

Supporting Information

Selective Hydrogenation of Biomass-Derived 2(5H)-Furanone to γ -Butyrolactone over Ni-Based Bimetallic Catalysts

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(11 Pages including **Equations (E1)~(E5)**, **Tables S1~S4** and **Figures S1~S5**)

The supported catalysts were evaluated for the liquid-phase hydrogenation of 2(5H)-furanone. The conversion of 2(5H)-furanone and selectivity to GBL were calculated as:

$$\text{Conversion of 2(5H)-furanone (\%)} = (C_{F,0} - C_F) / C_{F,0} \times 100 \quad (\text{E1})$$

$$\text{Selectivity to GBL (\%)} = C_G / (C_{F,0} - C_F) \times 100 \quad (\text{E2})$$

where $C_{F,0}$ is the initial concentration of 2(5H)-furanone in the reactor, and C_G and C_F are the concentrations of GBL and 2(5H)-furanone, respectively.

With the reaction order assumed to be 1.0, the apparent reaction rate constant k_r was determined by fitting C_F as a function of the reaction time based on Equation (3), which showed a good agreement with the experimental data for all the catalysts ($R^2 > 0.96$).

$$\ln(C_{F,0} / C_F) = k_r \times t \quad (\text{E3})$$

To further compare the catalyst activity per metal active sites, turnover frequency (TOF) for the hydrogenation of 2(5H)-furanone is defined as:

$$\text{TOF}_1(\text{s}^{-1}) = (k_r \times n_{F,0} / n_{M,\text{CO}}) \times S_{\text{initial GBL}} \quad (\text{E4})$$

$$\text{TOF}_2(\text{s}^{-1}) = (k_r \times n_{F,0} / n_{M,\text{TEM}}) \times S_{\text{initial GBL}} \quad (\text{E5})$$

Where $n_{F,0}$ is the initial mole of 2(5H)-furanone loaded into the reactor; $n_{M,\text{CO}}$ and $n_{M,\text{TEM}}$ are the moles of metal active sites estimated by CO and TEM, respectively; and $S_{\text{initial GBL}}$ is the initial selectivity to GBL at a low 2(5H)-furanone conversion.

Table S1 Physical properties of the SiO₂ supported Ni-based catalysts

Entry	Catalyst	$S_{\text{BET}}^{[b]}$ (m ² ·g ⁻¹)	Pore volume ^[c] (cm ³ ·g ⁻¹)	Average pore size ^[c] (nm)
1 ^[a]	SiO ₂	140	0.52	8.53
2	Ni5.0/SiO ₂	131	0.51	8.52
3	Ni4.0-Fe1.0/SiO ₂	133	0.50	8.52
4	Ni4.0-Co1.0/SiO ₂	131	0.50	8.52
5	Ni4.0-Cu1.0/SiO ₂	128	0.49	8.51
6	Ni4.0-Zn1.0/SiO ₂	130	0.51	8.53

^[a] The bare SiO₂ support was pre-treated by calcination in air at 723 K for 3 h;

^[b] The specific surface area was calculated using the BET method;

^[c] The pore volume and average pore size were calculated using the BJH method.

Table S2 Characterization results and metal dispersions of the Ni-based catalysts

Entry	Catalyst	$d_{\text{XRD}}^{[\text{a}]}$	$d_{\text{TEM}}^{[\text{b}]}$	$U_{\text{CO uptake}}$ ($\mu\text{mol} \cdot \text{g}^{-1}$)	Metal dispersion (%) ^[c, d]		
		(nm)	(nm)		D_{XRD}	D_{TEM}	D_{CO}
1	Ni5.0	7.5	6.5	26.3	9.1	10.5	3.1
2	Ni4.0-Fe1.0	6.9	6.1	19.2	9.9	11.2	2.3
3	Ni4.0-Co1.0	7.0	6.3	26.8	9.7	10.8	3.2
4	Ni4.0-Cu1.0	7.6	7.0	18.2	8.7	9.4	2.2
5	Ni4.0-Zn1.0	9.0	7.3	16.6	7.6	9.3	2.0

^[a] The crystalline size was calculated from the characteristic peak of NiO at 43.5° based on the XRD pattern using the Scherer equation, assuming that the metal composition is uniform.

^[b] The average metal particle size was determined by TEM.

^[c] The metal dispersion based on CO uptake was calculated with an adsorption coefficient of 1.0.

^[d] D_{XRD} , D_{TEM} and $D_{\text{CO uptake}}$ are the total metal dispersions estimated by the XRD crystalline size, TEM metal particle size and CO uptake, respectively.

Table S3 Ni2p_{3/2} and Fe2p_{3/2} binding energies of the Ni/SiO₂ and Ni-Fe/SiO₂ catalysts

Entry	Catalyst ^[a]	Binding Energy (eV)	
		Ni 2p _{3/2}	Fe 2p _{3/2}
1	Ni/SiO ₂	854.9	—
2	Ni-Fe/SiO ₂	855.1	710.2

^[a] As the partial re-oxidation in air is inevitable during the delivery and transfer of the reduced samples, the unreduced samples were used for the XPS analysis.

Table S4 Metal compositions and average metal particle sizes of Ni-Fe bimetallic catalysts

with different Fe/(Ni+Fe) ratios

Entry	Catalyst	Fe/(Ni+Fe) ratio		$d_{\text{TEM}}^{[a]}$ (nm)
		Theoretical	TEM-EDS	
1	Ni5.0/SiO ₂	0.00	N.A.	6.5
2	Ni4.5-Fe0.5/SiO ₂	0.10	0.07	6.0
3	Ni4.0-Fe1.0/SiO ₂	0.20	0.17	6.1
4	Ni2.5-Fe2.5/SiO ₂	0.50	0.42	5.9
5	Ni3.5-Fe1.5/SiO ₂	0.70	N.A.	N.A.
6	Ni1.0-Fe4.0/SiO ₂	0.80	0.76	6.6
7	Fe5.0/SiO ₂	1.00	N.A.	6.7

^[a] The average metal particle size was determined by TEM.

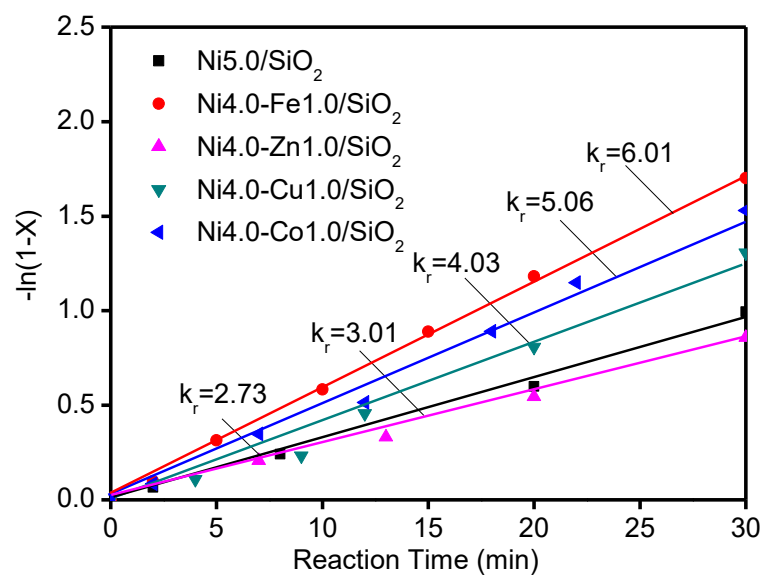


Fig. S1 Correlation of $-\ln(1-X)$ versus reaction time for Ni-based catalysts. Reaction conditions: 2(5H)-furanone (6.0 g), catalyst (0.15 g), 100 mL of methanol as the solvent, 353 K, 3.5 MPa H₂, 180 mL·min⁻¹ H₂ gas flow, 800 rpm stirring. The data was collected at the beginning reaction stage within 30 min.

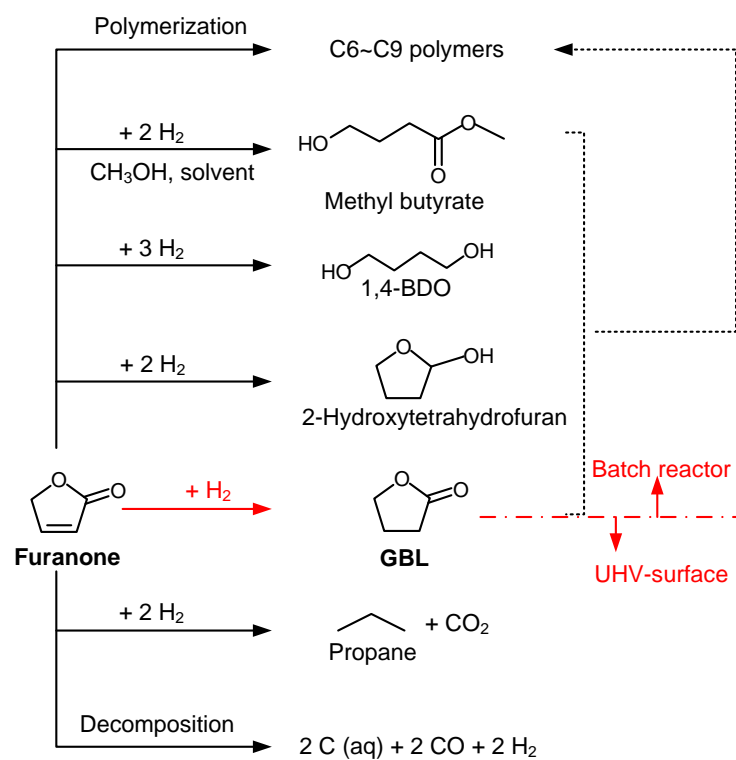


Fig. S2 Scheme for the side reactions in batch reactor and UHV experiments.

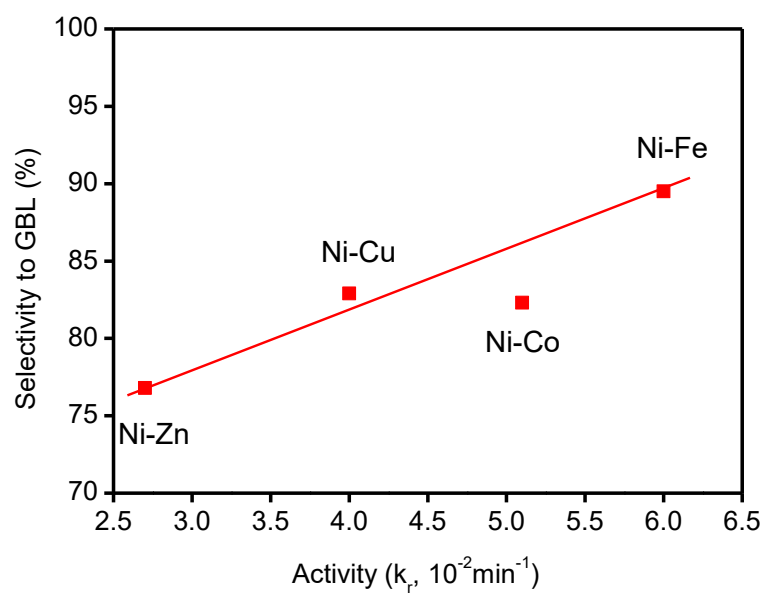


Fig. S3 Correlation of the selectivity to GBL with the reaction rate constant for the Ni-based bimetallic catalysts.

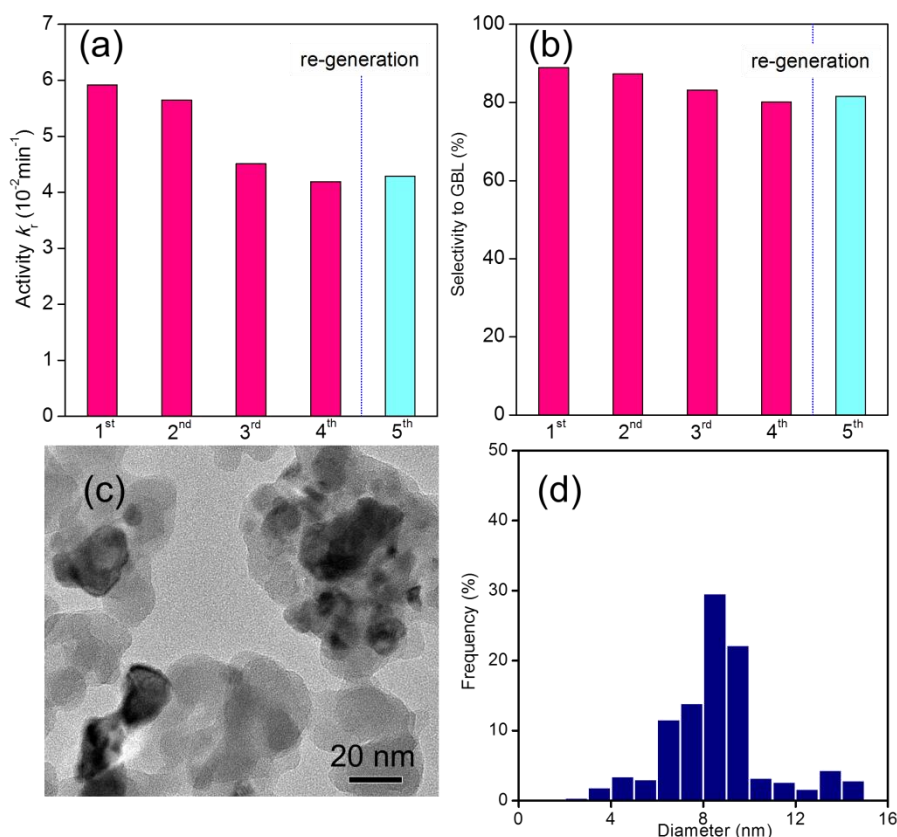


Fig. S4 Reuse of the Ni-Fe/SiO₂ bimetallic catalyst: (a) activity, (b) selectivity, (c) TEM image of the re-generated catalyst and (d) metal particle size distribution of the re-generated catalyst. Reaction conditions: 2(5H)-furanone (6.0 g), catalyst (0.15 g), 100 mL of methanol as the solvent, 353 K, 3.5 MPa H₂, 180 mL·min⁻¹ H₂ gas flow, 800 rpm stirring. The catalyst was washed with methanol and filtrated after each run (1st-4th run) and re-reduced in 30% H₂/He at 723 K for 3 h (5th run).

The reaction rate constant decreases from 0.060 min⁻¹ to 0.042 min⁻¹ after four runs. The significant decrease in the activity of Ni-Fe/SiO₂ was most likely caused by the partial oxidation of metal active sites in the process of washing and drying after each run. Additionally, a gradual decrease in the selectivity to GBL was also observed in the recycling experiments, as only 80.3% of selectivity to GBL was obtained over the forth-run Ni-Fe/SiO₂ catalyst. The spent catalyst was then re-reduced and only a 0.043 min⁻¹ of reaction rate constant was obtained. The sample after catalyst regeneration was characterized by TEM, as shown in Figures S4 (c) and (d), suggesting that sintering of metal particles occurred, which was responsible for the deactivation of the re-reduced Ni-Fe/SiO₂.

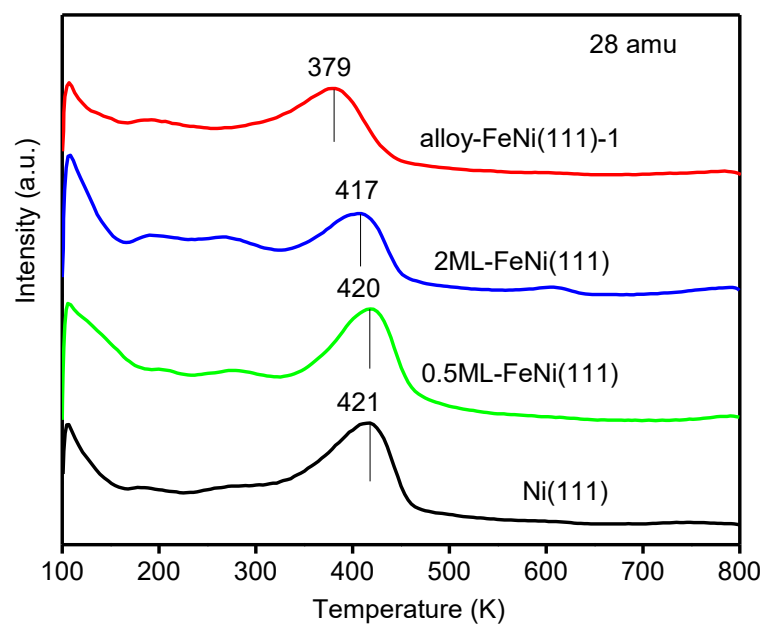


Fig. S5 TPD spectra of CO following the exposure of 3 L of CO with no reactions.