

Supported bimetallic catalysts for the solvent-free hydrogenation of levulinic acid to γ -valerolactone: Effect of metal combination (Ni-Cu, Ni-Co, Cu-Co)

Mahlet N. Gebresillase^{1†}, Reibelle Q. Raguindin^{1†}, Hern Kim¹, Jeong Gil Seo^{2*}

¹ Department of Energy Science and Technology, Myongji University, 116 Myongji-ro, Cheoin-gu, Yongin-si, Gyeonggi-do 17058, Republic of Korea

² Department of Chemical Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul 04763, Republic of Korea

* Corresponding author: +82-2-2220-0520, jgseo@hanyang.ac.kr

Table S1: List of the synthesized catalysts.

Ni-Cu/Al₂O₃	Ni-Co/Al₂O₃	Co-Cu/Al₂O₃
Mono Ni/Al ₂ O ₃	Mono Co/Al ₂ O ₃	Mono Cu/Al ₂ O ₃
[1:1] Ni-Cu/Al ₂ O ₃	[1:1] Ni-Co/Al ₂ O ₃	[1:1] Co-Cu/Al ₂ O ₃
[1:2] Ni-Cu/Al ₂ O ₃	[1:2] Ni-Co/Al ₂ O ₃	[1:2] Co-Cu/Al ₂ O ₃
[2:1] Ni-Cu/Al ₂ O ₃	[2:1] Ni-Co/Al ₂ O ₃	[2:1] Co-Cu/Al ₂ O ₃

Table S2: The textural properties of the bimetallic catalysts at different metal ratio.

Catalysts	S_{BET}(m²/g)^b	Pore volume (cm³/g)^c	Pore diameter (nm)^c
[1:1] Ni-Cu/Al ₂ O ₃	151.3	0.40	12.1
[1:2] Ni-Cu/Al ₂ O ₃	154.0	0.42	13.0
[1:1] Ni-Co/Al ₂ O ₃	163.2	0.44	12.7
[1:2] Ni-Co/Al ₂ O ₃	174.6	0.49	15.4
[1:1] Co-Cu/Al ₂ O ₃	166.0	0.43	12.6
[1:2] Co-Cu/Al ₂ O ₃	171.9	0.48	11.7

^b BET Surface Area calculated from N₂ adsorption-desorption isotherms using BET.

^c Pore volume and pore diameter calculated from N₂ adsorption-desorption isotherms using BJH.

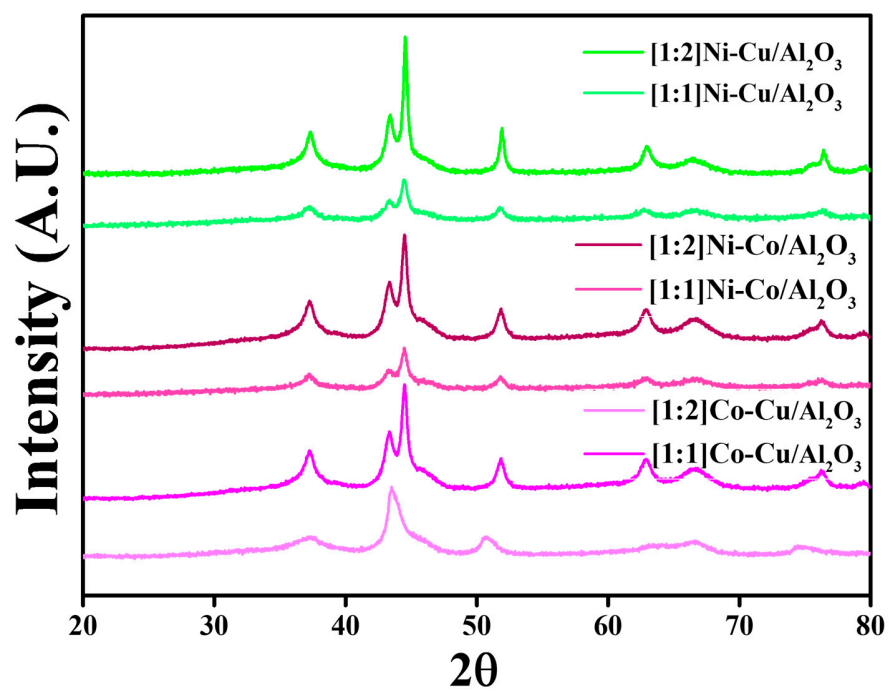


Figure S1: The XRD patterns of the bimetallic catalysts at different metal ratio.

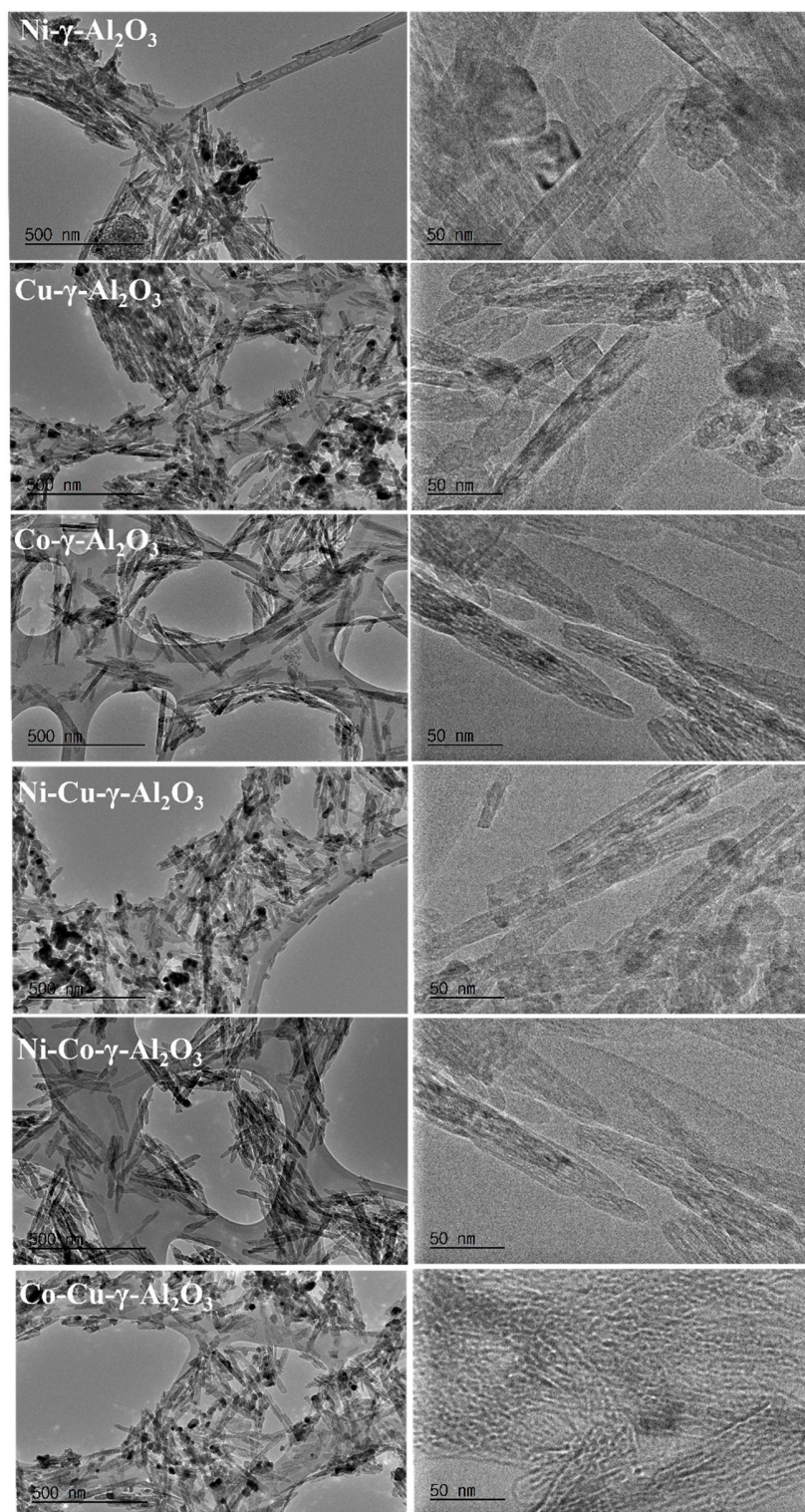


Figure S2: TEM images of selected catalysts at 500 nm and 50 nm.

Table S3: Metal loading screening

LA to GVL (Solvent-Free, 20 ml LA, 1 g catalyst) over Ni-Cu/ γ -Al ₂ O ₃				
Entry	Catalyst	LA Conversion (%)	GVL Selectivity (%)	GVL Yield (%)
1	10 wt.%	40.0	<99.0	39.6
2	20 wt.%	53.0	<99.0	52.5
3	30 wt.%	66.0	<99.0	65.3
4	35 wt.%	80.0	<99.0	79.2
5	40 wt.%	78.0	92.0	71.8
6	50 wt.%	72.5	67.0	48.6
Reaction Conditions: 220°C, 30 bar H ₂ pressure, 4 hrs				

Table S4: Metal leaching analysis

Catalysts	Ni (%)	Cu (%)	Co (%)	Total Metal Leached %
[2:1] Ni-Cu/Al ₂ O ₃	0.03	0.11	0.0	0.14
[2:1] Ni-Co/Al ₂ O ₃	0.03	0.0	0.04	0.07
[2:1] Co-Cu/Al ₂ O ₃	0.00	0.10	0.08	0.18

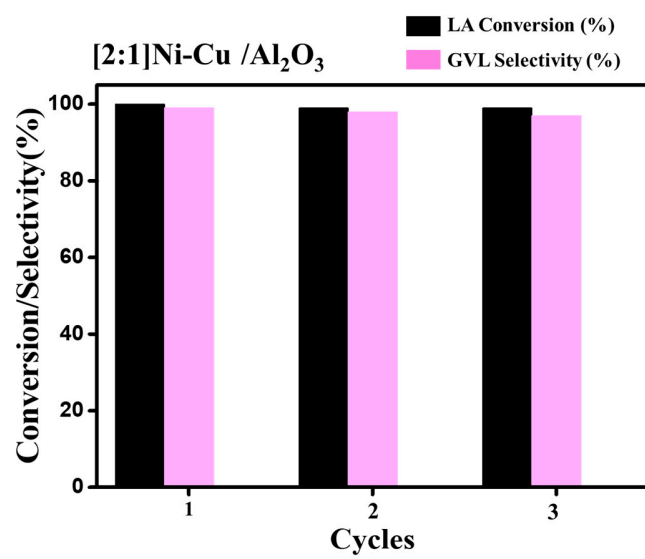


Figure S3. The recyclability test over [2:1] Ni-Cu/Al₂O₃. Reaction conditions: 20mL LA, 1g catalyst, 220 °C, 30 bar H₂ pressure and 6 h reaction time.