Efficient synthesis of $\gamma$-valerolactone from ethyl levulinate over Ni/V$_2$O$_5$

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Abstract: $\gamma$-valerolactone (GVL) has been recognized as one of the most value-added chemicals derived from biomass. In this work, an efficient Ni/V$_2$O$_5$ catalyst was prepared via solid phase grinding and in-situ reduction. The Ni/V$_2$O$_5$ catalyst was employed for catalytic transfer hydrogenation (CTH) of ethyl levulinate (EL) to GVL using 2-propanol as a hydrogen source. An excellent GVL selectivity of 93.04% at EL conversion of 97.40% could be achieved at 180 °C in 4 h using 30% Ni/V$_2$O$_5$ as the catalyst. This catalyst was able to be reused for five times with the GVL selectivity decreased a little. A possible adsorption mechanism of generate active H species in CTH of EL over Ni/V$_2$O$_5$ was proposed.

1. Introduction

As demand for chemicals and fuels increases and fossil resources are about to be depleted, it is imperative to find sustainable alternatives for petroleum-based products. $\gamma$-valerolactone (GVL) is an important platform compound derived from renewable biomass [1-5], which may find use as a green solvent, a fuel additive, precursor to alkene based transportation fuels or an intermediate compound to prepare functionalized materials because of its excellent physical and chemical properties such as high boiling point, low volatility, easy degradation, and low toxicity. Thus, the synthesis of GVL is one of the pivotal steps in the transformation of biomass resources into liquid fuels and high-value chemicals.

The biomass derivative levulinic acid (LA) and its esters are direct starting materials for synthesis of GVL. Extensive catalytic routes for the synthesis of GVL from LA/levulinate esters have been continuously improved in recent years [6, 7]. As well-known, metal catalysts have good catalytic activities for the hydrogenation reaction. The Pd [8, 9], Pt [10], Ru [11-13], Ir [14], Rh [15] are the most common precious metals used for the hydrogenation of LA/levulinate esters to GVL, and they exhibited fairly satisfactory catalytic performance under an optimal reaction condition. Even though the precious metal catalysts show good catalytic effects, the high economic cost cannot be ignored. So, much attention has been focused to the nonprecious metal catalysts.
Among the nonprecious metal catalysts, Cu [16], Co [17], Ni [18] catalysts exhibited considerable catalytic performances in this reaction, especially the Ni supported catalysts. Ni supported [19] by Al₂O₃, SiO₂, ZnO, ZrO₂, TiO₂ and MgO were prepared to investigate the synthetic efficiency of GVL from LA. 30 % Ni/SiO₂ can achieve the highest GVL yield of nearly 90 % at 250 °C in the vapor phase at atmospheric pressure. Sakakibara et al. [20] reported Ni/ZrO₂ for the transfer hydrogenation of methyl levulinate (ML) and LA to GVL using 2-propanol as a hydrogen donor to show the yield of 94 % and 92 %, respectively. Fang et al. [21] reported in situ synthesis of biomass-derived Ni/C catalyst for the hydrogenation of LA to GVL, and a high yield of 94.5 % can be obtained. The CTH of ethyl levulinate (EL) to GVL over Cu-Ni bimetallic catalyst with 2-butanol as the hydrogen donor was carried out and provided a 97% yield of GVL product in 12 h at 150 °C [22]. Activated carbon-supported bimetallic nickel-iron catalyst (Ni-Fe/AC) was employed to catalyse the EL converting into GVL in the liquid phase. At 100 °C, 4 MPa H₂, the reaction was carried out for 6 h, and the EL was completely converted, and the obtained GVL yield was 99% [23]. Most of the reported metal based catalysts prepare by impregnation or coprecipitation followed by reduction in H₂ gas. To the best of our knowledge, the Ni loaded V₂O₅ catalyst prepared via a solid phase grinding and in-situ reduction method hasn’t been reported in transfer hydrogenation of EL into GVL yet.

With the aim of developing new active, stable catalytic systems through cost effective system, in this work, this green and simple preparation method for metal supported catalyst was used to produce Ni/V₂O₅ catalysts. This method needs no solvent or reductive H₂ gas. No extra reduction is needed before using the metal catalysts. High catalytic activity of the Ni/V₂O₅ catalysts was obtained in synthesis of GVL from ethyl levulinate.

2. Material and Methods

2.1. Materials

Ethyl levulinate (EL, 99%), γ-valerolactone (GVL, 98%), and n-dodecane (98%) were purchased from Aladdin industrial corporation (Shanghai, China). 2-propanol (A.R.) was purchased from Hunan hui-hong reagent co., Ltd (Hunan, China). Citric acid monohydrate (A.R.), nickel nitrate hexahydrate (A.R.), aluminum nitrate nonahydrate (A.R.) and nitrate ferric nitrate (A.R.) were purchased from Sino pharm Chemical Reagent Co., Ltd. Vanadium pentoxide (A.R.) was purchased from Xiangzhong Chemical Reagent Development Center. All chemicals were used as received without further purification.

2.2. Catalysts preparation

Ni/V₂O₅ was prepared by solid phase grinding and in situ reduction method [24]. In a typical procedure, Ni(NO₃)₂·6H₂O (1.455 g) and citric acid monohydrate (1.26 g), were mixed and grinded at room temperature for 0.5 h to form the nickel citrate complex. Then V₂O₅ (0.685 g) was added and grinded for another 0.5 h. The paste precursor dried in a drying oven for 12 h and calcined for 3 h at 350 °C with ramp rate of 3 °C/min under nitrogen atmosphere. The catalyst was described as 30% Ni/V₂O₅, represents the loading of Ni in wt% is 30%. Ni/V₂O₅ catalyst with different loading of 5%, 10%, 20%, and 40% were prepared by changing the V₂O₅ feeding amount.

The preparation procedure of Ni/Al₂O₃ and Ni/Fe₂O₃ were very similar to that of Ni/V₂O₅ except that the corresponding nitrates of Al₂O₃ and Fe₂O₃ were added to the nickel citrate complex.

All catalysts were stored in vacuum desiccator and used directly.

2.3. Catalytic activity

Catalytic conversion of EL to GVL was carried out in a 100 mL autoclave with Teflon lined reactor under magnetic stirring. In a typical experiment, the batch was loaded with ethyl levulinate (EL, 5 mmol), 2-propanol (19 mL) as a hydrogen donor and solvent, n-dodecane (1 mmol) as an internal standard and the catalyst (216 mg), and then purged five times with N₂ at atmospheric conditions. The reaction mixture was heated to the prescribed temperature for a desired reaction time with stirring at
500 rpm. After reaction, the reactor was cooled down to room temperature, and the reaction mixture was separated from the catalyst magnetically. The reaction mixture was analyzed by a Flame Ionization Detector (FID) equipped gas chromatograph, GC 2014 (Shimadzu Instruments, Japan) with HP-5 column (30.0 m×0.50 mm×0.32 μm) and the products were confirmed by GCMS-QP2010 (Shimadzu Instruments, Japan).

Generally, EL conversion and selectivity of GVL, ethyl 4-hydroxypentanoate (4-HPE), and isopro-pyl levulinate (IPL) are calculated using the following formula:

\[
EL\;conversion\;(%)=\left(1-\frac{\text{Mole of EL after reaction}}{\text{Initial mole of EL}}\right)\times100\quad(1)
\]

\[
GVL\;selectivity\;(%)=\frac{\text{Mole of GVL produced}}{\text{Mole of EL converted}}\times100\quad(2)
\]

\[
4\text{-HPE}\;selectivity\;(%)=\frac{\text{Mole of 4\text{-HPE} produced}}{\text{Mole of EL converted}}\times100\quad(3)
\]

\[
IPL\;selectivity\;(%)=\frac{\text{Mole of IPL produced}}{\text{Mole of EL converted}}\times100\quad(4)
\]

2.4. Recycle experiments
The stability of the 30%Ni/V2O5 was tested in conversion of EL to GVL under the optimal condition. Autoclave containing the separated catalyst was evacuated and again charged with fresh EL solution for a subsequent catalytic cycle.

2.5. X-Ray Diffraction analysis
XRD patterns of Ni/V2O5 catalysts were recorded with an Ultima-IVX-ray powder diffractometer (Rigaku Corporation, Japan) using Ni filtered Cu Ka radiation (λ= 1.5406 Å). Samples were scanned in the 2θ range of 5~80° at 40 kV and 40 mA with a scan speed of 2°/min.

3. Results and discussion

3.1. XRD characterization of Ni/V2O5

![Figure 1. XRD patterns of the Ni/V2O5 catalysts with different Ni content](image)

The Crystal structures of the Ni/V2O5 catalysts with different Ni loading as well as V2O5 support were detected by X-ray powder diffractometer, and results were shown in Fig. 1. Compared with the XRD pattern of V2O5, the XRD patterns of all the supported catalysts showed metallic Ni and NiO phases. XRD reflections at 44.49° (111), 51.85° (200) and 76.38° (220) correspond to metallic Ni with a face-
centered cubic geometry (ICDD. No. 04-002-3695) and the diffraction peaks at 37.24° (111), 43.28°(200) and 62.85° (220) corresponding to NiO phase (ICDD. No. 97-002-8834)[25, 26]. The intensity of these peaks increased as the Ni loading in the catalysts increased.

3.2. Catalytic performance of Ni supported catalysts in hydrogenation of EL to GVL

![Scheme 1. The pathway of CTH of EL to GVL using 2-propanol as the hydrogen donor.](image)

Table 1. Catalytic transfer hydrogenation of EL to GVL by Ni supported catalysts.

| Entry | Catalysts   | Conversion /% | Selectivity /% | GVL | 4-HPE | IPL |
|-------|-------------|---------------|----------------|-----|-------|-----|
| 1     | Ni/Al₂O₃    | 29.70         | 88.57          |     |       |     |
| 2     | Ni/Fe₂O₃    | 81.24         | 89.12          | 4.39|       | 2.10|
| 3     | Ni/V₂O₅     | 97.40         | 94.50          | 2.72|       | 2.78|

Reaction conditions: ethyl levulinate 5 mmol (0.721 g), 19 mL 2-propanol, 216 mg catalyst, reaction temperature 180 °C, reaction time 4 h.

Three different metal oxides Al₂O₃, Fe₂O₃, and V₂O₅ were chosen as the supports to prepare Ni based catalysts. Their catalytic activities were tested in transfer hydrogenation of EL to GVL using 2-propanol as a hydrogen source and solvent. Results were shown in Table 1. All the catalysts showed good selectivity of main product GVL while had a significantly difference on conversion of EL. The high selectivity of GVL in all reactions may benefit to the highly selective reduction of carbonyl groups to alcoholic hydroxyl groups in the presence of 2-propanol as hydrogen donors [1]. Ni/V₂O₅ prepared from an acidic oxide support gave the highest EL conversion of 97.40%. In addition to the main product GVL, ethyl 4-hydroxypentanoate (4-HPE) as well as isopropyl levulinate (IPL) were detected by GC and identified by GC-MS. No other intermediate or by-products were detected. The intermediate product 4-HPE is produced by the hydrogenation of EL, which could be esterified and cyclized to synthesize GVL [27]. The pathway of catalytic transfer hydrogenation of EL to GVL using 2-propanol as the hydrogen donor was shown in Scheme 1. By-product IPL generated from the transesterification of EL and 2-propanol under the action of acidic active sites provided by NiO, V₂O₅ or Al₂O₃. However, the superior EL conversion in Ni/V₂O₅ catalytic system may also due to the appropriate amount acidic active sites in Ni/V₂O₅ to promote the lactonization of 4-HPE. More results discussed in the following part further proved this point. Furthermore, literatures [28, 29] also proved that modulating the Lewis acid or base contents of the catalysts is an effective measure to promote the lactonization efficiency of the catalysts in the CTH of alkyl levulinate to GVL.

In a subsequent experiment, Ni/V₂O₅ was selected as a catalyst to explore the reaction conditions required for its optimum catalytic activity.

3.3. Effect of Ni loading on the hydrogenation of EL

Table 2. Effect of Ni/V₂O₅ with different Ni loading on hydrogenation of EL to GVL

| Entry | Load/% | Conversion/% | Selectivity /% | GVL | 4-HPE | IPL |
|-------|--------|--------------|----------------|-----|-------|-----|
| 1     | 5      | 25.26        | 2.56           |     |       |     |
| 2     | 10     | 16.86        | 5.67           |     |       |     |
| 3     | 20     | 16.42        | 14.26          |     |       |     |

Table 2. Effect of Ni/V₂O₅ with different Ni loading on hydrogenation of EL to GVL
increased slightly with the increase of the Ni content continued to increase with the loading amount, there were enough metal active sites to reduce EL to the intermediate 4-HPE, which further generated GVL. So the EL conversion rate and selectivity of GVL increased. Obviously, Ni/V₂O₅ with 30% Ni loading has an appropriately ratio of metal active sites to acid active sites. 30% was chosen as the optimal loading amount.

3.4. Effect of catalyst dosage on the hydrogenation of EL

| Entry | Dosage/% | Conversion/% | Selectivity/% |
|-------|----------|--------------|---------------|
|       |          |              | GVL | 4-HPE | IPL |
| 1     | 5        | 36.39        | 36.13 | 35.16 | 28.71 |
| 2     | 10       | 70.35        | 72.58 | 14.25 | 13.59 |
| 3     | 20       | 93.12        | 68.15 | 18.05 | 13.14 |
| 4     | 30       | 97.40        | 94.50 | 2.72  | 2.78  |
| 5     | 40       | 96.14        | 80.75 | 17.57 | 1.68  |

Reaction conditions: ethyl levulinate 5 mmol (0.721 g), 19 mL 2-propanol, catalyst 30% Ni/V₂O₅, reaction temperature 180 °C, reaction time 4 h.

Catalyst dosages from 5% to 30% based on the mass of the substrate were investigated and results were seen from Table 3. The EL conversion and GVL selectivity gradually increased, while the intermediate product 4-HPE gradually decreased. Correspondingly, selective of the acid catalysed product IPL decreased with the Ni active centres increased. These results indicate the good catalytic activity of Ni active centres in transfer hydrogenation reaction. However, with the continuous increase of the catalyst dose to 40%, GVL selectivity declined and 4-HPE increased. The possible reason may as follows: the catalytic action of acidic sites on the Ni/V₂O₅ may be suppressed in the presence of too much Ni active centres in the reaction system, so that it delayed transformation of the intermediate into GVL. This, on the contrary, proved the catalytic action of the acid sites on the lactonization of 4-HPE, which discussed in section 3.2. Within the range examined, the optimum catalyst dosage was 30%.

3.5. Effect of reaction time on the hydrogenation of EL

Reaction time has a great influence on the EL conversion and products’ selectivities, the trends were shown in Table 4. The catalytic reaction trend along with the reaction time in CTH of EL to GVL over Ni/V₂O₅ is very similar to that of catalyst dosage. When prolonging reaction time to 4 h, the EL can be transferred into GVL nearly completely, with very little 4-HPE and IPL existed.
Table 4. Effect of reaction time on hydrogenation of EL to GVL over Ni/V₂O₅.

| Entry | Time/h | Conversion/% | Selectivity/% | GVL | 4-HPE | IPL |
|-------|--------|--------------|---------------|-----|-------|-----|
| 1     | 1      | 21.22        | 36.325        | 46.73 | 16.95 |
| 2     | 2      | 86.74        | 85.35         | 10.11 | 4.53  |
| 3     | 4      | 97.40        | 94.50         | 2.72  | 2.78  |
| 4     | 6      | 98.63        | 92.07         | 6.53  | 1.40  |

Reaction conditions: ethyl levulinate 5 mmol (0.721 g), 19 mL 2-propanol as solvent, catalyst 30% Ni/V₂O₅, reaction temperature 180 °C.

3.6. Effect of reaction temperature on the hydrogenation of EL

Table 5. Effect of reaction temperatures on hydrogenation of EL to GVL over Ni/V₂O₅

| Entry | temperature/°C | Conversion/% | Selectivity/% | GVL | 4-HPE | IPL |
|-------|----------------|--------------|---------------|-----|-------|-----|
| 1     | 150            | 7.00         | 2.11          | -   | 97.89 |
| 2     | 160            | 79.78        | 67.76         | 26.35 | 5.89  |
| 3     | 170            | 93.48        | 79.08         | 19.07 | 1.85  |
| 4     | 180            | 97.40        | 94.50         | 2.72  | 2.78  |
| 5     | 190            | 97.87        | 86.83         | 11.52 | 1.65  |

Reaction conditions: ethyl levulinate 5 mmol (0.721 g), 19 mL 2-propanol, catalyst 30% Ni/V₂O₅, reaction time 4 h.

Reaction temperature is also an important condition effect the catalytic activity of the catalyst. Catalytic active of Ni/V₂O₅ were investigated in different reaction temperature in the range of 150 to 190 °C. The results were shown in Table 5. EL conversion was only 7.00% when the reaction was carried out at 150 °C, and the product was mainly IPL, which means the Ni/V₂O₅ catalyst almost had no activity under the reaction temperature of 150 °C. Interestingly, when increasing the reaction temperature to 160 °C, conversion rate of EL and selectivity of GVL were significantly increased to 79.8% and 67.76%, and continuing increasing the reaction temperature to 180 °C, both values kept increasing. In the meantime, the intermediate 4-HPE decreased gradually with the reaction temperature increasing. Based on the above results, only the reaction temperature reached 160 °C can provide sufficient energy to over the catalytic energy barrier in this reaction, and high reaction temperature promoted the catalytic reaction rate. Thus, the suitable reaction temperature is 180 °C.

3.7. Recycling experiments

Table 6. Results of recycling experiments

| Entry | Usage times | Conversion/% | Selectivity/% | GVL | 4-HPE | IPL |
|-------|-------------|--------------|---------------|-----|-------|-----|
| 1     | 1           | 97.04        | 94.50         | 2.72 | 2.78  |
| 2     | 2           | 92.11        | 88.40         | 7.77 | 3.72  |
| 3     | 3           | 90.87        | 81.03         | 12.03 | 5.57  |
| 4     | 4           | 86.34        | 76.08         | 16.63 | 5.94  |
| 5     | 5           | 88.92        | 72.29         | 19.39 | 5.64  |

Reaction conditions: substrate 5 mmol (0.721 g) ethyl levulinate, 19 mL 2-propanol, 216 mg Ni/V₂O₅, reaction temperature 453 K, reaction time 4 h.
To investigate the recyclability of the 30%Ni/V₂O₅ catalyst, recycle tests for the CTH of EL to GVL were performed under the optimized reaction condition. After each run, the catalyst was separated by magnet, and washed with 2-propanol for 3 times. Then it subjected to the next run. The results are presented in table 6. The catalyst was reused for four catalytic runs with only a slight decrease in the EL conversion. But GVL selectivity decreased from 94.50 % to 72.29 %, and the selectivity of intermediate 4-HPE increased from 2.72 % to 19.39 % in the 5 runs, namely the lactonization of intermediate product 4-HPE to synthesize GVL was slowing down or be blocked. These results indicated that the metal active sites kept well while the acidic active sites may be covered or reduced in the recycle experiments.

3.8. The adsorption mechanism in CTH of EL over Ni/V₂O₅

Based on the above results, the synthesis of GVL from EL catalyzed by Ni/V₂O₅ using 2-propanol as a hydrogen source has two step reactions. Firstly, ethyl levulinate was hydrogenated under the action of Ni catalytic active sites and then the intermediate 4-HPE esterified and cyclized to generate GVL catalyzed by the acidic active sites, as shown in scheme 1. The use of secondary alcohols as hydrogen sources in CTH is different from the traditional hydrogenation. Thus, the possible adsorption mechanism in CTH of EL over Ni/V₂O₅ to generate the reductive H species was proposed in scheme 2. Firstly, the hydroxyl group of 2-propanol was adsorbed on the Ni metal active sites to make a cleavage of O-H bond and generate a surface alkoxy group on the Ni surface. At the same time, 2-propanol is easily undergoing the β-H elimination step after the generation of an alkoxy group on the Ni surface. During the elimination process, a ketone molecule was released and two H-atoms remained on the Ni surface which was the active species for transfer hydrogenation. Then, this was helpful in the transfer of the adsorbed atomic hydrogen to the keto group of EL which was present on the same surface/adjacent surface sites, resulting in the formation of the intermediate 4-HPE on the Ni surface.

4. Conclusions

In this work, the efficient Ni/V₂O₅ catalysts were prepared via a solid phase grinding and in-situ reduction method. An excellent GVL selectivity of 93.04 % at EL conversion of 97.40 % could be achieved at 180°C in 4 h using Ni/V₂O₅ with 30 % Ni loading as a catalyst in CTH of EL to GVL. The catalyst can be reused for 5 times with the GVL selectivity decreased. A possible adsorption mechanism of generating H active species in CTH of EL over Ni/V₂O₅ was proposed. This work provided a green and efficient catalytic route for the synthesis of GVL from bio-derived ethyl levulinate. The solid phase grinding and in-situ reduction can be used as a green and efficient method for preparation of metal supported catalysts in numerous of hydrogenation reactions.

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