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*Electronic Supplementary Information (ESI) for*

# Highly efficient synchronized production of phenol and 2,5-dimethylfuran through a bimetallic Ni-Cu catalyzed dehydrogenation-hydrogenation coupling process without external hydrogen and oxygen supply

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## Experimental section

### Materials.

$Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$ were purchased from Sinopharm Chemical Reagent Co. Ltd. NaOH and $Na_2CO_3$ were supplied by Beijing Chemical Reagent Company. The reaction solvent and substrates (i. e. 1,4-dioxane, HMF, 2,5-DMF, CHL, CHN, CHO, phenol, and various substituted phenols) were purchased from TCI or J&K Scientific Ltd. All these chemicals were used as received.

### Preparation of Catalysts.

NiCuAl-LDH precursors with different Ni/Cu ratios were prepared by a simple separate nucleation and aging steps method developed by our group.[1] In a typical process, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$ with a $[M^{2+}]/[M^{3+}]$ molar ratio of 3 : 1 ($[M^{3+}] = 0.20$ M) and a $[Ni^{2+}]/[Cu^{2+}]$ molar ratio of $x/y$ ($x/y = 3/0$, 2/1, 1.5/1.5, 1/2, and 0/3) were well dissolved in 100 mL of deionized water. Then NaOH and $Na_2CO_3$ (maintain $[OH^-] = 1.6[M^{2+} + M^{3+}]$ and $[CO_3^{2-}] = 2[M^{3+}]$) were dissolved in another 100 mL of deionized water. Subsequently, the above two solutions were simultaneously added to a rotating liquid-film reactor with the rotor speed of 3000 rpm and mixed for 3 min. The resulting suspension was placed into a water bath and aged at 60 °C for 6 h. Then centrifugation and washing were performed for several times with deionized water until pH = 7.0. The resulting LDH solids were denoted as $Ni_xCu_yAl$-LDH and dried at 70 °C overnight. Subsequently, the LDH precursors were calcined in static air at 500 °C for 4 h, and the calcined samples were denoted as C-$Ni_xCu_y$. For catalytic tests, the obtained C-$Ni_xCu_y$ samples were loaded into the reactor and reduced *in situ* in 10% v/v $H_2$/Ar atmosphere at 600 °C for 4 h at a ramping rate of 2 °C $min^{-1}$ (see the **Catalytic test** section for details). For characterization, the C-$Ni_xCu_y$ samples were reduced in a tube furnace under the same conditions as the test samples. The obtained reduced catalysts were denoted as $Ni_xCu_y$.

For comparison, the $Ni/Al_2O_3$, $Cu/Al_2O_3$, and $Ni$-$Cu/Al_2O_3$ catalysts were also prepared by the conventional impregnation method using $Al_2O_3$ as supports. The loading amounts of metals and the calcination/reduction conditions were the same as that of the $Ni_xCu_y$ catalysts.

## Characterization.

The elemental analysis was performed using a Shimadzu ICPS-75000 inductively coupled plasma atomic emission spectrometer (ICP-AES). XRD patterns of samples were obtained on a Shimadzu XRD-6000 diffractometer with graphite-filtered $Cu_{K\alpha}$ source ($\lambda = 0.15418$ nm) at 40 kV and 40 mA. HRTEM and HAADF-STEM were carried out on a JEOL 2010F instrument combined with an X-ray energy dispersive spectroscopy (EDS) system. $N_2$ adsorption-desorption isotherms of samples were obtained on a Micromeritics ASAP 2020 sorptometer apparatus at -196 °C. $H_2$-TPR measurements were performed on a Micrometric ChemiSorb 2920 chemisorption instrument with a thermal conductivity detector (TCD). The calcined sample (0.1 g) was loaded in a quartz U-tube reactor and degassed at 200 °C for 2 h under argon flow (30 mL $min^{-1}$). Then TPR was conducted in a stream of 10 % v/v $H_2/Ar$ (30 mL $min^{-1}$) with a heating rate of 5 °C $min^{-1}$ up to 900 °C. XPS were recorded on a Thermo VG ESCALAB 250 X-ray photoelectron spectrometer using monochromatic Al Kα X-ray as the excitation source (1486.6 eV). The samples were transferred to the vacuum chamber immediately after reduction.

**Catalytic test.**

The vapor-phase coupling reaction of CHL and HMF was performed in an integral fixed-bed tubular reactor with an inner diameter of 10 mm under atmospheric pressure. The calcined samples (3.0 g) were loaded into the middle of the reactor with quartz powders (20-40 mesh) packed in both sides of the catalyst bed, and reduced *in situ* in a flow of 10 % v/v $H_2/Ar$ (30 mL $min^{-1}$) under atmospheric pressure at 600 °C for 4 h prior to the reaction. After cooling down to the reaction temperature, a mixture of the reactants (with CHL/HMF molar ratio of 2) was dissolved in 1,4-dioxane (HMF mass fraction as 20 % wt.%) and fed into the reactor controlled by a sampling pump. The initial $N_2$/mixture molar ratio was set as 13.0 and the LHSV values were set from 0.4 to 1.6 $h^{-1}$ during the reaction. All the reaction results (i.e. conversions and selectivities) in all figure or tables are collected when the reaction process reached the steady state.

Gas chromatography (Agilent GC-7890B) equipped with a DB-WAX capillary column (30.0 m×250 μm×0.25 μm) using flame ionization detector was employed for the analysis of the liquid products. The products were identified by comparison with known standards, and biphenyl was used as an internal standard to quantitatively analyze liquid products.

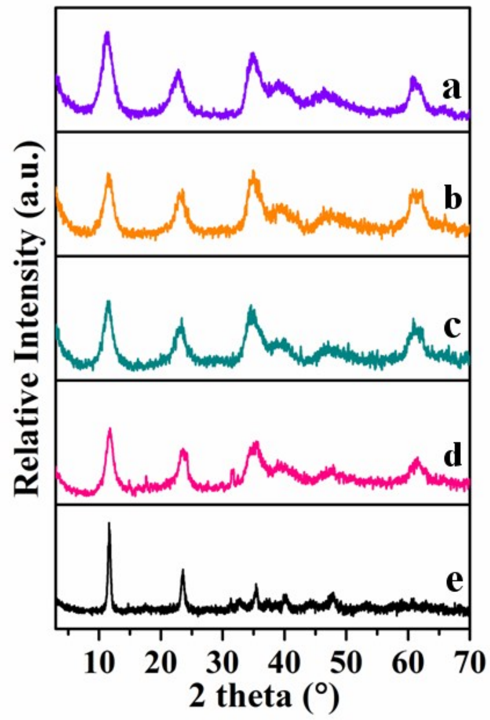


**Fig. S1** XRD patterns of NiCuAl-LDH precursors with different Ni/Cu molar ratio of (a) 3:0, (b) 2:1, (c) 1.5:1.5, (d) 1:2 and (e) 0:3.

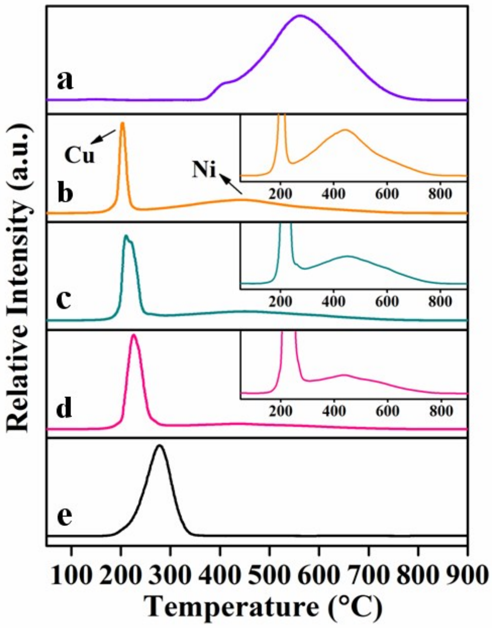


**Fig. S2** TPR profiles of calcined C-Ni$_x$Cu$_y$ samples: (a) C-Ni$_3$Cu$_0$, (b) C-Ni$_2$Cu$_1$, (c) C-Ni$_{1.5}$Cu$_{1.5}$, (d) C-Ni$_1$Cu$_2$, and (e) C-Ni$_0$Cu$_3$. The insets in (b-d) show the enlarged views.

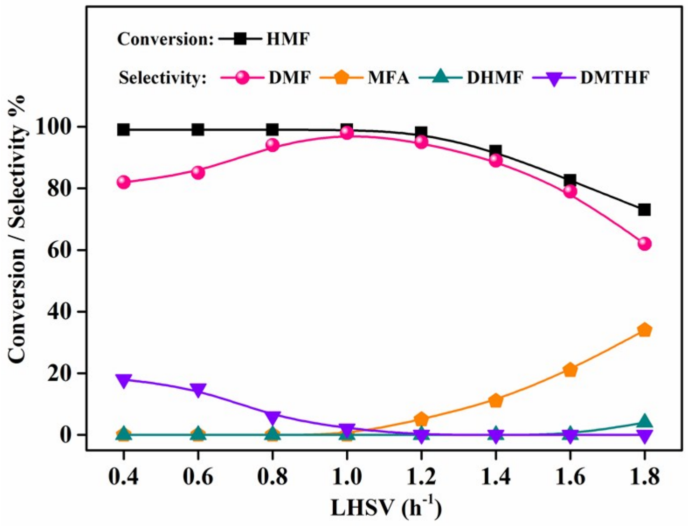
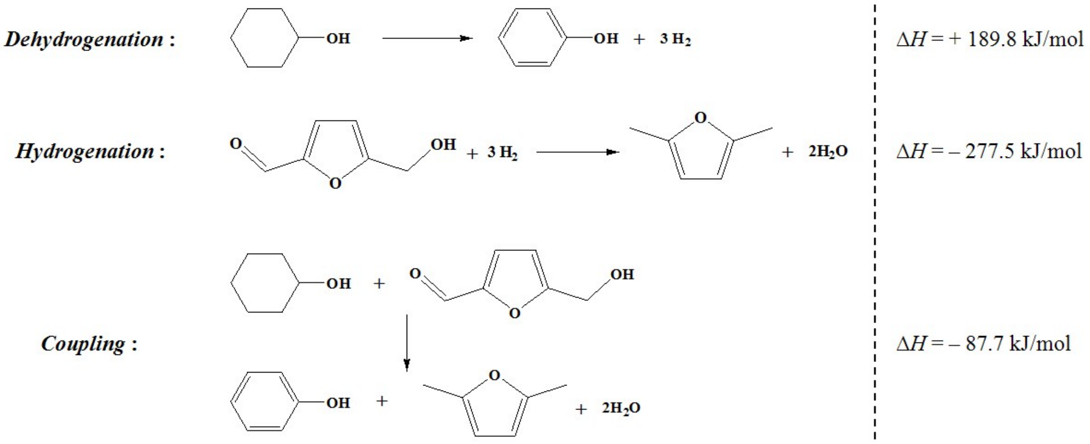


**Fig. S3** Change in the conversions and the selectivies over the $Ni_2Cu_1$ catalyst with the LHSV value in the single HMF hydrogenation using external $H_2$. Reaction conditions: $H_2$: 1 atm, $H_2$/HMF = 13 (in mole), $T$ = 240 °C.



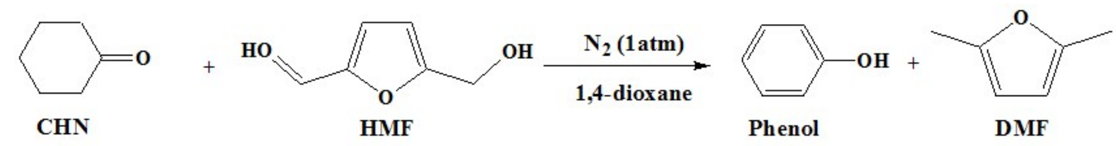
**Scheme S1** Reaction enthalpies of single dehydrogenation, single hydrogenation, and coupling process. [2,3]

**Table S1** Textural properties of different catalysts

| Entry | Catalyst | $S_{BET}$ [a]($m^2/g$) | Average pore size (nm) |
|---|---|---|---|
| 1 | $Ni_3Cu_0$ | 90 | 4.6 |
| 2 | $Ni_2Cu_1$ | 87 | 5.1 |
| 3 | $Ni_{1.5}Cu_{1.5}$ | 85 | 5.9 |
| 4 | $Ni_1Cu_2$ | 76 | 6.0 |
| 5 | $Ni_0Cu_3$ | 74 | 6.2 |

[a] BET specific surface area.

**Table S2** Catalytic performance of the coupling reaction between CHN and HMF over various catalysts [a]



| Entry | Catalyst | Con.% (CHN) | Con.% (HMF) | Selectivity % [b] | | Selectivity % [c] | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Phenol | CHO | DMF | MFA | DHMF |
| 1 | $Ni_3Cu_0$ | 99 | 97 | 92 | 8 | 92 | 8 | 0 |
| 2 | $Ni_2Cu_1$ | 99 | 99 | 99 | 1 | 95 | 5 | 0 |
| 3 | $Ni_{1.5}Cu_{1.5}$ | 78 | 92 | 90 | 10 | 75 | 19 | 6 |
| 4 | $Ni_1Cu_2$ | 43 | 81 | 86 | 14 | 57 | 25 | 18 |
| 5 | $Ni_0Cu_3$ | 11 | 39 | 72 | 28 | 29 | 33 | 38 |
| 6 | $Ni/Al_2O_3$ | 72 | 88 | 78 | 22 | 72 | 28 | 0 |
| 7 | $Cu/Al_2O_3$ | 5 | 19 | 64 | 36 | 16 | 32 | 52 |
| 8 | $Ni\text{-}Cu/Al_2O_3$ | 76 | 90 | 88 | 12 | 80 | 20 | 0 |
| 9 [d] | $Ni_3Cu_0$+$Ni_0Cu_3$ | 78 | 92 | 85 | 15 | 77 | 15 | 8 |

[a] Reaction conditions: $N_2$: 1 atm, $T = 240$ °C, CHN/HMF = 2 (in mole), $N_2$/(CHN + HMF) = 13 (in mole), LHSV(CHN + HMF) = 1.0 $h^{-1}$. [b] Selectivity of the dehydrogenation part. [c] Selectivity of the hydrogenation part. [d] The physical mixture of $Ni_3Cu_0$ and $Ni_0Cu_3$.

## References

1 Y. Zhao, F. Li, R. Zhang, D. G. Evans and X. Duan, *Chem. Mater.*, 2002, **14**, 4286–4291.

2 CRC handbook of chemistry and physics, CRC press, 2014.

3 Breaking the Chemical and Engineering Barriers to Lignocellulosic Biofuels: Next Generation Hydrocarbon Biorefineries (Ed.: G. H. Huber) NSF, 2008.