Supplementary Information

Effect of Pd/Cu(Co) ratio on catalytic performance of PdCu(Co)/NC bimetallic catalysts for furfural selective hydrogenation

Xin Duan [1], Yu Fang [1], Ziwei Cao, Jingbao Zhang, and Lihua Zhu *

Jiangxi Province Key Laboratory of Functional Crystalline Materials Chemistry, College of Chemistry and Chemical Engineering, Faculty of Materials Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou 341000, Jiang Xi, China.

Corresponding author: zhulihua@jxust.edu.cn (Lihua Zhu)

[1]These authors contributed equally to this work.

1. Experimental section

1.1. Materials

The reagents (cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$), FF ($C_5H_4O_2$), FA ($C_5H_6O_2$), ammonium tetrachloropalladate(II) (($NH_4)_2PdCl_4$), carbon black (C), hexane (C_6H_{14}), THFA ($C_5H_{10}O_2$), anhydrous ethanol (C_2H_6O), melamine ($C_3H_6N_6$), copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$)) were acquired from Aladdin.

1.2. Catalyst synthesis

Synthesis of the NC support: 1.800 g of melamine and 1.800 g of carbon black were added to 100 mL ethanol (carbon black:melamine mass ratio of 1:1). The solution was rotated to dryness at 80 °C in the rotary evaporator and transferred to a muffle furnace, then calcined at 500 °C for 2 h to obtain the NC support.

Synthesis of Pd_3/NC: 200 mg of the NC support was dispersed in 100 mL deionized water, sonicated for 10 min, and then stirred for 0.5 h. 4.0 mL aqueous $(NH_4)_2PdCl_4$ solution (0.0136 mol/L) was added dropwise to the dispersed NC mixture. Rotating the above solution to dryness at 80 °C in the rotary evaporator, then it was dried at 110 °C (3 h). Then it was heated to 400 °C for 2 h in $10\%H_2+90\%N_2$ to obtain Pd_3/NC.

Synthesis of Cu_{10}/NC: 200 mg of the NC support was dispersed in 100 mL deionized water, sonicated for 10 min, and then stirred for 0.5 h. 53 mg $CuCl_2 \cdot 2H_2O$ was added to deionized water to form a 20 mL solution, ultrasound for 10 min and then it was added dropwise to the dispersed the above mixture. Rotating the above solution to dryness at 80 °C in the rotary evaporator, then it was dried at 110 °C (3 h). Then it was heated to 400 °C for 2 h in $10\%H_2+90\%N_2$ to obtain Cu_{10}/NC.

Synthesis of Pd_xCu_y/NC and Pd_xCo_y/NC: Take Pd_3Cu_7/NC as an example, the above Cu_{10}/NC was dispersed in 100 mL water, sonicated for 10 min, and then stirred for 0.5 h. 4.0 mL aqueous $(NH_4)_2PdCl_4$ solution (0.0136 mol/L) was added dropwise to the

above solution. The solution was stirred under ice bath conditions for 6 h. After being filtered, it was dried in vacuum to obtain Pd_3Cu_7/NC. Pd_xCu_y/NC and Pd_xCo_y/NC (x/y represented the mass ratio of Pd/Cu (or Co) with different loadings were also synthesized according to the above method and steps, except that the amount of the precursors added is different. ICP-MS (Agilent ICP-MS 4500-300) was used to determine the metals contents in the catalysts (as listed in Table S1).

Table S1. The mental contents in different catalysts.

Catalyst	Pd loading (wt%)	Cu loading (wt%)	Co loading (wt%)
Pd_3/C	2.46	/	/
Pd_3/NC	2.61	/	/
Cu_{10}/NC	/	9.22	/
Pd_1Cu_9/NC	0.93	8.30	/
Pd_2Cu_8/NC	1.74	7.47	/
Pd_3Cu_7/NC	2.66	6.54	/
Co_{10}/NC	/	/	9.07
Pd_1Co_9/NC	0.91	/	8.14
Pd_2Co_8/NC	1.78	/	7.29
Pd_3Co_7/NC	2.70	/	6.39

1.3. Characterization

With Cu *Ka* radiation (λ = 1.54 Å, 40 kV, 30 mA), the high-speed array detection system, Rigaku Ultima IV (X-ray diffractometer) was used to collect the XRD patterns of the samples. MLA 650F (FEI) collected scanning electron microscope (SEM) images. To analyze the nanostructures and shapes of the catalysts, TEM images were obtained using a JEM-F200 micro-scope. HAADF-STEM and STEM-EDX elemental maps of the samples were obtained using a TECNAI F30. XPS spectra of the catalysts

were collected on a PHI Quantum 2000 scanning ESCA microprobe. The ability of the materials to adsorb and activate hydrogen was tested by H_2-TPD. The procedure was as follows. The samples were firstly treated in argon for 2 h (150 °C) and then cooled to 30 °C in argon before hydrogen adsorption in $5\%H_2+95\%Ar$ (2 h, 30 °C). At the end of the adsorption, the tubes were purged with 50 mL/min Ar until the signal stabilized. The desorption temperature was increased from 30 °C to 800 °C in 50 mL/min Ar. The tubes were returned to ambient temperature at the end of the H_2-TPD.

1.4. Measurement of the catalytic performance

The catalytic performance of the catalysts for FF hydrogenation reaction was evaluated in a stainless steel autoclave (MS-50-316L with a polytetrafluoroethylene lining) with different catalysts. A polytetrafluoroethylene liner containing ethanol FF solution (10 mL) and catalyst (0.03 g) was placed in the autoclave, purged with H_2 for 2 min and sealed by increasing the pressure to 1.5 MPa. The reactor was stirred with a rotor at 870 revolutions per minute and the temperature was raised to 40 °C and held in an H_2 atmosphere (1.5 MPa) for a certain period of reaction time. The reactor was rapidly cooled to 5 °C when the reaction was complete. The liquid phase products were analyzed by Agilent GC 7820A and Agilent GC-MS 597X.

The formulas for calculating the conversion of furfural, selectivity to furfuryl alcohol, and tetrahydrofurfuryl alcohol are as follows:

$$X = \frac{n_{converted\ furfural}}{n_{total\ furfural}} \times 100\% \tag{1}$$

$$S_{furfuryl\ alcohol} = \frac{m_{furfuryl\ alcohol} \times \dfrac{M_{furfural}}{M_{furfuryl\ alcohol}}}{m_{converted\ furfural}} \times 100\% \tag{2}$$

$$S_{tetrahydrofurfuryl\ alcohol} = \frac{m_{tetrahydrofurfuryl\ alcohol} \times \dfrac{M_{furfural}}{M_{tetrahydrofurfuryl\ alcohol}}}{m_{converted\ furfural}} \times 100\% \tag{3}$$

where $n_{converted\ furfural}$, $n_{total\ furfural}$, $m_{furfuryl\ alcohol}$, $m_{converted\ furfural}$, $m_{tetrahydrofurfuryl\ alcohol}$, $M_{furfural}$, $M_{furfuryl\ alcohol}$, $M_{tetrahydrofurfuryl\ alcohol}$, is moles of consuming furfural, moles of total furfural, mass of furfuryl alcohol, mass of consuming furfural, mass of tetrahydrofurfuryl alcohol, relative molecular weight of furfural, relative molecular weight of furfuryl alcohol, relative molecular weight of tetrahydrofurfuryl alcohol, respectively. X is the conversion of furfural, $S_{tetrahydrofurfuryl\ alcohol}$ and $S_{furfuryl\ alcohol}$ was the selectivity of furfuryl alcohol and tetrahydrofurfuryl alcohol, respectively. The mass of different reactants and products were determined by the gas chromatography analysis (Agilent GC 7820A).
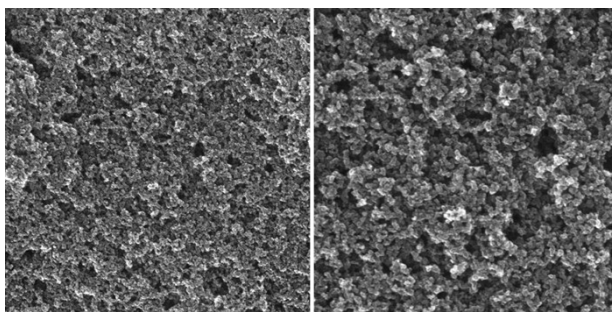
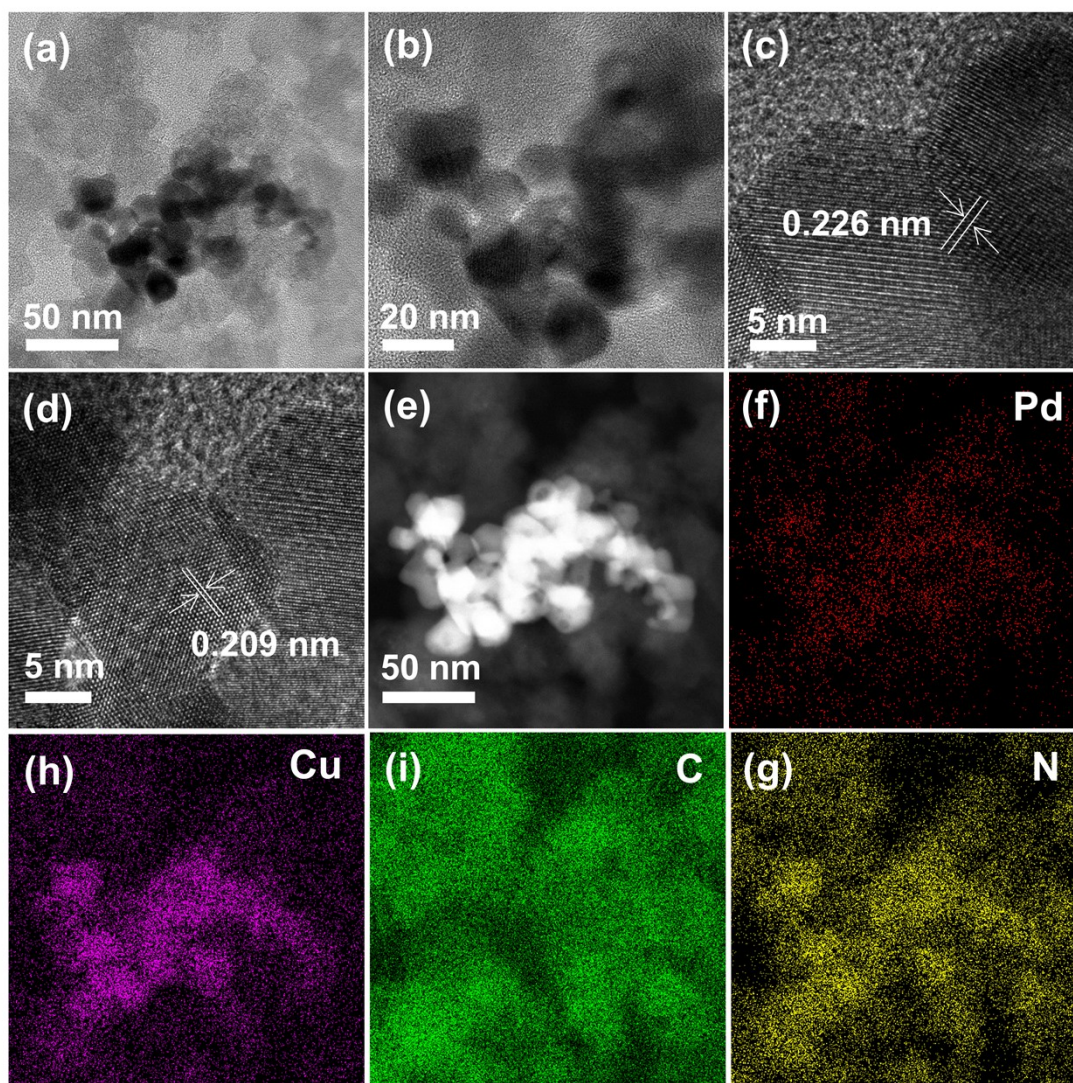## 2. Characterization results

Fig. S1. SEM images of Pd$_3$Cu$_7$/NC.

Fig. S2. (a, b) TEM, (c, d) HRTEM, (e) HAADF-STEM images and (f-g) STEM-EDX elemental mapping of Pd_3Cu_7/NC, Pd, Cu, C, and N.
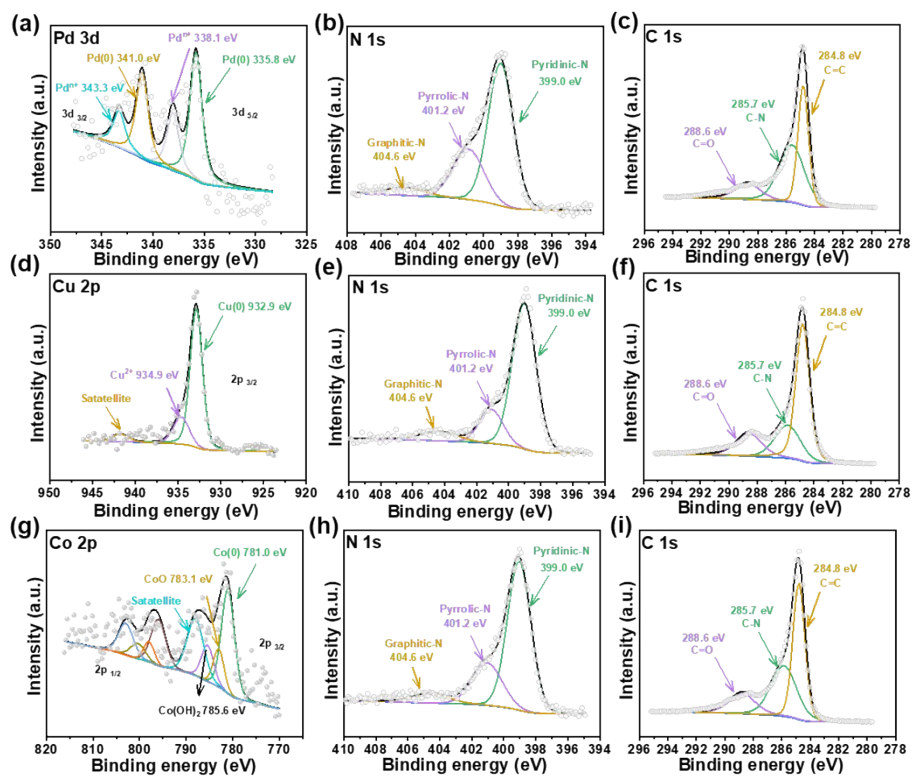
Fig. S3. (a) Pd 3d of Pd$_3$/NC, (d) Cu 2p of Cu$_{10}$/NC, (g) Co 2p of Co$_{10}$/NC, (b, e, h) N 1s XPS spectra of Pd$_3$/NC, Cu$_{10}$/NC, Co$_{10}$/NC, (c, f, i) C 1s XPS spectra of Pd$_3$/NC, Cu$_{10}$/NC, Co$_{10}$/NC XPS spectra of Pd$_3$/NC, Cu$_{10}$/NC, Co$_{10}$/NC.
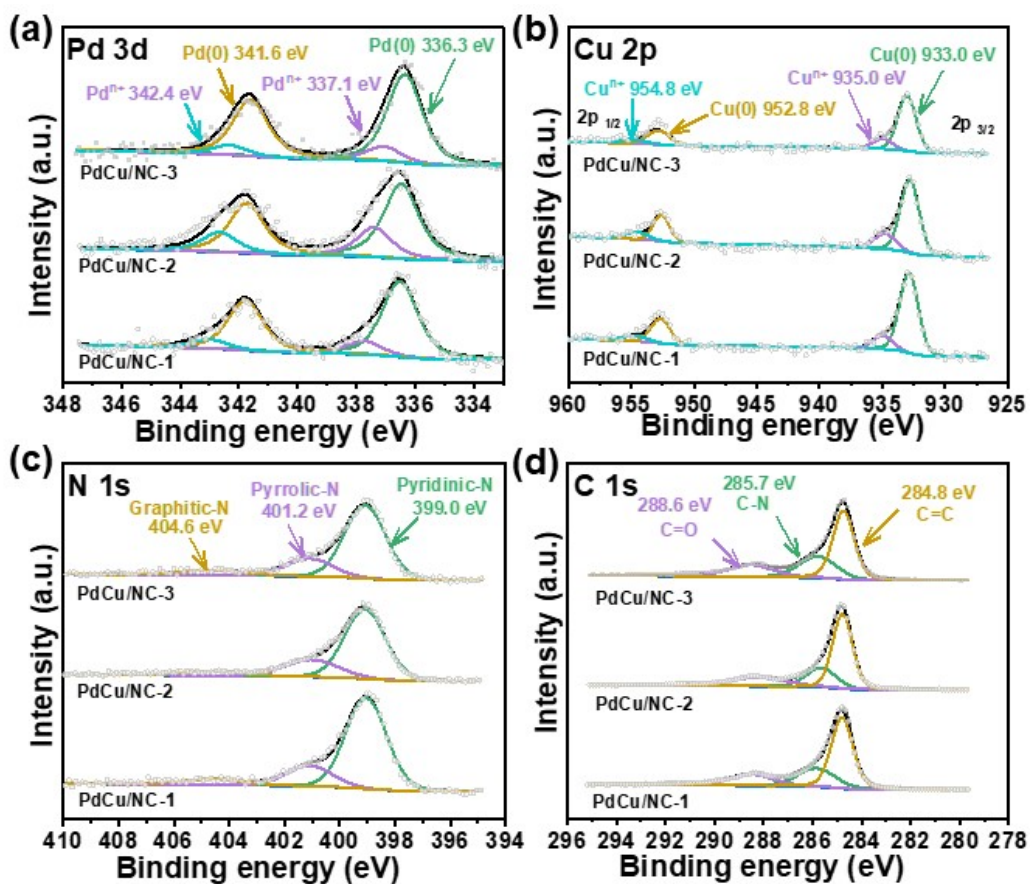
Fig. S4. (a) Pd 3d, (b) Cu 2p, (c) N 1s and (d) C 1s XPS spectra of Pd_1Cu_9/NC, Pd_2Cu_8/NC and Pd_3Cu_7/NC.
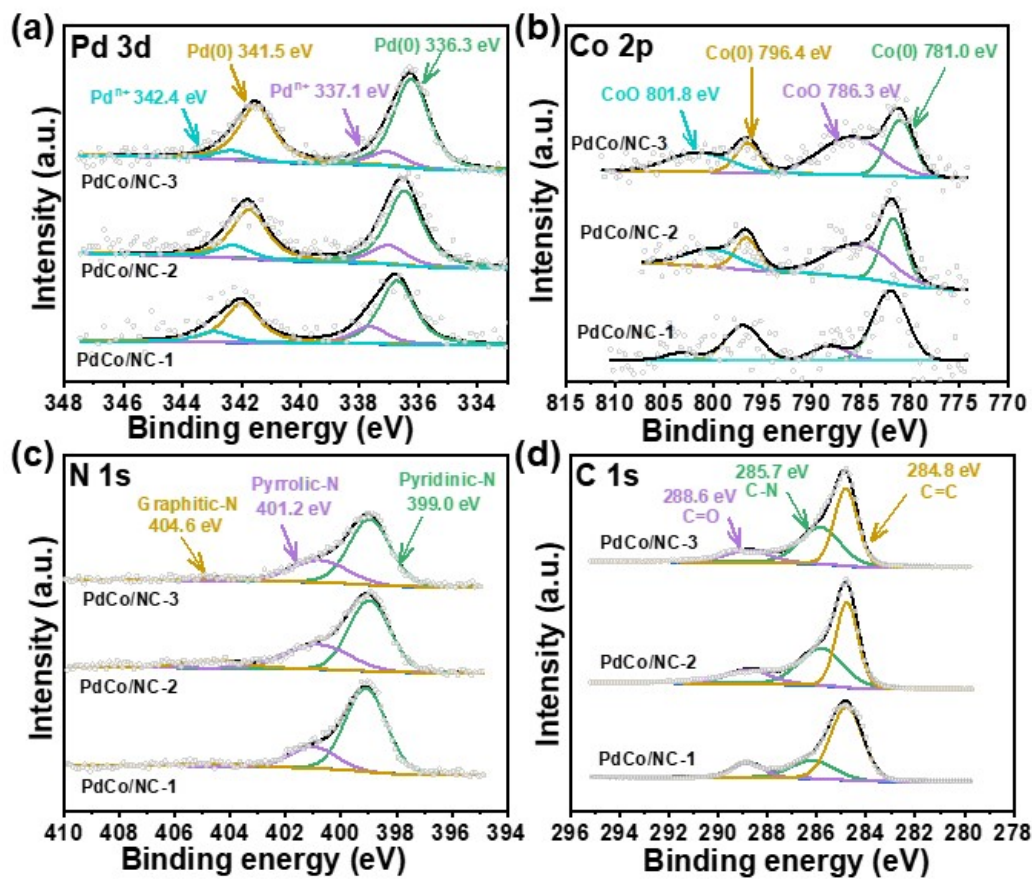
Fig. S5. (a) Pd 3d, (b) Co 2p, (c) N 1s and (d) C 1s XPS spectra of Pd_1Co_9/NC, Pd_2Co_8/NC and Pd_3Co_7/NC.