

Supplementary Materials

The transfer hydrogenation of levulinic acid to  $\gamma$ -valerolactone over CuNiAl catalyst

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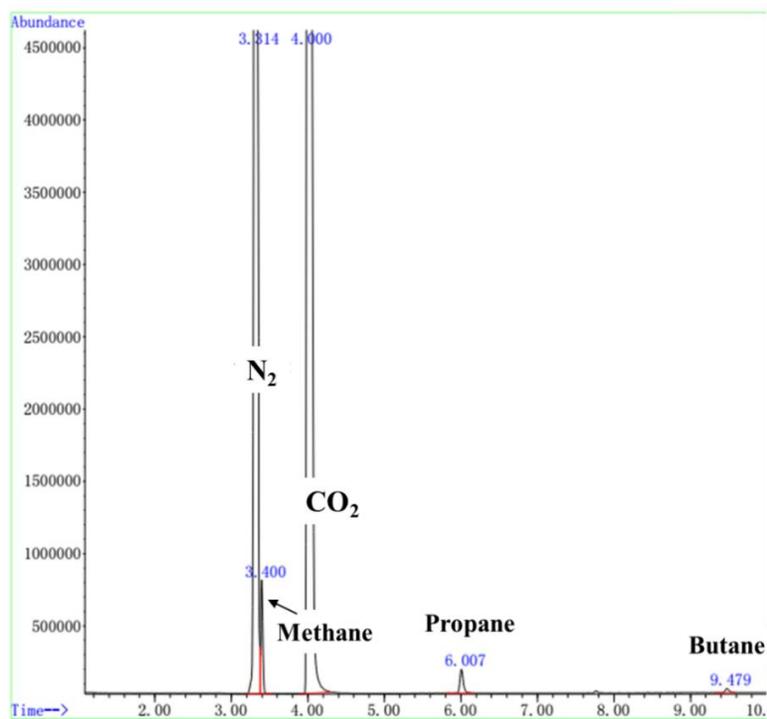
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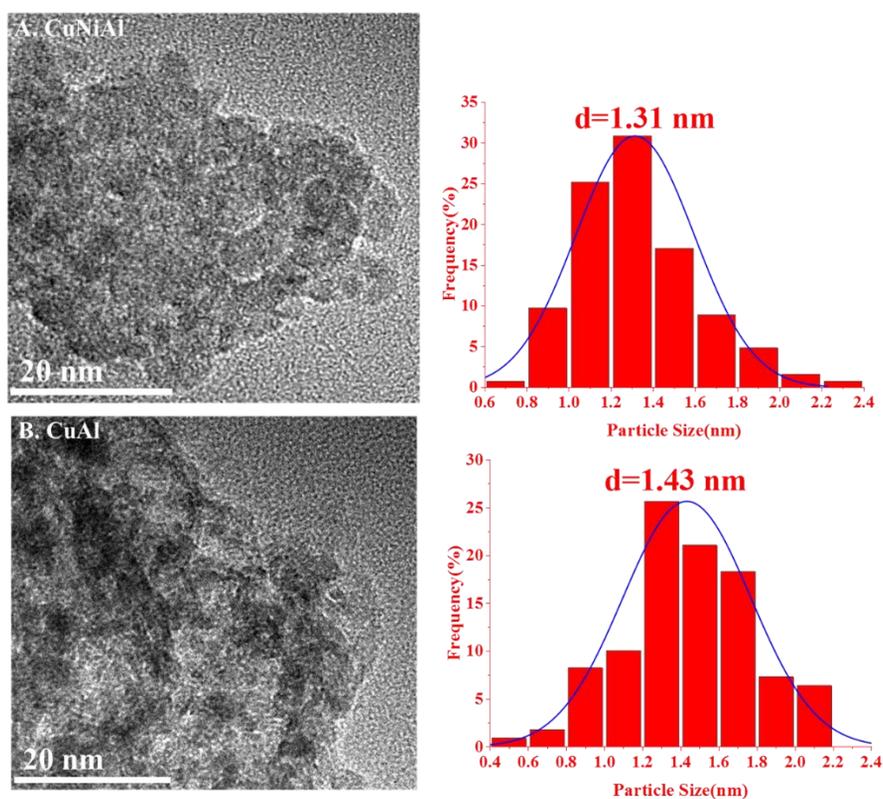
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## Supplementary Figures



Supplementary Figure 1. GC-MS analysis for gas products on CuNiAl catalyst.



Supplementary Figure 2. TEM images of (A) CuNiAl and (B) CuAl catalysts.

**Supplementary Tables****Supplementary Table 1. The amount of total acid sites and basic sites of catalysts**

| Samples | Acidity ( $\mu\text{mol}\cdot\text{g}^{-1}$ ) <sup>a</sup> | Basicity ( $\text{mmol}\cdot\text{g}^{-1}$ ) <sup>b</sup> |
|---------|--|---|
| CuAl    | 0.39   | 0.49  |
| NiAl    | 0.50   | 0.54  |
| CuNiAl  | 0.30   | 0.31  |

<sup>a</sup>The acidity was estimated by the amount of  $\text{NH}_3$  desorption [Figure 5A]; <sup>b</sup>The basicity was estimated by the amount of  $\text{CO}_2$  desorption [Figure 5B].

**Supplementary Table 2. The surface ratio of  $\text{Cu}^{2+}/\text{Cu}^{+0}$  estimated from Cu 2p XPS spectra**

| Samples              | $\text{Cu}^{2+}/\text{Cu}^{+0}$ |
|----------------------|---------------------------------|
| CuNiAl               | 0.35                            |
| CuAl                 | 0.42                            |
| CuNiAl-used six runs | 0.56                            |
| CuAl-used four runs  | 0.81                            |

**Supplementary Table 3. Comparison of the catalytic performances of non-noble metal catalysts in the transfer hydrogenation of LA to GVL with formic acid as hydrogen donor**

| Catalyst                             | Amount of catalyst (g) | LA (mmol) | FA/LA | T (°C) | Time (h) | Conv. (%) | Sel. (%) | GVL forming rate (mmol·g <sub>catal</sub> <sup>-1</sup> ·h <sup>-1</sup> ) <sup>a</sup> | Ref.      |
|--------------------------------------|------------------------|-----------|-------|--------|----------|-----------|----------|---|-----------|
| <b>Continuous fixed bed reaction</b> |                        |           |       |        |          |           |          |   |           |
| 20Ni60Cu/SiO <sub>2</sub>            | 1                      | 31.73     | 1     | 285    | 100      | 99        | 96       | 0.30  | 1         |
| 30Ni/SiO <sub>2</sub>                | 1                      | 97.60     | 5     | 250    | 10       | 99        | 92       | 8.88  | 2         |
| 30Ni/SiO <sub>2</sub>                | 1                      | 97.60     | 5     | 250    | 10       | 98        | 91.8     | 8.78  | 3         |
| 10Cu/Fe <sub>2</sub> O <sub>3</sub>  | 1                      | -         | 2     | 250    | -        | 100       | 100      | -   | 4         |
| 6Cu/SiO <sub>2</sub>                 | 0.5                    | 43.50     | 3     | 250    | 10       | 56        | 87       | 4.24  | 5         |
| HTC MgAl (3:1)                       | 0.4                    | -         | 5     | 270    | 30       | 100       | 98       | -   | 6         |
| 5Ni/CeO <sub>2</sub>                 | 0.2                    | 20.51     | 3     | 275    | 14       | 72.6      | 90.1     | 4.79  | 7         |
| MgO-UBE                              | 0.5                    | -         | 2     | 270    | -        | 100       | 100      | -   | 8         |
| <b>Batch reaction</b>                |                        |           |       |        |          |           |          |   |           |
| 20Cu/ZrO <sub>2</sub> -OG            | 0.24                   | 18        | 1     | 200    | 5        | 100       | 100      | 15  | 9         |
| 20Ni/ZrO <sub>2</sub>                | 0.5                    | 43        | 1     | 220    | 5        | 34.3      | 99       | 5.84  | 10        |
| Raney-Ni                             | 0.02                   | 1         | 4     | 200    | 48       | 100       | 68.5     | 0.71  | 11        |
| MnCo(20:1) oxide                     | 0.2                    | 1.5       | 10    | 230    | 20       | 78.9      | 76.7     | 0.23  | 12        |
| ZnAl(2:1) oxide                      | 1                      | 41.5      | 5     | 140    | 6        | 87        | 100      | 6.02  | 13        |
| 16Cu42NiAl                           | 0.05                   | 5         | 2     | 210    | 6        | 100       | 97.3     | 16.17   | This work |

<sup>a</sup>The forming rate was calculated by the moles of GVL produced (mmol)/catalyst mass (g)/Reaction time (h).

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