Supplementary Information:

New Journal of Chemistry

One-pot synthesis of 1-butylpyrrolidine and its derivatives from aqueous ammonia and 1,4-butandiol over CuNiPd/ZSM-5 catalyst

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Catalyst characterization:

The metal contents were analyzed by using graphite furnace atomic absorption spectroscopy (GF-AAS, contrAA700, Germany).

X-ray diffraction (XRD) was measured on a Siemens D/max-RB powder X-ray diffractometer. Diffraction patterns were recorded with Cu Kα radiation (40 mA, 40 kV) over a 2θ range of 5° to 90° and a position-sensitive detector using a step size of 0.01° and a step time of 0.15 s.

Surface analysis of the catalysts was performed by X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB210 spectrometer using Mg Kα radiation at a pass energy of 20 eV.The energy scale was calibrated and corrected for charging using the C 1s (285.0 eV) line as the binding energy (BE) reference.

Transmission electron microscope (TEM) analysis was carried out using a TF20 field emission transmission electron microscope operating at 300 kV. Single-particle EDX mapping analysis was performed using a TF20 field emission TEM in the STEM mode.

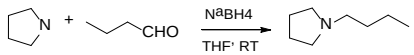
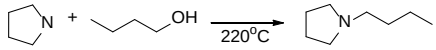
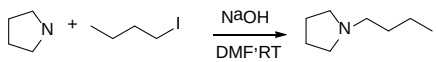
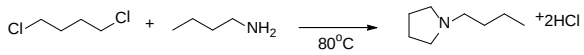
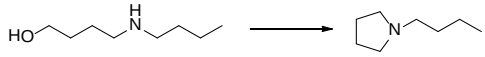
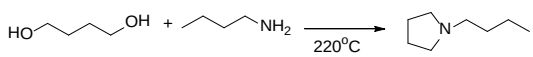
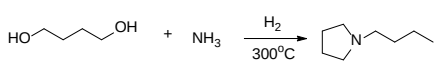
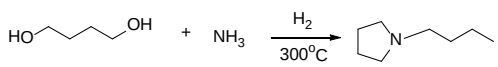
General procedures for the preparation of 3Cu-3Ni-0.2Pd/ZSM-5:

The 3%Cu-3%Ni-0.2Pd/ZSM-5 catalyst was prepared by incipient wetness method using $Cu(NO_3)_2{\cdot}3H_2O$, $Ni(NO_3){\cdot}6H_2O$ and H_2PdCl_4 (Sinopharm Chemical Reagent Co., Ltd, China) aqueous solution ([Pd] 0.1g/mL) as starting materials. 1.14g $Cu(NO_3)_2{\cdot}3H_2O$ (0.3g Cu) and 1.5g $Ni(NO_3){\cdot}6H_2O$ (0.3g Ni) dissolved in 3mL water, then 0.2ml H_2PdCl_4 aqueous solution was added, 10g HZSM-5 zeolite (Si/Al ratio of 80, surface area of 360 m^2/g, supplied by the catalyst plant of NanKai University, China) with continuous stirring at room temperature. After 2h stirring and 2h aging, the resulted precipitate was dried at 110 ºC for 12h. Then, the precursors were calcined at 500 ºC for 3h in air. Then, the obtained catalyst precursor was reduced at 300 ºC under hydrogen atmosphere for 3h. The catalyst was denoted as 3Cu-3Ni-0.2Pd/ZSM-5. Other catalysts were prepared via similar method, and the carrier USY (Si/Al ratio of 5.4, surface area of 700 m^2/g) Beta (Si/Al ratio of 40, surface area of 680 m^2/g), HZSM-5 (Si/Al ratio of 25, surface area of 340 m^2/g) and HZSM-5 (Si/Al ratio of 300, surface area of 370 m^2/g) zeolites were also purchased from the catalyst plant of NanKai University, China.

Synthesis of 1-BP:

The catalytic reactions were carried out in a 100 ml stainless steel autoclave with a magnetic stirrer. In a typical process, BDO 18g (0.2 mol), aqueous NH_3 6.8g (0.1 mol, 25 wt% solution) and catalyst (1.8 g) were charged in the autoclave, which was then filled with H_2 at 4 MPa pressure. The reactor was heated to 300 °C and magnetically stirred constantly during the reaction, and the final pressure was 10 Mpa. After reaction, the qualitative and quantitative analyses of the resulting liquid mixture were conducted with GC-MS (Agilent 6890/5973) and GC (Agilent 7890) equipped with a SE-54 capillary column and a FID detector. The GC-MS chromatogram of the products under optimization conditions, the scan and standard mass spectra of 1-butylpyrrolidine were illustrated in Fig. S1.

Table S1 The comparison of different routes for synthesis of 1-BP

Entry	Route	Catalyst	Yield	Ref.
1[a,b]		Silica gel supported H_2SO_4	90% [d]	1
2[a]		$RuCl_3$	80% [d]	2
3[a,b]		-	62% [d]	3
4[b]		Hydrotalcite	82% [e]	4
5[a]		$RhH(PPh_3)_4$	56% [d]	5
6		$RuCl_3$	36% [d]	2
7[c]		Reduced, fused iron	38% [e]	6
8		CuNiPd/ZSM-5	**76%** [e]	**This work**

[a] Involving relatively expensive raw materials

[b] Using relatively toxic reactants or yielding waste acid (or salt)

[c] 1-BP just is one of the products, and not the target product

[d] Isolated yield

[e] GC yield

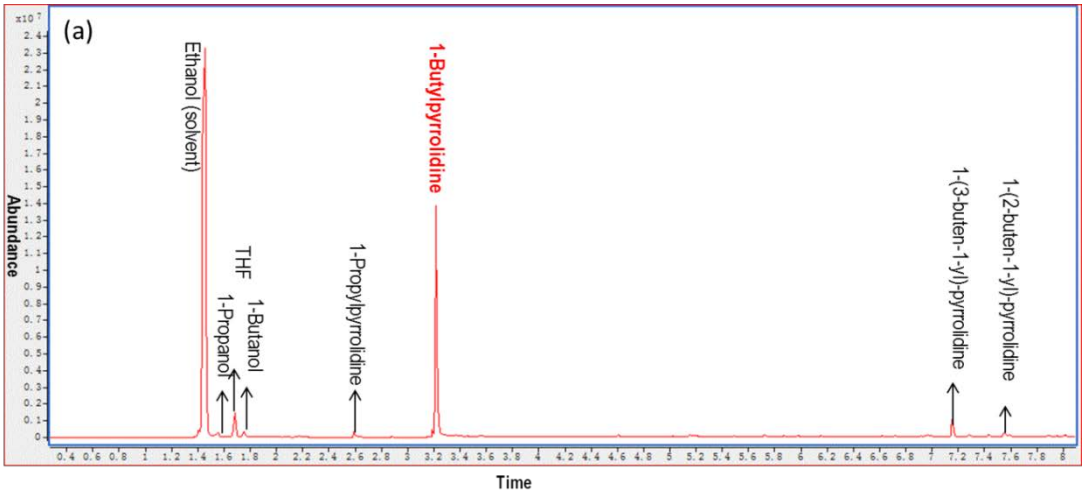
Table S2 The contents of Cu, Ni and Pd measured by AAS

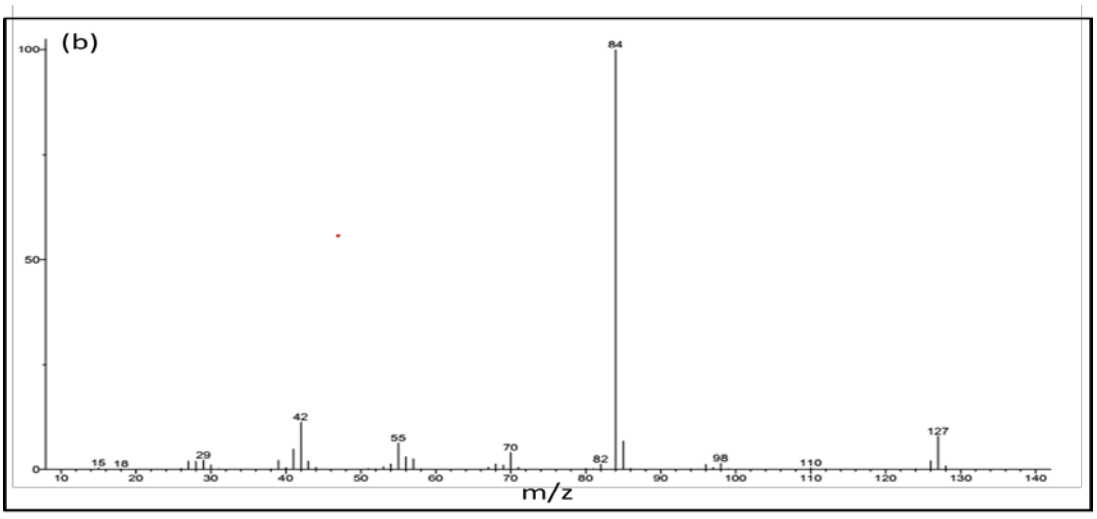
catalyst	Content wt%		
	Cu	Ni	Pd
3Cu-3Ni/ZSM-5	2.91	2.88	
3Cu-3Ni-0.2Pd/ZSM-5	2.92	2.86	0.19
3Cu-3Ni-0.2Pd/ZSM-5*	1.76	2.68	0.18

* 2nd run

Table S3 XPS peak table of 3%Cu-3%Ni-0.2/ZSM-5

Name	Start BE	Peak BE	End BE	Atomic %
C1s	298.88	284.78	280.08	93.16
Cu2p	970.88	932.83	926.08	3.38
Ni2p	890.88	855.76	846.08	3.19
Pd3d	352.08	336.15	330.28	0.26





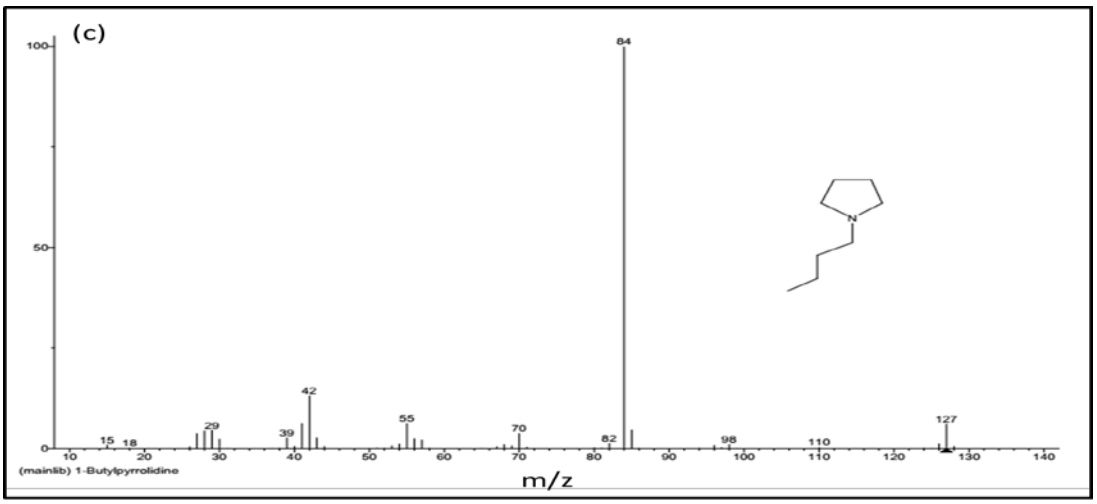


Fig. S1 (a) GC-MS chromatogram of the products under optimization conditions, (b) scan mass spectrum of 1-butylpyrrolidine, (c) standard mass spectrum of 1-butylpyrrolidine

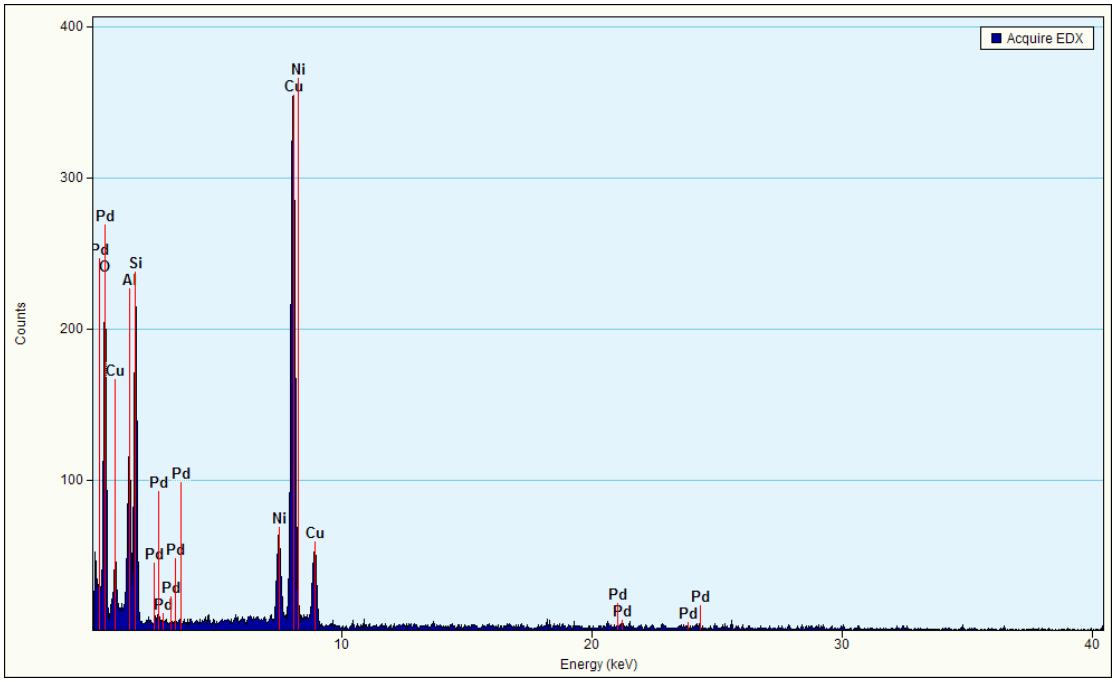


Fig. S2 the EDX pattern of 3Cu-3Ni-0.2Pd/ZSM-5

References

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