

# Supporting information

## **Highly Efficient Conversion of Biomass-derived Levulinic Acid into $\gamma$ -Valerolactone over Ni/MgO Catalyst**

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## Experimental section

### Product analysis

The products were quantitatively analyzed by GC [Agilent 7890A, FID detector, DB-FFAP (30m×250μm×0.25μm) capillary column] with calibrated area normalization method and qualitatively analyzed by GC-MS (Agilent 5979C).

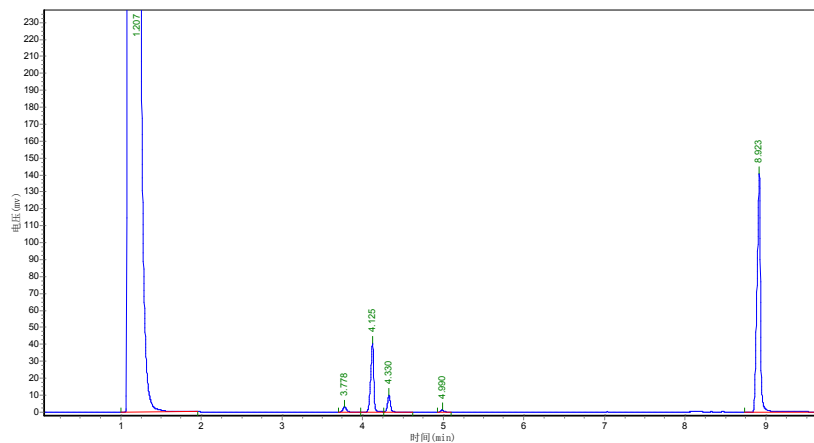


Fig.S1 The chromatogram for hydrogenation of LA

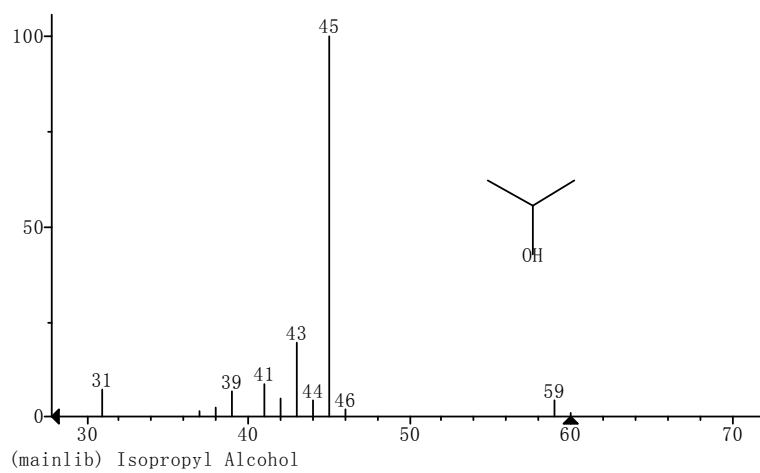


Fig.S2 The mass spectrum for isopropanol

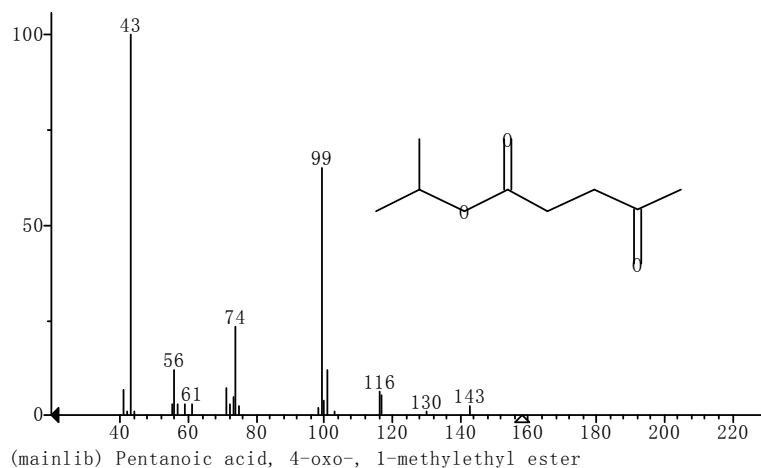


Fig.S3 The mass spectrum for isopropyl levulinate

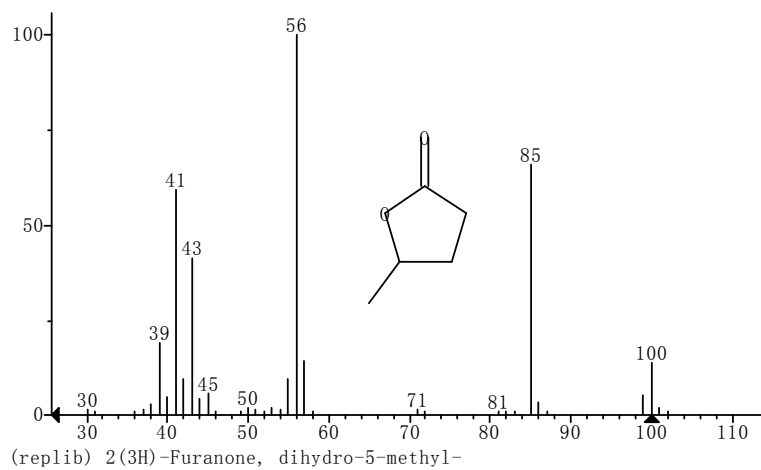


Fig.S4 The mass spectrum for  $\gamma$ -valerolactone

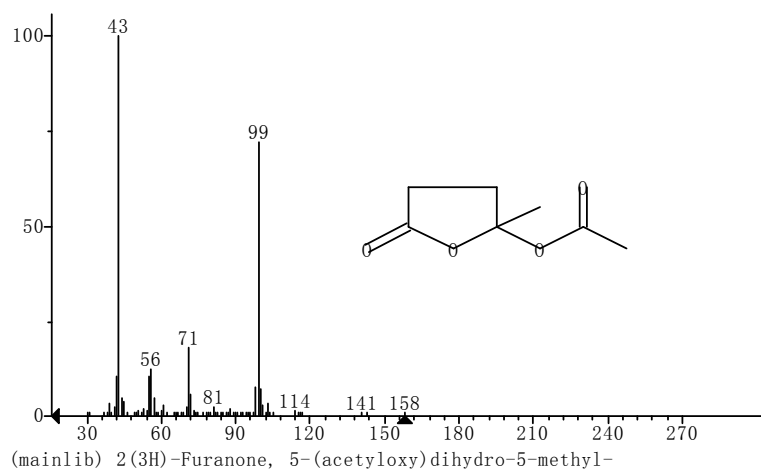


Fig.S5 The mass spectrum for isopropyl Pseudo-levulinate

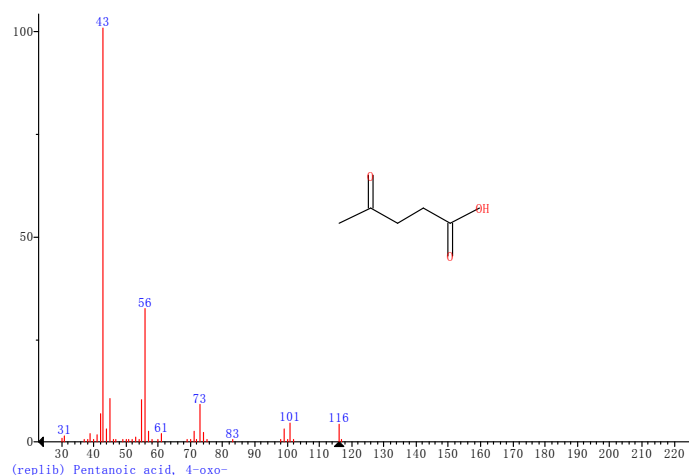


Fig.S6 The mass spectrum for Levulinic acid

### The calculations and XRD characterization of the precipitation process

The XRD patterns of Ni/MgO with different precipitants were shown in new Fig. S7. In the patterns of KOH, Na<sub>2</sub>CO<sub>3</sub> and NaOH, three sharp peaks appeared at 2θ = 44.5 °, 51.8 ° and 76.4 °, with respect to (111), (200) and (220) facets of Ni lattice reflection. Using Scherrer's equation, the average crystalline sizes of Ni were estimated to be about 9.1 nm, 14.8 nm and 9.9 nm respectively. But in the patterns of NH<sub>3</sub>·H<sub>2</sub>O, CO(NH<sub>2</sub>)<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, the peaks of Ni turned much weaker and even partly covered by MgO's peak. The average crystalline sizes of Ni were estimated to be about 8.0 nm, 4.4 nm and 4.2 nm respectively. It indicated that the Ni particles are well dispersed on supports and particles size of Ni prepared by NH<sub>3</sub>·H<sub>2</sub>O, CO(NH<sub>2</sub>)<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> are smaller than other sample.

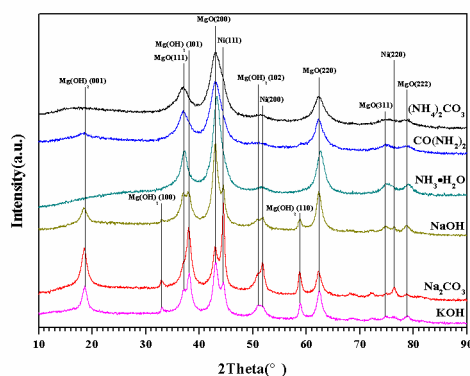


Fig. S7 XRD patterns of Ni/MgO with different precipitants, Ni loading is 44wt%

Based on the equation:  $K_{sp}[\text{Ni}(\text{OH})_2] = [\text{c}(\text{Ni}^{2+})] \times [\text{c}(\text{OH}^-)]^2$ , Ni(OH)<sub>2</sub> generated when pH ≥ 7.45 and the precipitation process was completed  $[\text{c}(\text{Ni}^{2+}) < 10^{-5} \text{ mol} \cdot \text{L}^{-1}]$  when pH ≥ 9.15. So Ni<sup>2+</sup> ions could be completely converted into Ni(OH)<sub>2</sub> when using NaOH or KOH as precipitants (Entry 1 and 2). Obviously, it provided a lower activity, which might be caused by the migration and aggregation of Ni particles when Ni(OH)<sub>2</sub> was reduced by H<sub>2</sub> flow at 500 °C, exceeding to the melting point of Ni(OH)<sub>2</sub>.

When Na<sub>2</sub>CO<sub>3</sub> was used as a precipitant, Ni(OH)<sub>2</sub> and NiCO<sub>3</sub> might be obtained due to the coexists of OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> in the solution. If it is Ni(OH)<sub>2</sub>,

$$[\text{c}(\text{OH}^-)] = \sqrt{\frac{K_{sp}(\text{Ni}(\text{OH})_2)}{[\text{c}(\text{Ni}^{2+})]}} = 3.4 \times 10^{-7} \quad (1);$$

If it is NiCO<sub>3</sub>,

$$[c(\text{CO}_3^{2-})] = \frac{K_{sp}(\text{NiCO}_3)}{[c(\text{Ni}^{2+})]} = 3.88 \times 10^{-7} \quad (2);$$

$$\frac{[c(\text{CO}_3^{2-})]}{[c(\text{OH}^-)]} = 1.14 \quad (3);$$

In this study, pH was 11.26 for Na<sub>2</sub>CO<sub>3</sub> solution (Entry 3). So [c(OH<sup>-</sup>)]=10<sup>11.26-14</sup>=0.00182, [c(CO<sub>3</sub><sup>2-</sup>)]≈0.017-0.00182=0.0152,

$$\frac{[c(\text{CO}_3^{2-})]}{[c(\text{OH}^-)]} = 8.35 \quad (4);$$

So NiCO<sub>3</sub> was firstly obtained when Na<sub>2</sub>CO<sub>3</sub> was dropwise added into the suspension. However, another reaction for transformation of precipitation continuously happened: NiCO<sub>3</sub> + 2OH<sup>-</sup> ⇌ Ni(OH)<sub>2</sub> + CO<sub>3</sub><sup>2-</sup> and

$$k = \frac{K_{sp}(\text{NiCO}_3)}{K_{sp}(\text{Ni(OH)}_2)} = \frac{6.6 \times 10^{-9}}{2 \times 10^{-15}} = 3.3 \times 10^6 \quad (2);$$

The equilibrium constant value is very large with 10<sup>6</sup>, which meaning that the precipitation process is complete. So Ni(OH)<sub>2</sub> was obtained at last and it also provided a low activity using Na<sub>2</sub>CO<sub>3</sub> as a precipitant.

### Effects of DP time and Drying Time

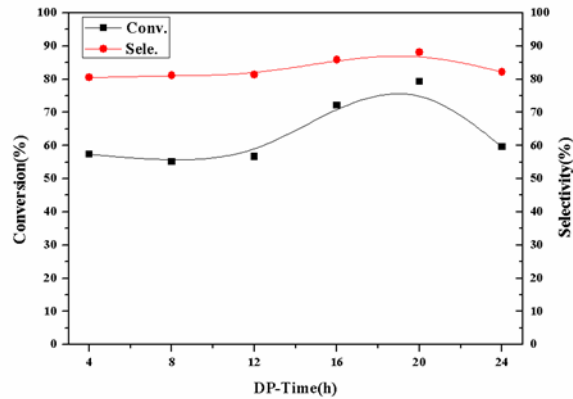


Fig. S8 Hydrogenation of LA with Ni/MgO (0.4604 g LA, 20 mL *i*-PrOH, 0.01 g catalyst, 150 °C, 1.0 MPa, 120 min, Ni loading is 44wt%)

Table S1 Hydrogenation of LA to GVL on catalysts with different Dry-Time

Entry	Drying-Time/h	Conv./%	Sel./%			
			Ester	GVL	P-LA	Others
1	6	70.4	6.0	85.9	4.3	3.9
2	12	68.1	7.0	85.2	4.0	3.8
3	18	74.7	5.4	87.0	3.3	4.3
4	24	79.3	4.8	88.1	3.3	3.8

The Deposition-Precipitation time (DP-time) was studied for the preparation of Ni/MgO catalyst and the catalytic performance was shown in Fig. S8. As the DP-time was extended, both conversion of LA and selectivity of GVL gradually increased then decreased under the same reaction conditions. Generally, Deposition–Precipitation is a complex reaction process and it might contain several key steps, such as precipitation, diffusion, deposition, transformation of precipitation, dissolution-reprecipitation et al.<sup>1</sup>. So an appropriate reaction time is necessary. When DP-time was set as 20 h, the highest conversion was obtained in this study.

Furthermore, the drying time was investigated for the preparation of Ni/MgO. In the process, it could efficiently remove water from the sample before reduction, preventing the sintering of the oxide phase. The more water is eliminated, the smaller metal particles could be obtained<sup>2</sup>. In this study, we got four different drying times (6 h ~24 h) for the catalyst preparation and results were showed in Table S1. It may be noted that after 24 h of drying, the highest 79.3% conversion of LA and 88.1% selectivity of GVL were obtained.

### The possibility of MPV reaction

In this study, *i*-PrOH and 1,4-dioxane appeared to be more appropriate than MeOH, EtOH and H<sub>2</sub>O as solvents. When there were acetyl group of LA, catalyst and *i*-PrOH, the Meerwein-Ponndorf-Verley (MPV) reaction might happen as reported<sup>3, 4</sup>. According to the references<sup>5, 6</sup>, MgO can be used as the catalyst for the MPV reaction. So a contrast test was designed with nitrogen replacing hydrogen. 23.7% conversion and 54.9% selectivity to GVL were obtained in Table S2. When H<sub>2</sub> is absence, isopropyl alcohol provides a hydrogen source and it is converted into acetone. Because acetone couldn't be removed out in the closed reactor, there is a reversible hydride transfer from alcoholate to carbonyl acceptor. It is not enough for *i*-PrOH to afford all the hydrogenation of LA to GVL. As a whole, *i*-PrOH acted as double roles not only solvent but also hydrogen donator. So when *i*-PrOH is solvent, we got the highest activity.

Table S2 Contrast test with nitrogen replacing hydrogen<sup>a</sup>

Entry	Conv./%	Sel./%			
		Ester	GVL	P-LA	others
1	100	1.5	93.3	0.8	4.4
2 <sup>b</sup>	23.7	23.6	54.9	19.8	1.7
3 <sup>c</sup>	3.3	60.6	3.0	36.4	-

<sup>a</sup> Reaction Conditions: 0.2302 g LA, 20 mL *i*-PrOH, 0.01 g Ni/MgO, 150 °C, 1.0 MPa H<sub>2</sub>, 120 min, Ni loading amount is 44wt%. <sup>b</sup> H<sub>2</sub> was replaced by N<sub>2</sub>; <sup>c</sup> Ni/MgO was replaced by MgO.

### References

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