Supporting Information

Catalytic Selective Hydrogenation and Rearrangement of 5-Hydroxymethylfurfural to 3-Hydroxymethyl-cyclopentone over Bimetallic Nickel-Copper Catalyst in Water

Shujing Zhang[a,b], Hong Ma[a*], Yuxia Sun[a,b], Yang Luo[a,b], Xin Liu[a,b], Meiyun Zhang[a,b], Jin Gao[a], Jie Xu[a]*

[a.] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Dalian 116023, P. R. China;

[b.] University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

E-mail: xujie@dicp.ac.cn, mahong@dicp.ac.cn

Table of Contents

1 The quantification of products

When 5-HMF was employed as substrate, the conversion and yields of FDA, HCPN, HHD, HHCPEN, and THFDA were calculated with internal standard method as follows:

$$\text{Conversion of 5-HMF(mol\%)} = \left(1 - \frac{\text{moles of unreacted 5-HMF}}{\text{moles of starting 5-HMF}}\right) \times 100\%$$

$$\text{Yield of FDA (mol\%)} = \frac{\text{moles of formed FDA}}{\text{moles of starting 5-HMF}} \times 100\%$$

$$\text{Yield of HCPN (mol\%)} = \frac{\text{moles of formed HCPN}}{\text{moles of starting 5-HMF}} \times 100\%$$

$$\text{Yield of HHD (mol\%)} = \frac{\text{moles of formed HHD}}{\text{moles of starting 5-HMF}} \times 100\%$$

$$\text{Yield of HHCPEN (mol\%)} = \frac{\text{moles of formed HHCPEN}}{\text{moles of starting 5-HMF}} \times 100\%$$

$$\text{Yield of THFDA (mol\%)} = \frac{\text{moles of formed THFDA}}{\text{moles of starting 5-HMF}} \times 100\%$$

Yield to others (non-identified products) = 100% - total yield for all identified products.

2 Schematic illustration of the preparation procedure for Ni-Cu/C catalyst

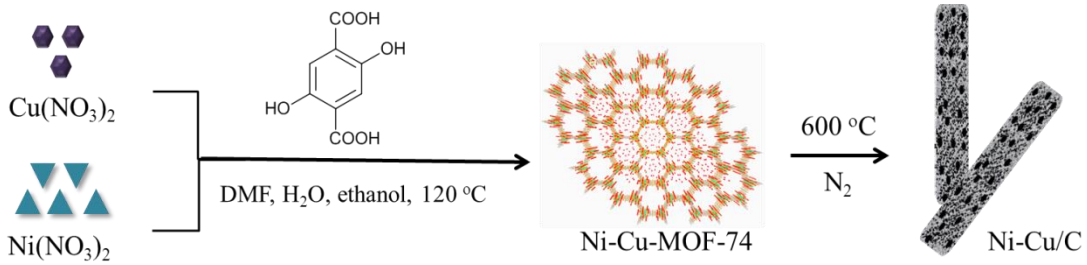


Figure S1. Schematic illustration of the preparation procedure for Ni-Cu/C catalyst.

3 Time course for the hydrogenation and rearrangement of 5-HMF

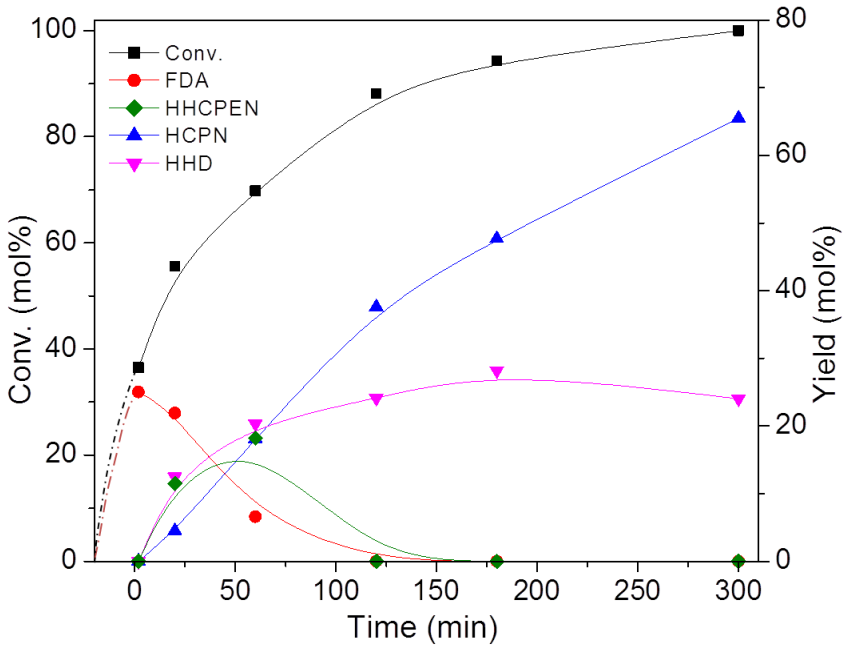


Figure S2. Time course for selective hydrogenation and rearrangement of 5-HMF in water over Ni-Cu/C catalyst.

4 The influence of initial pH values on the colors of the reaction solutions

Figure S3. The influence of initial pH values on the colors of the reaction solutions.

5 Mass spectra of 5-HMF and the hydrogenation and rearrangement products

5.1 Mass spectrum of 5-HMF

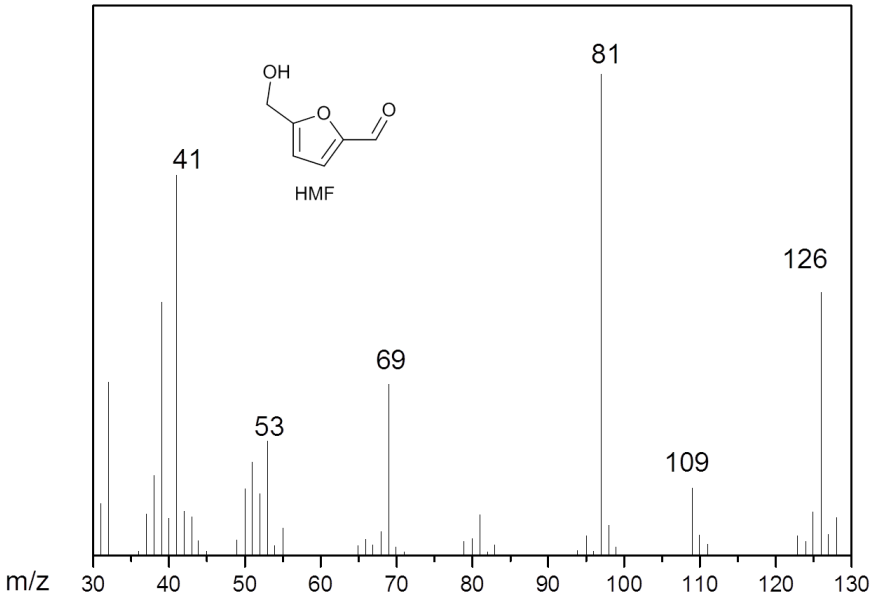


Figure S4. Mass spectrum of 5-HMF.

5.2 Mass spectrum of FDA

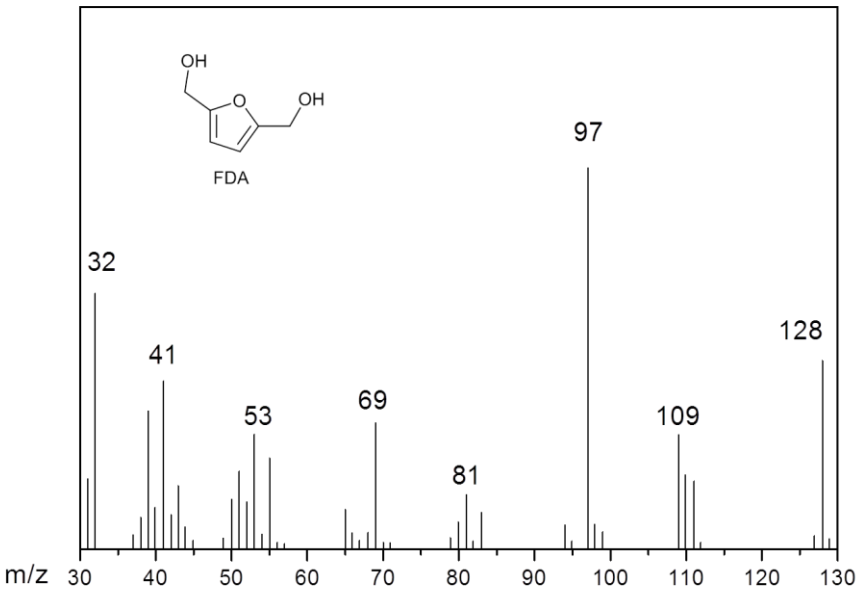


Figure S5. Mass spectrum of FDA.

5.3 Mass spectrum of HCPN

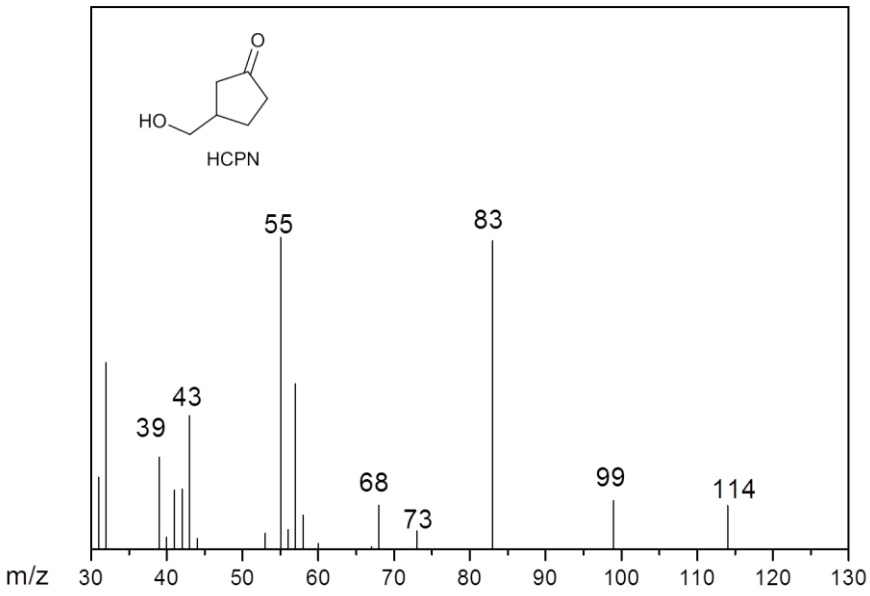


Figure S6. Mass spectrum of HCPN.

5.4 Mass spectrum of HHD

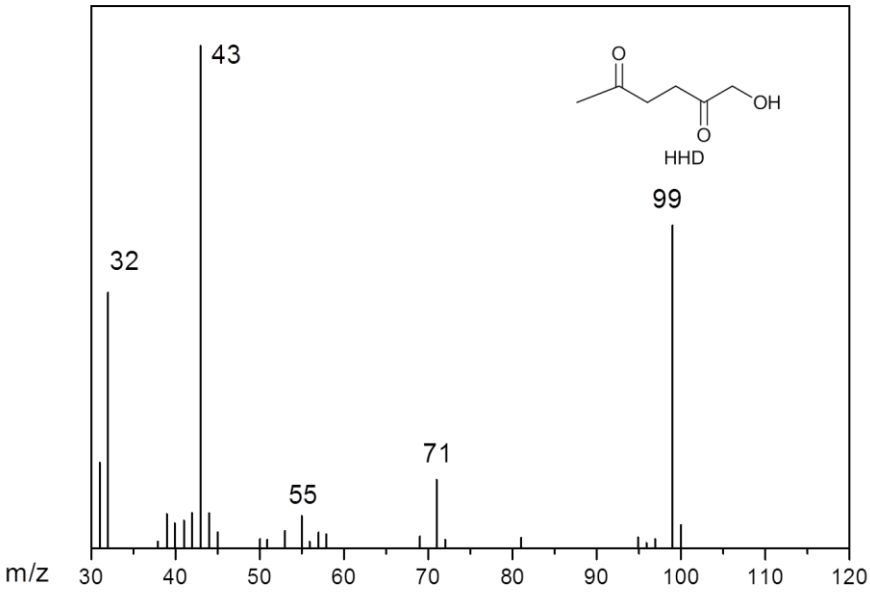


Figure S7. Mass spectrum of HHD.

5.5 Mass spectrum of HHCPEN

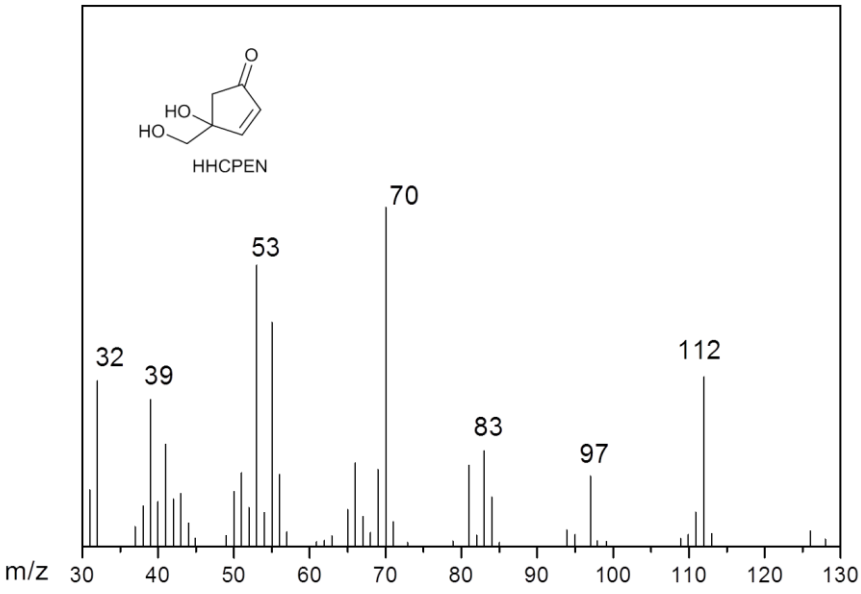


Figure S8. Mass spectrum of HHCPEN.

5.6 Mass spectrum of THFDA

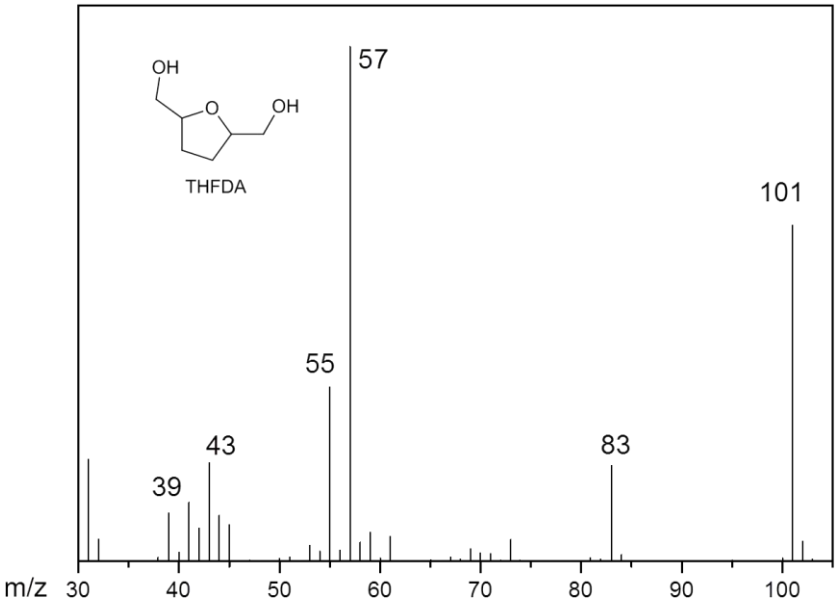


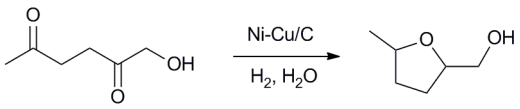
Figure S9. Mass spectrum of THFDA.

6 Hydrogenation and rearrangement of HHD

6.1 Experiments for the hydrogenation and rearrangement of HHD

The hydrogenation and rearrangement experiment over Ni-Cu/C catalyst using HHD as the starting substrate were performed, and the catalytic procedure was as follows: 0.0738 g (0.56 mmol) HHD, 5 mL of water, and 12.5 mg Ni-Cu/C catalyst were added into a 50 mL Parr autoclave, and then the autoclave was sealed. After charging H_2, the reaction mixture was stirred and heated to the specified temperature. The reaction was stopped after desired hours, and then quantitatively analyzed by gas chromatograph (Aligent GC-7890) with internal standard method and qualitatively analyzed by the mass spectrometry using an Agilent 6890N GC/5973 MS instrument.

6.2 Schematic illustration of hydrogenation and rearrangement of HHD



Scheme S1. Hydrogenation and rearrangement of HHD by Ni-Cu/C in water.

6.3 Mass spectrum of 5-methyl-2-hydroxymethyl-tetrafuran

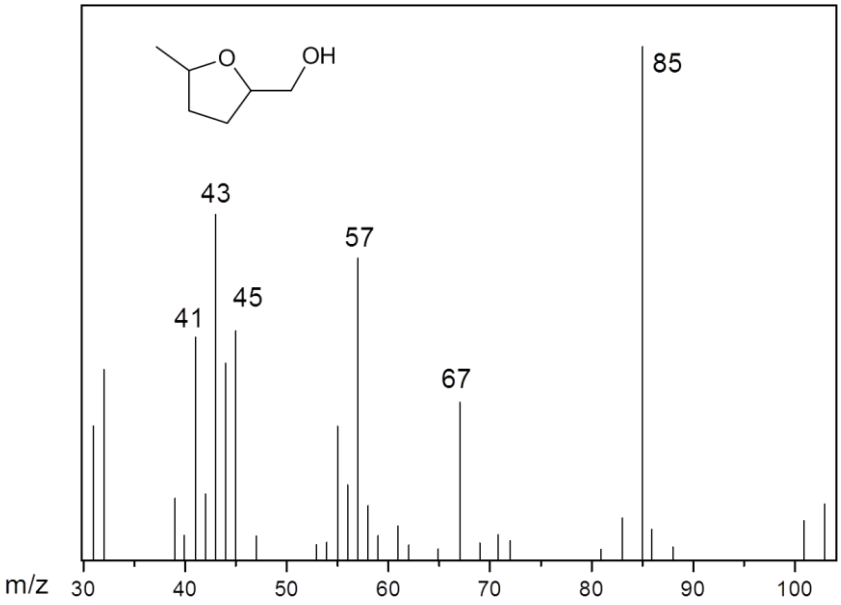


Figure S10 Mass spectrum of 5-methyl-2-hydroxymethyl-tetrafuran.

7 Detection of HCPEN

7.1 Experiment for detection of HCPEN

The enlarged experiment was conducted to verify the existence of HCPEN. The hydrogenation and rearrangement experiment of 5-HMF over Ni-Cu/C catalyst was performed, and the catalytic procedure is as follows: 1.0 g (8 mmol) 5-HMF, 40 mL of water, and 160 mg Ni-Cu/C catalyst were added into a 120 mL stainless autoclave, and then the autoclave was sealed. After charging H_2, the reaction mixture was stirred and heated to 140 ^{o}C. The reaction was stopped after 10 h, and then analyzed by the mass spectrometry using an Agilent 6890N GC/5973 MS instrument. HCPEN was isolated from the reaction solution, were purified by column chromatography on silica gel eluted with ethylacetate/petroleum ether (1:1) and measured by ^{1}H NMR and ^{13}C NMR.

7.2 Mass spectrum of HCPEN

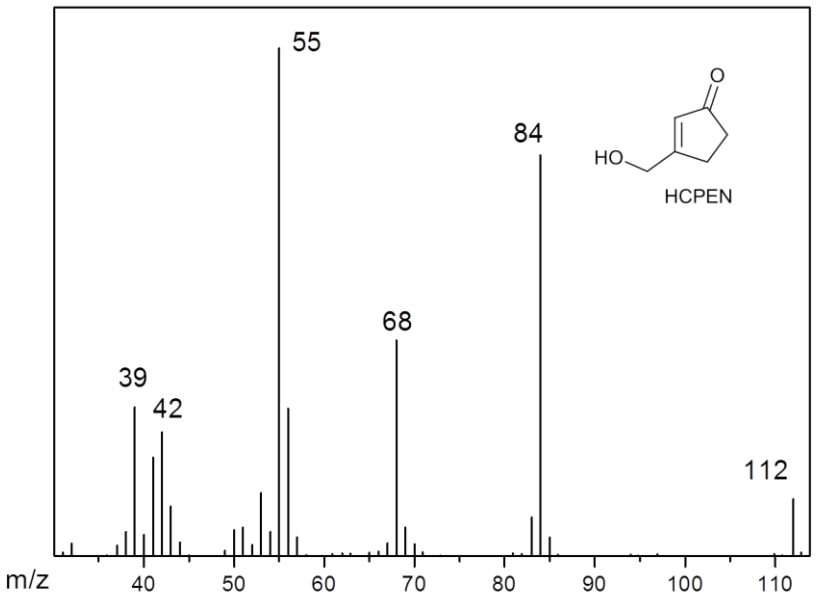
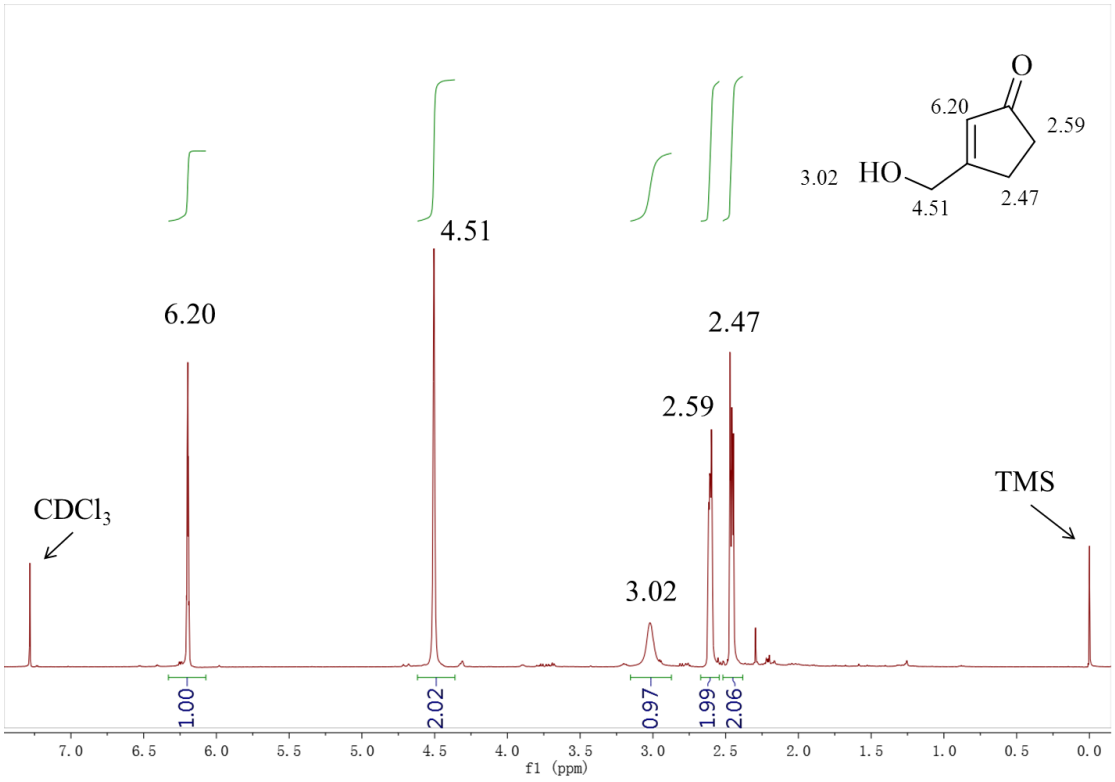


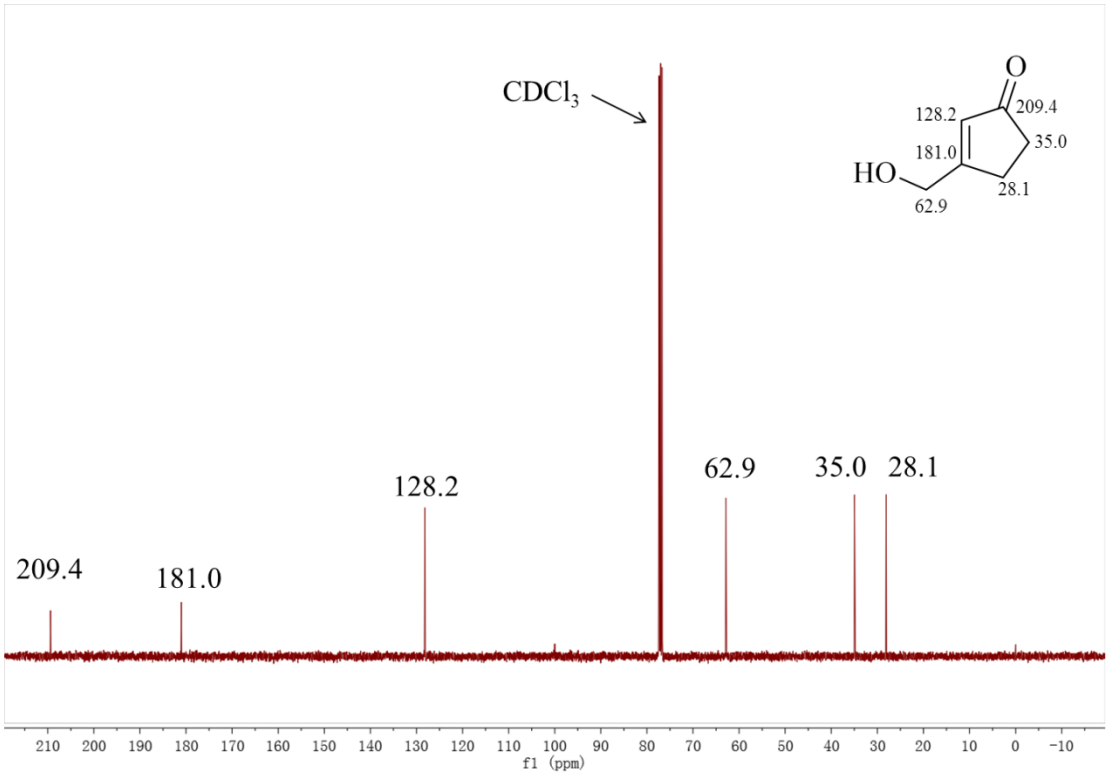
Figure S11. Mass spectrum of HCPEN.

7.3 ^{1}H NMR and ^{13}C NMR of HCPEN



^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.20 (m, 1H), 4.51 (s, 2H), 3.02 (d, 1H), 2.59 (m, 2H), 2.47 (m, 2H).

Figure S12. ^{1}H NMR of HCPEN



^{13}C NMR (101 MHz, $CDCl_3$) δ = 209.4, 181.0, 128.2, 62.9, 35.0, 28.1.

Figure S13. ^{13}C NMR of HCPEN

8. Calculated concentration of H^+ and pH value of water at different temperatures

Table S1. Calculation concentration of H^+, and pH, dependence of K_w according to literature [1]

T(^{o}C)	logK_w	K_w (mol^2/kg^2)	C_{H^+} (mol/kg)	pH
100	-12.264	5.4325×10^{-13}	7.37×10^{-7}	6.13
125	-11.914	1.21899×10^{-12}	1.22×10^{-6}	5.96
150	-11.642	2.28034×10^{-12}	1.49×10^{-6}	5.82

K_w: molality of H^+ ion times molality of OH^-

$C_{H+}=\sqrt{K_w}$

$pH=-\log(C_{H+})$

9. The XPS analysis of different Cu element valence states in catalysts

Table S2. The XPS analysis of different Cu element valence states in catalysts

Catalyst	XPS analysis (%)		
	Cu(I)	Cu(II)	Cu(0)
	932.5 eV	934.6 eV	932.7 eV
Cu/C	39.28	30.96	29.76
Ni-Cu/C	88.26	11.74	-

10. The XPS analysis of different Ni element valence states in catalysts

Table S3. The XPS analysis of different Ni element valence states in catalysts

Catalyst	XPS analysis (%)		
	Ni(II)	Ni(III)	Ni(0)
	854.2 eV	856 eV	852.8 eV
Ni/C	37.05	17.66	45.29
Ni-Cu/C	71.79	12.86	15.35

11. The XRD patterns of Cu/C and Ni/C

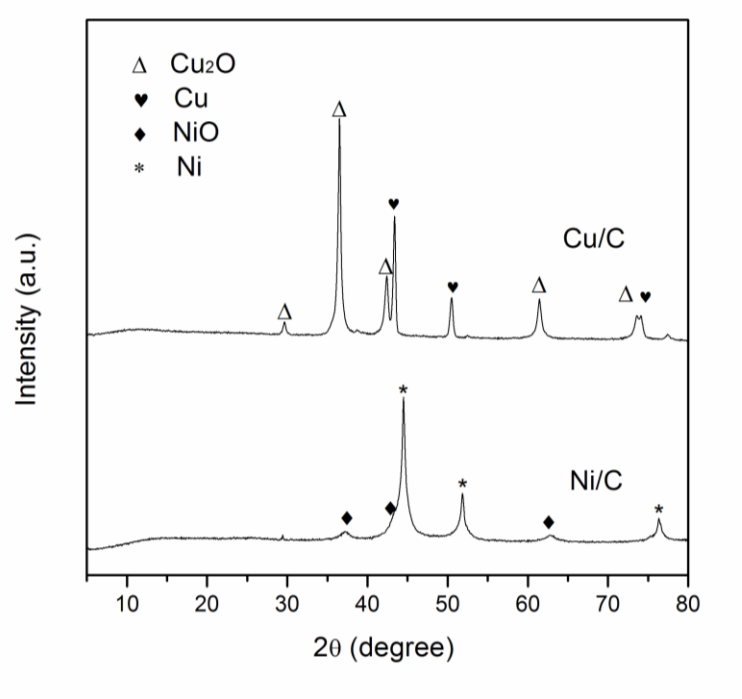


Figure S14. XRD patterns of Cu/C and Ni/C.

12. The Cu 2p and Ni 2p XPS spectrum of different catalysts

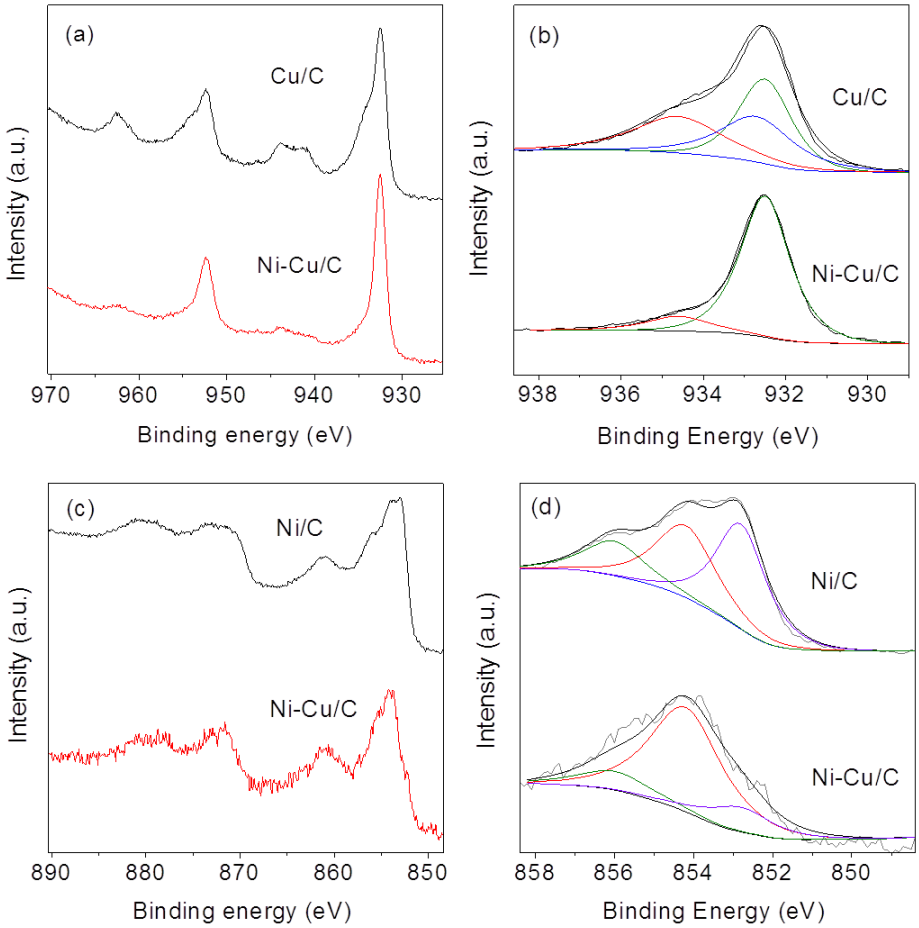


Figure S15. (a) The Cu 2p XPS spectra of Cu/C and Ni-Cu/C, (b) The Cu $2p_{3/2}$ XPS spectra of Cu/C and Ni-Cu/C, (c) The Ni 2p XPS spectra of Ni/C and Ni-Cu/C (d) The Ni $2p_{3/2}$ XPS spectra of Ni/C and Ni-Cu/C

Reference:

1 W. L. Marshall and E. U. Franck, *J. Phys. Chem. Ref. Data*, 1981, **10**, 295-304.

2 P. Prieto, V. Nistor, K. Nouneh, M. Oyama, M. Abd-Lefdil, R. D ́ıaz, *Appl. Surf. Sci.* 2012, **258**, 8807–8813

3 R. Q. Hang, X. B. Huang, L. H. Tian, Z. H. He, B. Tang, *Electrochim. Acta* 2012, **70**, 382–393

4 V. Hayez, A. Franquet, A. Hubin, H. Terryn, *Surf. Interface Anal.* 2004, **36**, 876–879

5 R. W. Fu, N. Yoshizawa, M. S. Dresselhaus, G. Dresselhaus, J. H. Satcher Jr., T. F. Baumann, *Langmuir* 2002, **18**, 10100-10104