

Time (h)	Yield (%)	Conversion (%)
1	84.02	89.29
2	93.88	96.9
3	87.71	89.94
4	86.73	88.75
5	86.60	88.46
6	86.20	87.91
7	85.64	87.42
Average	87.25	89.81

[a] Pt/V molar ratio = 1:0.5, temperature = 210 ºC, pressure of H_2 = 20 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

Table S5 The yields of N-methylpyrrolidine every hour at 200 ºC [a]

Time (h)	Yield (%)	Conversion (%)
1	77.68	81.81
2	93.47	95.29
3	84.76	85.57
4	59.38	59.91
5	58.94	59.35
6	60.60	60.91
7	58.99	59.30
Average	70.55	71.73

[a] Pt/V molar ratio = 1:0.5, temperature = 200 ºC, pressure of H_2 = 20 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

Table S6 The yields of N-methylpyrrolidine every hour at 230 ºC [a]

Time (h)	Yield (%)	Conversion (%)
1	78.47	83.97
2	79.47	91.99
3	79.86	93.16
4	81.03	94.25
5	81.01	93.69
6	59.69	63.15
7	72.43	80.87
Average	75.99	85.87

[a] Pt/V molar ratio = 1:0.5, temperature = 230 ºC, pressure of H_2 = 20 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

Table S7 The yields of N-methylpyrrolidine every hour at 240 ºC [a]

Time (h)	Yield (%)	Conversion (%)
1	56.57	77.19
2	71.77	90.31
3	69.46	87.90
4	70.51	92.02
5	69.82	92.33
6	71.37	91.60
7	71.39	93.65
Average	68.70	89.29

[a] Pt/V molar ratio = 1:0.5, temperature = 240 ºC, pressure of H_2 = 20 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

Table S8 The yields of N-methylpyrrolidine every hour at 30 bar [a]

Time (h)	Yield (%)	Conversion (%)
1	83.78	90.69
2	93.67	96.52
3	68.10	73.94
4	66.85	68.35
5	67.11	68.07
6	80.29	81.49
7	76.78	77.77
Average	76.65	79.55

[a] Pt/V molar ratio = 1:0.5, temperature = 210 ºC, pressure of H_2 = 30 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

Table S9 The yields of N-methylpyrrolidine every hour at 25 bar [a]

Time (h)	Yield (%)	Conversion (%)
1	76.68	77.92
2	80.49	81.30
3	79.27	80.24
4	85.42	89.79
5	89.38	92.17
6	81.09	82.15
7	65.91	66.88
Average	79.75	81.49

[a] Pt/V molar ratio = 1:0.5, temperature = 210 ºC, pressure of H_2=25 bar, flow rate of H_2=100 sccm, WHSV = 1.2 h^{-1}

Table S10 The yields of N-methylpyrrolidine every hour at 15 bar [a]

Time (h)	Yield (%)	Conversion (%)
1	73.40	75.65
2	79.82	82.00
3	80.06	82.23
4	81.21	83.39
5	79.58	82.17
6	80.52	82.70
7	80.93	83.08
Average	79.36	81.60

[a] Pt/V molar ratio=1:0.5, temperature = 210 ºC, pressure of H_2=15 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

Table S11 The yields of N-methylpyrrolidine every hour at 10 bar [a]

Time (h)	Yield (%)	Conversion (%)
1	73.08	77.75
2	78.68	81.44
3	73.10	76.17
4	67.20	71.10
5	71.12	74.80
6	69.77	73.39
7	69.87	73.43
Average	71.83	75.44

[a] Pt/V molar ratio = 1:0.5, temperature = 210 ºC, pressure of H_2 = 10 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

Table S12 The yields of N-methylpyrrolidine every hour at 0 sccm [a]

Time (h)	Yield (%)	Conversion (%)
1	22.88	24.15
2	10.82	10.88
3	6.89	8.30
4	7.47	8.75
5	7.72	10.88
6	6.89	8.30
7	7.47	8.75
Average	10.02	11.43

[a] Pt/V molar ratio = 1:0.5, temperature = 210 ºC, pressure of H_2=20 bar, flow rate of H_2 = 0 sccm, WHSV = 1.2 h^{-1}

Table S13 The yields of N-methylpyrrolidine every hour at 50 sccm [a]

Time (h)	Yield (%)	Conversion (%)
1	59.24	69.39
2	56.60	63.88
3	53.33	55.44
4	38.71	39.97
5	47.81	48.95
6	42.72	43.89
7	42.11	43.44
Average	48.65	52.14

[a] Pt/V molar ratio = 1:0.5, temperature = 210 ºC, pressure of H_2 = 20 bar, flow rate of H_2 = 50 sccm, WHSV = 1.2 h^{-1}

Table S14 The yields of N-methylpyrrolidine every hour at 150 sccm [a]

Time (h)	Yield (%)	Conversion (%)
1	88.29	90.88
2	91.37	94.01
3	91.21	94.13
4	85.05	92.65
5	93.09	96.05
6	90.77	96.32
7	91.11	94.45
Average	90.13	94.07

[a] Pt/V molar ratio = 1:0.5, temperature = 210 ºC, pressure of H_2 = 20 bar, flow rate of H_2 = 150 sccm, WHSV = 1.2 h^{-1}

Table S15 The yields of N-methylpyrrolidine every hour at 200 sccm [a]

Time (h)	Yield (%)	Conversion (%)
1	87.89	92.18
2	91.08	95.09
3	91.00	96.48
4	89.18	96.18
5	92.60	96.31
6	93.60	97.07
7	91.17	95.50
Average	90.93	95.54

[a] Pt/V molar ratio=1:0.5, temperature=210 ºC, pressure of H_2=20 bar, flow rate of H_2 = 200 sccm, WHSV = 1.2 h^{-1}

Table S16 The yields of N-methylpyrrolidine every hour of entry 1 in Table 2 [a]

Time (h)	Yield (%)	Conversion (%)
1	53.36	54.63
2	59.45	61.20
3	66.08	66.33
4	62.11	62.40
5	68.58	68.82
6	68.80	69.10
7	68.44	68.72
Average	63.83	64.46

[a] Pt/V molar ratio = 1:0.5, temperature = 200 ºC, pressure of H_2 = 15 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

Table S17 The yields of N-methylpyrrolidine every hour of entry 2 in Table 2 [a]

Time (h)	Yield (%)	Conversion (%)
1	69.26	72.89
2	71.44	73.19
3	78.51	88.95
4	63.20	79.52
5	65.29	81.39
6	63.86	66.22
7	71.22	73.33
Average	68.97	76.50

[a] Pt/V molar ratio = 1:0.5, temperature = 220 ºC, pressure of H_2 = 15 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

Table S18 The yields of N-methylpyrrolidine every hour of entry 3 in Table 2 [a]

Time (h)	Yield (%)	Conversion (%)
1	78.50	83.81
2	71.32	71.73
3	72.04	73.67
4	61.16	62.19
5	57.14	62.84
6	57.39	57.74
7	42.98	43.29
Average	62.93	65.04

[a] Pt/V molar ratio = 1:0.5, temperature = 200 ºC, pressure of H_2 = 25 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

Table S19 The yields of N-methylpyrrolidine every hour of entry 4 in Table 2 [a]

Time (h)	Yield (%)	Conversion (%)
1	55.73	56.12
2	69.79	70.80
3	79.26	81.03
4	82.91	85.39
5	83.92	86.27
6	83.28	85.72
7	81.20	83.65
Average	76.57	78.43

[a] Pt/V molar ratio = 1:0.5, temperature = 220 ºC, pressure of H_2 = 25 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

Table S20 The yields of N-methylpyrrolidine every hour of entry 5 in Table 2 [a]

Time (h)	Yield (%)	Conversion (%)
1	48.77	50.31
2	32.64	33.53
3	29.48	29.63
4	29.85	30.17
5	27.43	28.03
6	26.50	26.81
7	28.45	26.81
Average	31.87	32.46

[a] Pt/V molar ratio = 1:0.5, temperature = 200 ºC, pressure of H_2 = 20 bar, flow rate of H_2 = 50 sccm, WHSV = 1.2 h^{-1}

Table S21 The yields of N-methylpyrrolidine every hour of entry 6 in Table 2 [a]

Time (h)	Yield (%)	Conversion (%)
1	47.41	48.46
2	48.44	49.89
3	47.31	48.45
4	44.88	47.57
5	39.48	41.43
6	38.48	39.71
7	34.95	36.47
Average	42.99	44.57

[a] Pt/V molar ratio = 1:0.5, temperature = 220 ºC, pressure of H_2 = 20 bar, flow rate of H_2 = 50 sccm, WHSV = 1.2 h^{-1}

Table S22 The yields of N-methylpyrrolidine every hour of entry 7 in Table 2 [a]

Time (h)	Yield (%)	Conversion (%)
1	82.57	84.30
2	69.00	70.03
3	85.85	86.15
4	71.60	71.91
5	82.18	82.29
6	70.45	70.56
7	68.81	68.89
Average	75.78	76.30

[a] Pt/V molar ratio = 1:0.5, temperature = 200 ºC, pressure of H_2 = 20 bar, flow rate of H_2 = 150 sccm, WHSV = 1.2 h^{-1}

Table S23 The yields of N-methylpyrrolidine every hour of entry 8 in Table 2 [a]

Time (h)	Yield (%)	Conversion (%)
1	71.27	71.78
2	77.53	81.35
3	86.16	92.20
4	71.18	73.10
5	70.43	71.26
6	81.80	88.17
7	55.51	58.08
Average	73.41	76.56

[a] Pt/V molar ratio = 1:0.5, temperature = 220 ºC, pressure of H_2 = 20 bar, flow rate of H_2 = 150 sccm, WHSV = 1.2 h^{-1}

Table S24 The yields of N-methylpyrrolidine every hour of entry 9 in Table 2 [a]

Time (h)	Yield (%)	Conversion (%)
1	71.20	75.26
2	49.31	55.77
3	41.42	43.74
4	30.83	36.89
5	33.18	37.57
6	37.99	39.53
7	34.04	35.52
Average	42.57	46.33

[a] Pt/V molar ratio = 1:0.5, temperature = 210 ºC, pressure of H_2 = 15 bar, flow rate of H_2 = 50 sccm, WHSV = 1.2 h^{-1}

Table S25 The yields of N-methylpyrrolidine every hour of entry 10 in Table 2 [a]

Time (h)	Yield (%)	Conversion (%)
1	31.33	36.01
2	29.01	31.57
3	44.53	46.40
4	47.17	51.82
5	45.44	49.65
6	41.63	46.09
7	41.26	42.62
Average	40.05	43.45

[a] Pt/V molar ratio = 1:0.5, temperature = 210 ºC, pressure of H_2 = 25 bar, flow rate of H_2 = 50 sccm, WHSV = 1.2 h^{-1}

Table S26 The yields of N-methylpyrrolidine every hour of entry 11 in Table 2 [a]

Time (h)	Yield (%)	Conversion (%)
1	45.75	46.73
2	72.16	74.21
3	78.11	80.67
4	72.16	72.88
5	80.33	81.29
6	76.70	77.83
7	80.26	81.73
Average	72.21	73.62

[a] Pt/V molar ratio = 1:0.5, temperature = 210 ºC, pressure of H_2 = 15 bar, flow rate of H_2 = 150 sccm, WHSV = 1.2 h^{-1}

Table S27 The yields of N-methylpyrrolidine every hour of entry 12 in Table 2 [a]

Time (h)	Yield (%)	Conversion (%)
1	69.58	72.06
2	87.88	89.99
3	90.40	91.80
4	80.61	81.68
5	81.37	82.09
6	74.03	74.48
7	82.45	83.20
Average	80.90	82.19

[a] Pt/V molar ratio = 1:0.5, temperature = 210ºC, pressure of H_2 = 25 bar, flow rate of H_2 = 150 sccm, WHSV = 1.2 h^{-1}

Table S28 The yields of N-methylpyrrolidine every hour of entry 14 in Table 2 [a]

Time (h)	Yield (%)	Conversion (%)
1	88.93	89.55
2	84.34	85.59
3	82.63	84.07
4	84.17	87.26
5	85.62	87.06
6	84.71	86.66
7	85.72	87.72
Average	85.16	86.85

[a] Pt/V molar ratio = 1:0.5, temperature = 210 ºC, pressure of H_2 = 20 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

Table S29 The yields of N-methylpyrrolidine every hour of entry 15 in Table 2 [a]

Time (h)	Yield (%)	Conversion (%)
1	88.85	93.55
2	85.89	95.26
3	88.55	91.74
4	87.64	90.18
5	87.65	90.03
6	85.96	89.11
7	89.98	93.66
Average	87.79	91.93

[a] Pt/V molar ratio = 1:0.5, temperature = 210 ºC, pressure of H_2 = 20 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

Table S30 The yields of N-methylpyrrolidine every hour of entry 16 in Table 2 [a]

Time (h)	Yield (%)	Conversion (%)
1	84.81	86.89
2	85.91	87.89
3	86.37	88.89
4	86.11	88.60
5	85.12	87.13
6	86.51	88.78
7	86.16	88.64
Average	85.86	88.12

[a] Pt/V molar ratio = 1:0.5, temperature = 210 ºC, pressure of H_2 = 20 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

Table S31 The yields of N-methylpyrrolidine every hour of entry 17 in Table 2 [a]

Time (h)	Yield (%)	Conversion (%)
1	86.66	88.60
2	85.84	87.47
3	84.96	86.95
4	85.60	87.70
5	86.21	88.53
6	86.36	89.23
7	86.19	87.42
Average	85.97	87.99

[a] Pt/V molar ratio = 1:0.5, temperature = 210 ºC, pressure of H_2 = 20 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

Table S32 The yields of N-methylpyrrolidine every hour at WHSV=0.4 [a]

Time (h)	Yield (%)	Conversion (%)
1	82.97	96.02
2	83.99	98.47
3	84.57	98.70
4	83.07	98.57
5	83.67	98.58
6	83.76	98.67
7	83.97	98.68
Average	83.71	98.24

[a] Pt/V molar ratio = 1:0.5, temperature = 211 ºC, pressure of H_2 = 21 bar, flow rate of H_2 = 123 sccm, WHSV = 0.4 h^{-1}

Table S33 The yields of N-methylpyrrolidine every hour at WHSV=0.8 [a]

Time (h)	Yield (%)	Conversion (%)
1	87.13	98.96
2	88.25	96.72
3	89.72	96.98
4	91.53	97.86
5	92.60	98.72
6	91.03	97.95
7	91.12	97.76
Average	90.20	97.85

[a] Pt/V molar ratio = 1:0.5, temperature = 211 ºC, pressure of H_2 = 21 bar, flow rate of H_2 = 123 sccm, WHSV = 0.8 h^{-1}

Table S34 The yields of N-methylpyrrolidine every hour at WHSV=1.6 [a]

Time (h)	Yield (%)	Conversion (%)
1	73.53	78.83
2	74.52	76.32
3	75.72	76.94
4	76.68	77.50
5	78.20	78.87
6	79.35	79.99
7	76.14	76.70
Average	76.31	77.88

[a] Pt/V molar ratio = 1:0.5, temperature = 211 ºC, pressure of H_2 = 21 bar, flow rate of H_2 = 123 sccm, WHSV = 1.6 h^{-1}

Table S35 The yields of N-methylpyrrolidine every hour at WHSV=2.0 [a]

Time (h)	Yield (%)	Conversion (%)
1	68.20	68.64
2	62.15	62.78
3	66.22	66.73
4	63.77	64.04
5	66.74	67.12
6	61.90	62.28
7	63.22	63.61
Average	64.60	65.03

[a] Pt/V molar ratio = 1:0.5, temperature = 211 ºC, pressure of H_2 = 21 bar, flow rate of H_2 = 123 sccm, WHSV = 2.0 h^{-1}

S3.4 Pt/V/HAP (Pt/V molar ratio=1:0.25)

Table S36 The yields of N-methylpyrrolidine every hour[a]

Time (h)	Yield (%)	Conversion (%)
1	47.18	48.03
2	59.86	62.08
3	53.56	72.17
4	66.15	69.60
5	69.13	71.10
6	59.55	63.77
7	42.31	43.71
Average	58.43	63.74

[a] Pt/V molar ratio = 1:0.25, temperature = 220 ºC, pressure of H_2=20 bar, flow rate of H_2 = 100 sccm, WHSV = 1.2 h^{-1}

S4. Identification of N-methylpyrrolidine

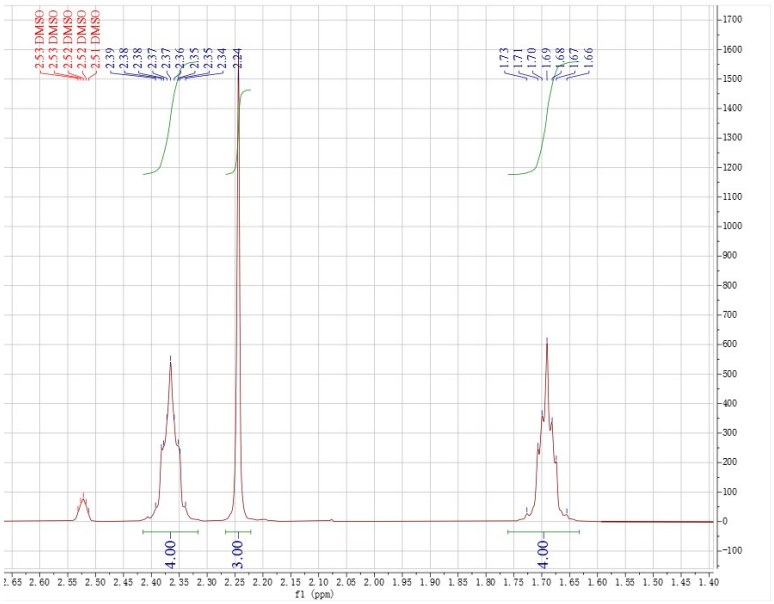

Fig.S1 The ^{1}H NMR spectrum of NMPD

^{1}H NMR (400 MHz, DMSO-D_6), δ: 1.66- 1.73 (m,4H),2.24(s,3H),2.34-2.39(m,4H)

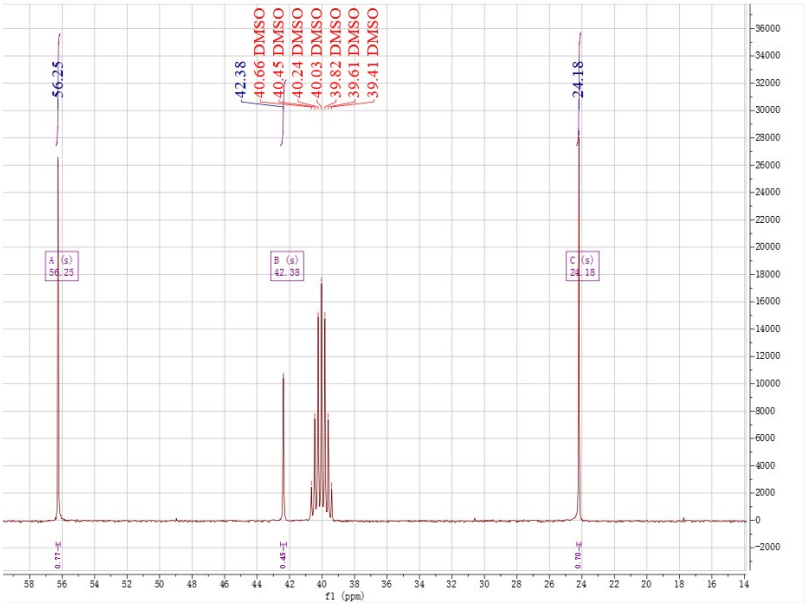

Fig.S2 The ^{13}C NMR spectrum of NMPD

^{13}C NMR (400 MHz, DMSO-D_6), δ: 24.18, 42.38, 56.25

S5. Identification of by-products

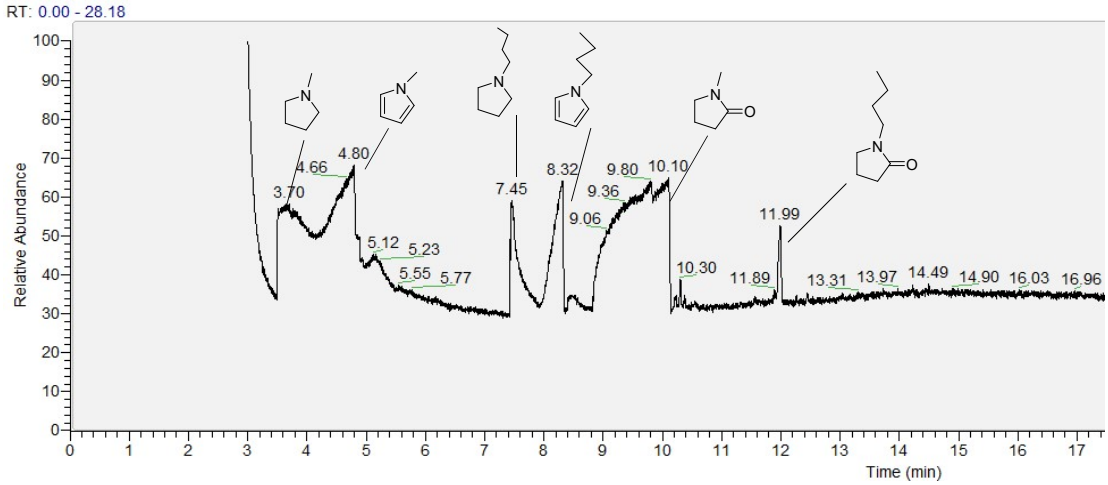

Fig.S3 The GC-MS of crude product

Some unexpected byproducts were synthesized under the condition of temperature = 340 °C, pressure of H_2 = 20 bar, flow rate of H_2 = 100 sccm, weight hourly space velocity = 1.2 h^{-1}, Pt/V/HAP (Pt/V molar ratio = 1:5) as the catalysts. The by-products, N-methylpyrrole, N-butylpyrrole, N-butylpyrrolidine and 1-butylpyrrolidine-2-one were detected. Probably because the exorbitant temperature could cause the dehydrogenation of NMPD to create N-methylpyrrole, at the same time, the ring of the NMPD was opened with the N-C bond broken, providing the n-butyl and prompting the N-butylpyrrole, N-butylpyrrolidine and 1-butylpyrrolidine-2-one formed.

References

S1 T. Mitsudome, K. Miyagawa, Z. Maeno, T. Mizugaki, K. Jitsukawa, J. Yamasaki, Y. Kitagawa, K. Kaneda, *Angew. Chem. Int. Ed.*, 2017, **129**, 9509-9513.