

Choline chloride-promoted efficient solvent-free hydrogenation of biomass-derived levulinic acid to γ -valerolactone over Ru/C

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Experimental section

Chemicals and materials

Methanol (MeOH), ethanol (EtOH), MBK, VA, acetone, methyl isobutyl ketone (MIBK), ChCl, and LiCl were purchased from Sinopharm Chemical Reagent Co. Ltd. Ru/C (5 wt%), Rh/C (5 wt%), Pd/C (5 wt%), Pt/C (5 wt%), LA (99%) and GVL (98%) were supplied by Aladdin Reagent Co. Ltd. (Shanghai, China). All the chemicals were analytical reagents and used without further purification.

Hydrogenation of LA to GVL with the presence of ChCl

The synthetic process of the LA/ChCl was carried out in a 50 mL round-bottomed flask equipped with a magnetic stirrer. The ChCl was dried over night to remove the adsorbed H₂O before use. LA and ChCl were mixed at a certain mass ratio (from 2:1 to 20:1 in this research). After heating at 80°C for 30 min, two compositions become the transparent liquid.

All the hydrogenation experiments were carried out in a 20 mL Hastelloy-C autoclave. The autoclave was charged with certain amounts of LA/ChCl and the catalyst, and then sealed and purged three times with N₂, pressurized with hydrogen at ambient temperature before heating to target temperature with stirring (500 rpm). The reactor was cooled to room temperature after the reaction, and the used catalyst was recovered by centrifugation, washed by MeOH and EtOH and then dried at 60 °C for two hours. The ChCl crystal was removal after evaporation of the water. The final liquid products were analyzed by gas chromatograph-mass spectrum (GC-MS) and gas chromatograph (GC) methods.

Products analysis

The product was detected on an Agilent 7890 series connected with a DB-Waxetr column and a flame ionization detector (FID) operating at 270 °C. The flow rate of carrier gas (N₂) was 1.0 mL/min. The mass of LA or GVL in acetone solution was calculated based on a standard curve. LA conversion (X_{LA} , %), GVL selectivity (S_{GVL} , %) after reaction are calculated by the following equations:

$$X_{LA} = \left(1 - \frac{\text{mol of LA in products}}{\text{initial mol of LA}}\right) \times 100\% \quad (\text{Eq. 1})$$

$$S_{GVL} = \left(\frac{\text{mol of GVL in products}}{\text{initial mol of LA} - \text{mol of LA in products}}\right) \times 100\% \quad (\text{Eq. 2})$$

The qualitative analysis of the liquid products was carried out with a Thermofisher Trace 1300 & ISQ LT GC-MS instrument with a TR-5MS column. The operating parameters of GC-MS analysis were consistent with those of GC analysis.

Fourier transform infrared (FTIR) spectroscopy was conducted using the Nicolet Is5 spectrometer at 298 ± 2 K in the range from 4000 to 400 cm⁻¹. Viscosity was analyzed

by a viscometer (LV model, Brookfield).

Density functional theory (DFT) calculations

Theoretical calculations of absorb energy and charge density of LA and LA/ChCl were performed using the Vienna Ab-Initio Simulation Package (VASP) [1-3]. The projector augmented plane wave (PAW) pseudo potential basis set and generalized gradient approximation (GGA) functional by the PBE parametrization was employed in these calculations[4]. The Monkhorst-pack method with the centered k-point grid $2 \times 2 \times 1$ was used for surface calculations. The reasonable vacuum layers were set around 15 Å in the z-direction for avoiding interaction between planes. A kinetic energy cutoff of 520 eV for the plane wave expansion is used for all systems. Geometry optimizations were pursued until the force on each atom falls below the convergence criterion of 0.02 eV/Å and energies were converged within 10^{-5} eV. The charge density difference (CDD) were obtained from the charge density file (CHACAR) using VASPKIT program [5] and then rendered using VESTA visualization program[6]. The Gaussian 09 package was used to model the atomic structure of LA/ChCl combination[7]. The structure of LA/ChCl mixture was fully optimized at the PBE0/def2tzvp level[8].

The adsorption energy (ΔE_{ads}) of the species on slab surface was determined by the following expression [9]:

$$\Delta E_{ads} = E_{ads/base} - E_{ads} - E_{base}$$

where $E_{ads/base}$, E_{ads} and E_{base} are the total energy of the adsorbed systems, the isolated HMF, and model, respectively. Accordingly, the negative ΔE_{ads} indicates the energetically favorable (exothermic) interaction between adsorbate and slab surface.

Results and discussion

Screening of catalysts in the synthesis of GVL

The reaction system developed in the present study consisted of LA, ChCl, H₂ and Ru/C. Various noble metal catalysts were tested for the hydrogenation in this reaction system. As shown in Table S1, the catalytic results of these catalysts vary greatly. The solvent-free LA was effectively converted to GVL with 100% S_{GVL} by only 1.75 wt % Ru/C catalyst at 150 °C (Table S1, entry 1). X_{LA} over Rh/C was slightly inferior, but its selectivity towards GVL was acceptably good. Pd/C and Pt/C turned out to be less effective for the production of GVL from solvent-free LA feedstock (Table S1, entries 3-4).

Table S1 LA hydrogenation in LA/ChCl over various noble catalysts

| Entry | Catalyst | X _{LA} (%) | S _{GVL} (%) | Y _{GVL} (%) |
|-------|----------|---------------------|----------------------|----------------------|
|-------|----------|---------------------|----------------------|----------------------|

| | | | | |
|---|------|------|-------|------|
| 1 | Ru/C | 80.1 | 100.0 | 80.1 |
| 2 | Rh/C | 76.2 | 98.8 | 75.3 |
| 3 | Pd/C | 23.6 | 54.9 | 13.0 |
| 4 | Pt/C | 14.4 | 62.3 | 9.0 |

Reaction conditions: 5 g LA/ChCl, 500 rpm, 1.75 wt % catalyst based on the LA, 10 h, 150 °C, 5 MPa H₂, mass ratio of LA to ChCl is 10:1.

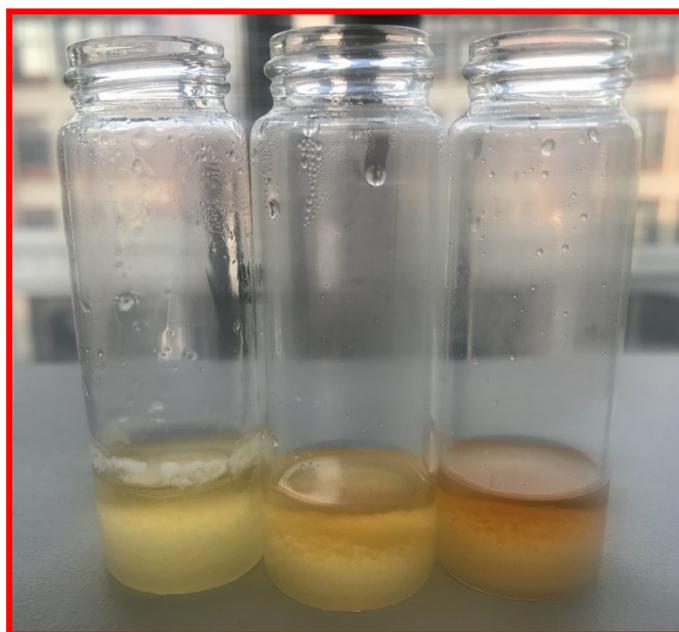


Figure S1. Crystallization of ChCl after reaction: recovered after 2nd, 4th and 6th run from left to right.



Figure S2. Recovered ChCl after washing and drying.

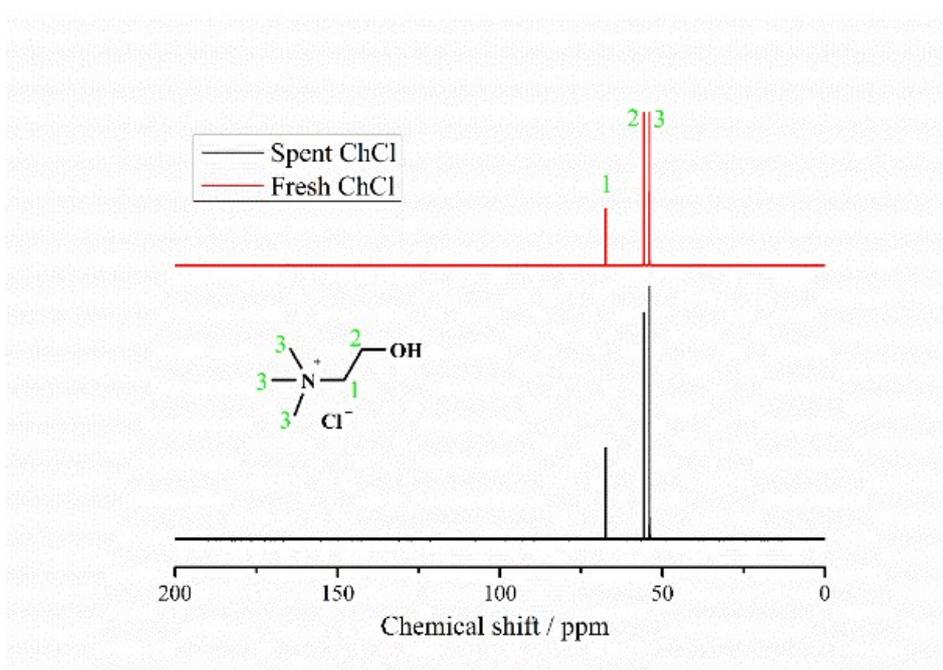


Figure S3. ^{13}C NMR of fresh and spent ChCl.

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