Development of Robust CuNi Bimetallic Catalysts for Selective Hydrogenation of Furfural to Furfuryl Alcohol under Mild Conditions

Deqin He [1,†], Zheng Liang [2,†], Juwen Gu [1], Xuechun Sang [1], Yujia Liu [1,3,4,*] and Songbai Qiu [1,3,4,*]

[1] School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China
[2] Guangzhou Key Laboratory of Clean Transportation Energy and Chemistry, Guangzhou 510006, China
[3] Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China
[4] Guangdong Provincial Key Laboratory of Plant Resources Biorefinery, Guangzhou 510006, China
* Correspondence: yujia.liu@gdut.edu.cn (Y.L.); qiusb@gdut.edu.cn (S.Q.)
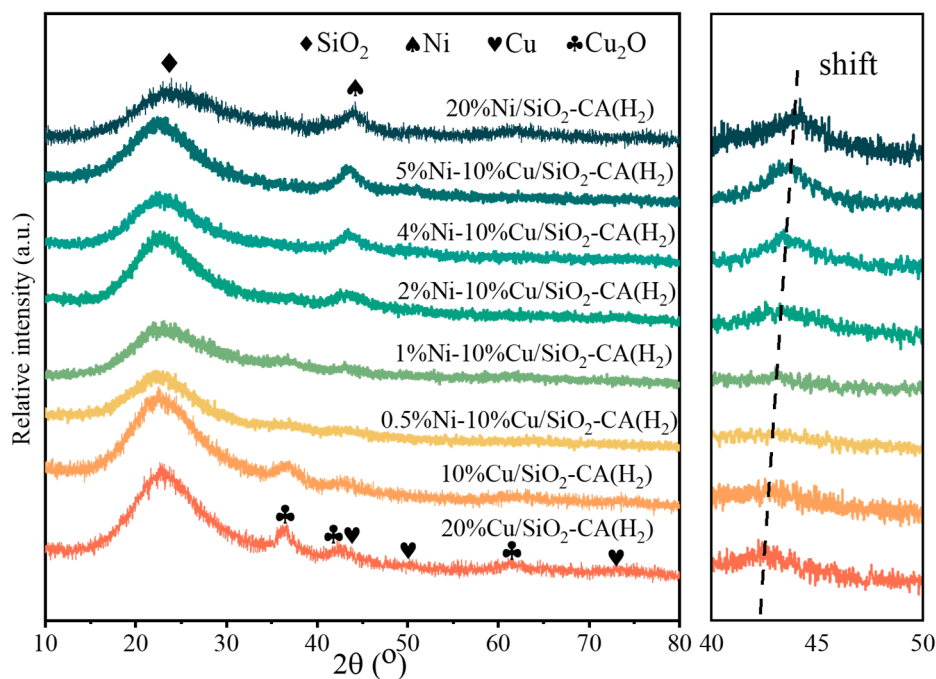† These authors contributed equally to this work.

Figure S1. XRD patterns of x%Ni-10%Cu/SiO$_2$-CA(H$_2$) with varying Ni contents.

X-ray powder diffraction (XRD) was conducted on a Japanese RigakuD/MiniFlex600 diffractometer utilizing a Cu Kα-ray source (40 kV and 30 mA) at a wavelength of λ = 1.54 nm. The scanning range (2θ) was 5 °~80 ° in steps of 0.027 °/s at a scanning speed of 10 °/min and a test temperature of 25 ℃.
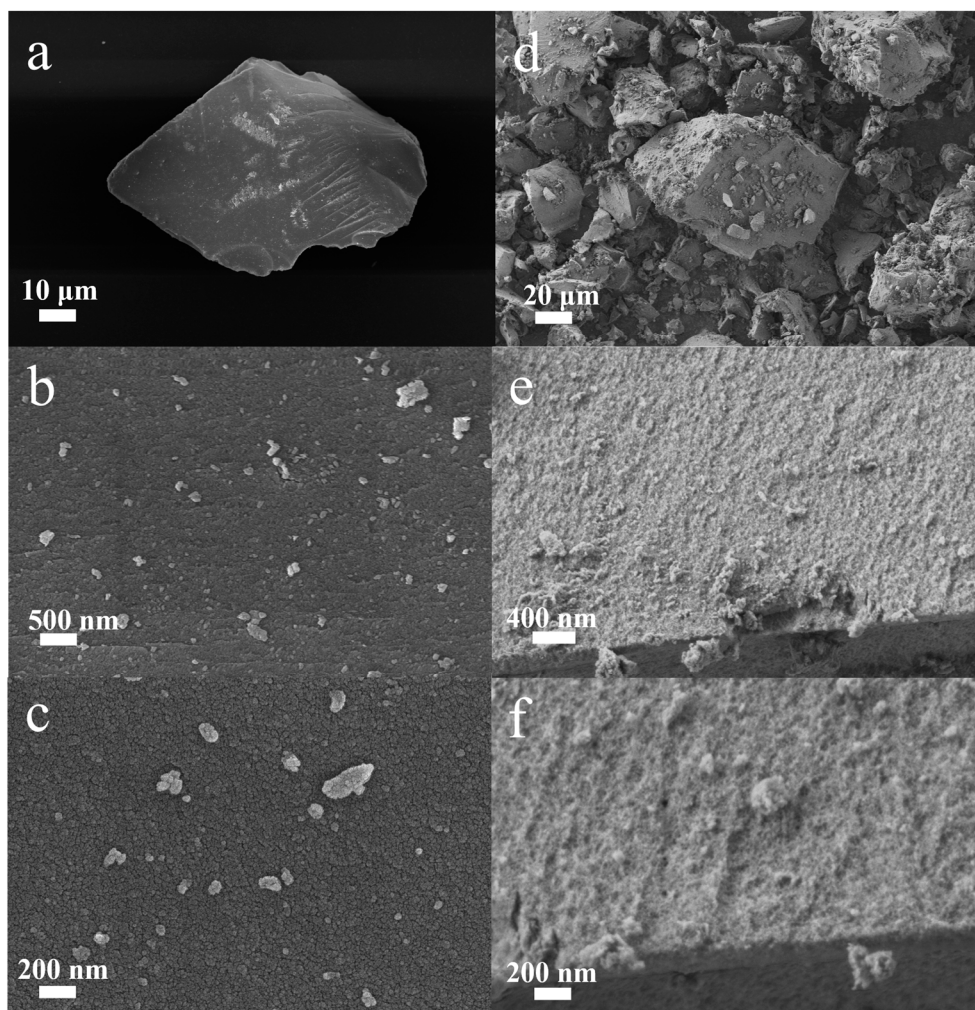
Figure S2. SEM images of (a-c) 10%Cu/SiO$_2$-CA(H$_2$) and (d-f) 0.5%Ni-10%Cu/SiO$_2$-CA(H$_2$).

A scanning electron microscope (SEM) of the MERLIN type was employed for the observation of sample morphology and the analysis of sample composition. Prior to testing, the samples were subjected to a fine grinding process and ensured to be well-dried. Subsequently, the samples were affixed to a sample stage and introduced into the instrument for analysis. As evidenced by the SEM images, both the 10%Cu/SiO$_2$-CA(H$_2$) and 0.5%Ni-10%Cu/SiO$_2$-CA(H$_2$) catalysts exhibit irregular lump-like structures. The addition of a small amount of Ni does not result in a notable alteration to the surface morphology of the catalysts. Following direct calcination under H$_2$ atmosphere, the catalyst surface undergoes a contraction, resulting in the formation of numerous spherical structures.
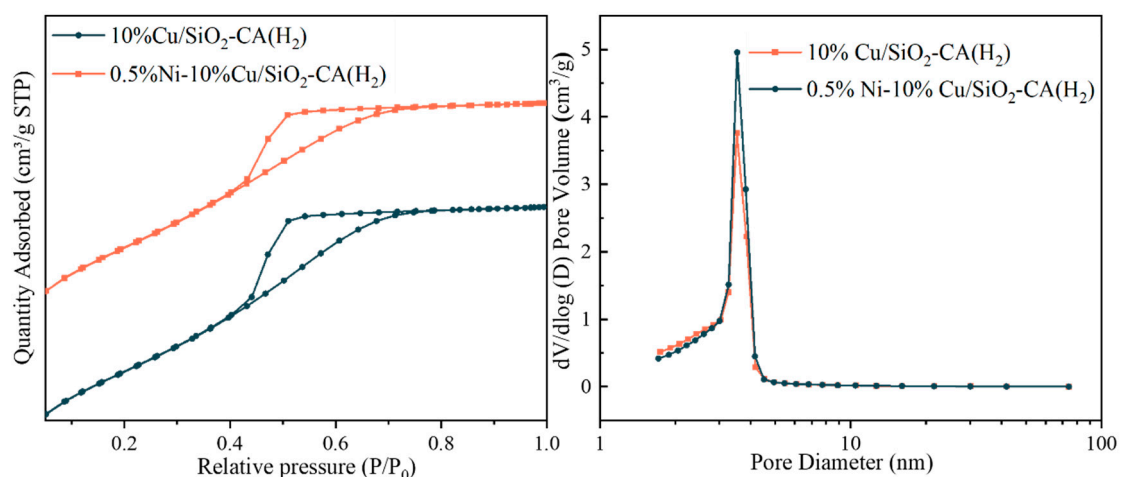
Figure S3. N_2 adsorption-desorption isotherms and pore size distributions of typical samples.

As illustrated in Figure S3, all the catalysts exhibit the characteristic IV-type isotherms with a discernible H2-type hysteresis loop, indicative of a mesoporous structure. Additionally, Figure S3 depicts that the Barret-Joyner-Halenda (BJH) pore size distributions of the catalysts are predominantly concentrated around 3.0 nm. Furthermore, the specific surface area, average pore volume, and pore size of the catalysts are summarized in Table S1.
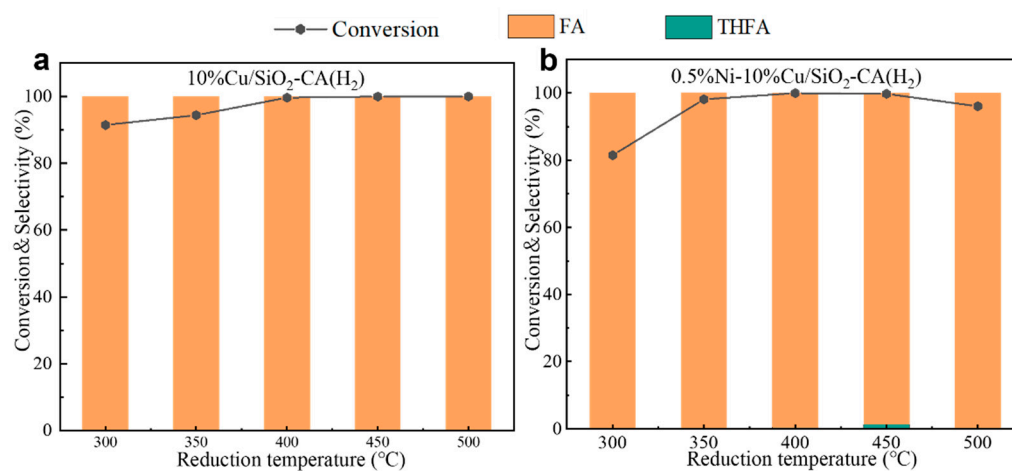
Figure S4. Catalytic performance of (a) 10%Cu/SiO$_2$-CA(H$_2$) and (b) 0.5%Ni-10%Cu/SiO$_2$-CA(H$_2$) at different calcination temperatures in H$_2$.

Reaction conditions: 0.32 g furfural, 2.88 g isopropanol, 0.089 g catalyst, 55 °C, 4 MPa H$_2$, 2 h.
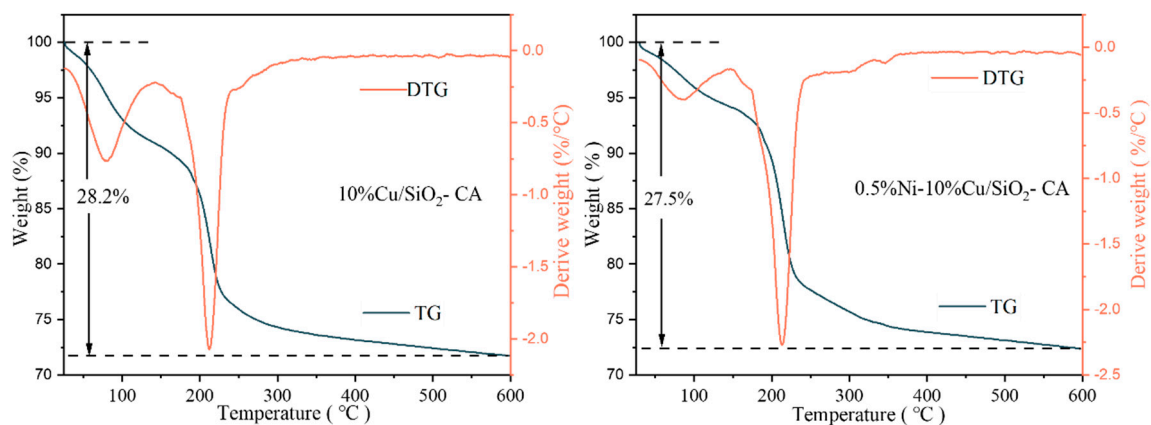
Figure S5. TG profiles of typical samples.

The mass changes during the carbonization of the samples were determined using a thermogravimetric analyzer. A STA449F5 thermogravimetric analyzer (NETZSCH, Germany) was used. Test method: the sample was placed in a crucible (made of Al_2O_3), the crucible was covered with a lid and the heating rate was 10 ℃/min, the temperature range was 50-900 ℃.
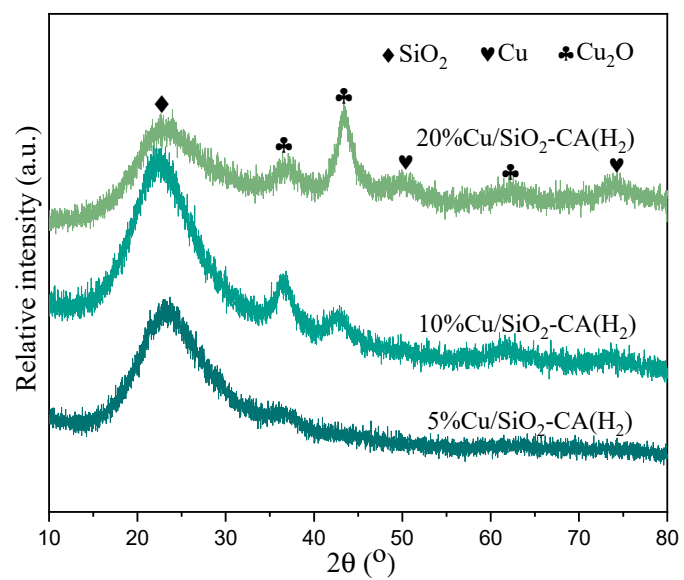
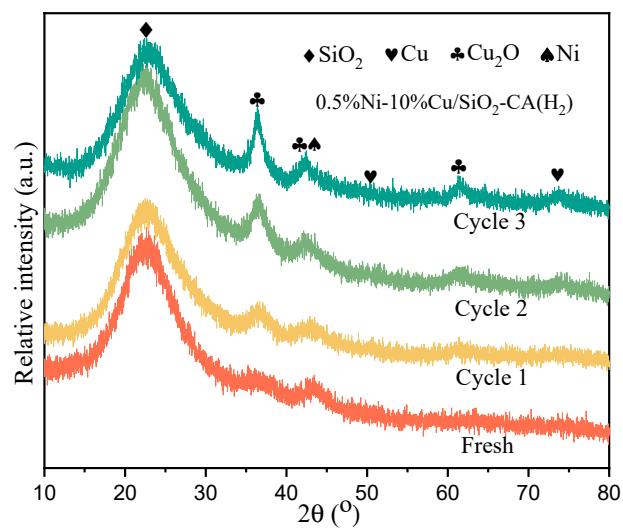Figure S6. XRD patterns of x%Cu/SiO$_2$-CA(H$_2$) catalysts with varying Cu contents.

Figure S7. XRD patterns of the 0.5%Ni-10%Cu/SiO$_2$-CA(H$_2$) catalyst after multiple reaction cycles.

Table S1. Textural properties of the typical samples.

Samples [a]	S_{BET} [b] (m^2/g)	Pore volume [c] (cm^3/g)	Pore diameter [c] (nm)
10%Cu/SiO$_2$-CA(H$_2$)	634.4	0.52	3.0
0.5%Ni-10%Cu/SiO$_2$-CA(H$_2$)	627.1	0.54	3.1

[a] The 10%Cu/SiO$_2$-CA(H$_2$) and 0.5%Ni-10%Cu/SiO$_2$-CA(H$_2$) samples were subjected to hydrogen reduction at 400 °C.

[b] The surface area of the various samples was calculated using the Brunner-Emmet-Teller (BET) method.

[c] The pore volume and average pore diameter of samples were calculated based on Barret-Joyner-Halenda (BJH) desorption method.

Table S2. Comparison of the catalytic performance of typical samples versus commercial catalysts.

Samples	H_2/(MPa)	Furfural conversion/(%)	Selectivity/(%)	
			Furfuryl alcohol	Tetrahydrofurfuryl alcohol
Commercial 5%Ru/C	4	93.5	97.3	2.7
Commercial 5%Pt/C	4	85.2	99.2	0.8
Commercial 5%Pd/C	4	99.7	0	100.0
Raney Ni	4	100	38.3	61.7
10%Cu/SiO$_2$-CA(H$_2$)	4	99.6	99.7	0.3
0.5%Ni-10%Cu/SiO$_2$-CA(H$_2$)	1	95.7	99.9	0
0.5%Ni-10%Cu/SiO$_2$-CA(H$_2$)	2	99.4	99.9	0

Reaction conditions: 0.32 g furfural, 2.88 g isopropanol, 0.089 g 0.5%Ni-10%Cu/SiO$_2$-CA(H$_2$), 0.16 g commercial 5%Ru/C, 0.16 g commercial 5%Pt/C, 0.16 g commercial 5%Pd/C and 0.50 g wet Raney Ni catalyst, 55 °C, 2 h.

Table S3. Chemical compositions of the catalysts.

Catalysts	Cu[a] (wt.%)	Ni[a] (wt.%)
10%Cu/SiO$_2$-CA	9.6502	0
0.5%Ni-10%Cu/SiO$_2$-CA	8.9219	0.4367

[a] Determined by ICP-OES analysis.

The Ni and Cu loadings were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using PerkinElmer Optima 8000 instrument. Before the measurement, the sample was dissolved in aqua regia and diluted with water.

Table S4. Quantitative analysis of Cu based on the XPS results.

Catalysts	Cu^0		Cu^+	
	B.E. [a] (eV)	Percentage [b] (%)	B.E. [a] (eV)	Percentage [b] (%)
10%Cu/SiO2-CA	569.2	61.30	572.8	38.70
0.5%Ni-10%Cu/SiO$_2$-CA	569.8	40.37	572.5	59.63

[a] Binding energy.

[b] The percentage of Cu^0 and Cu^+ peak areas was determined by deconvolution of Cu LMM AES spectra.

Table S5. Catalytic performance of Ni and Cu monometallic catalysts.

Samples	T (°C)	H$_2$ (MPa)	Furfural conversion (%)	Selectivity/(%)	
				Furfuryl alcohol	Tetrahydrofurfuryl alcohol
0.5%Ni/SiO$_2$-CA(H$_2$)	55	4	0.9	96.2	3.8
4%Ni/SiO$_2$-CA(H$_2$)	55	4	90.3	67.6	32.4
5%Cu/SiO$_2$-CA(H$_2$)	55	4	69.6	>99	0
10%Cu/SiO$_2$-CA(H$_2$)	55	4	99.9	>99	0
20%Cu/SiO$_2$-CA(H$_2$)	55	4	88.9	>99	0

Reaction conditions: 0.32 g furfural, 2.88 g isopropanol, 0.089 g catalysts, 2 h.

Table S6. Reusability of the 0.5%Ni-10%Cu/SiO$_2$-CA(H$_2$) catalyst.

catalyst	Number of cycles	T/°C	H$_2$/MPa	t/h	Furfural conversion/%	Furfuryl alcohol Selectivity/%
0.5%Ni-10%Cu/SiO$_2$-CA(H$_2$)	1	55	2	2	99.5	>99
	2	55	2	2	91.6	>99
	3	55	2	2	77.7	>99

Reaction conditions: 0.32 g furfural, 2.88 g isopropanol, 0.089 g catalyst.