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A novel Ni/AC catalyst prepared by MOCVD method for hydrogenation of ethyl levulinate to γ -valerolactone



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ABSTRACT

GVL (γ -valerolactone) is identified as an important biomass platform molecule due to its wide application. In this work, a series of novel supported Ni catalysts with different supports and Ni loading were synthesized via metalorganic chemical vapor deposition (MOCVD) method for the hydrogenation of EL (ethyl levulinate) to GVL. Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), nitrogen adsorption/desorption, inductively coupled plasma optical emission spectroscopy (ICP-OES) and transmission electron microscopy (TEM) were used to characterize the as-synthesized catalysts. The results showed that the 2 wt.% Ni/ AC(MOCVD) presented superior catalytic activity when compared with the catalyst prepared by impregnation method. This behavior is explained in terms of the smaller Ni nanoparticles (4.28 nm) and higher dispersion on 2 wt.% Ni/AC(MOCVD). Among the catalysts, the 2 wt.% Ni/AC catalyst exhibited the best catalytic performance with 99.7 % EL conversion and 79.8 % GVL yield under 1 MPa initial H₂ pressure (measured at room temperature) at 250 °C for 2 h. In addition, the reaction conditions were optimized and the stability of the catalyst were also investigated. The insights gained from this study in the design of high dispersed Ni particles with smaller particle size via MOCVD method will facilitate the metal-catalyzed hydrogenation of EL to GVL.

1. Introduction

With the rapid depletion of fossil fuels and its subsequent environmental deterioration, searching for clean and renewable energy resources has become particularly important. The research focused on biomass-derived platform molecules which have attracted considerable attention in recent years because of its unique physical and chemical properties. Biomass-derived platform molecules are considered as potential alternative to replace fossil-based resources [1,2], which can meet the increasing demand of energy for the production of fuels and chemicals. Biomass-derived platform molecules can be converted into a variety of valuable chemicals [3-6], such as 5-hydroxymethylfurfural (5-HMF), ethyl levulinate (EL), levulinic acid (LA), y-valerolactone (GVL), 2-methyl tetrahydrofuran (2-MTHF), etc. Among them, GVL is identified as an important building block due to its wide application [7-11]. As a non-toxic and coconut scented compound, GVL could be used as an additive of food and perfume, and proved to be an excellent solvent [12,13]. Besides, in consideration of the carbonyl and cyclic lactone groups on GVL, it could be directly used as raw material to prepare high calorific value liquid hydrocarbon fuels and fuel additives through ring-opening hydrogenation reaction [7]. Moreover, GVL could also be converted to epsilon-caprolactam, which is the raw material to produce nylon polymers [14]. Therefore, GVL has been known as one of the most important biomass platform molecules [10].

At present, many reports have focused on the preparation of GVL, especially on the hydrogenation of LA and its esters to GVL, which is one of the key steps in biomass conversion reactions [15,16]. The synthesis of GVL from LA or its esters can be divided as homogeneous reaction and heterogeneous reaction. Generally speaking, the catalysts used in homogeneous systems are mainly noble metal coordination compounds, such as Ru(acac)₃, [Ir(COE)₂Cl]₂ and so on [17,18], which showed excellent catalytic performances under mild conditions. For example, [Ir(COE)₂Cl]₂ achieved a 99 % yield of GVL under 5.0 MPa H₂ at 100 °C for 15 h, and Pd(DTBPE)Cl₂ obtained a almost 100 % yield of GVL under 0.5 MPa H₂ at 80 °C for 5 h. However, it is obvious that the recovery of the catalysts in the homogeneous system can be extremely difficult, which significantly limited its large-scale commercial application. Moreover, the complex synthesis methods for homogeneous catalysts could also constrain their application.

Hence, heterogeneous catalyst would be a more suitable choice for

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hydrogenation of LA and its esters to GVL. In heterogeneous reaction system, noble metal catalysts such as Ru, Ir, Pd and Au, etc. [19-22], could reach a considerable GVL yield under mild conditions. Du et al. [19] reported that the Ir/AC catalyst obtained a 95 % GVL production under 5.5 MPa H₂ at 150 °C for 2 h. Nonetheless, a common sense is that the noble metal catalysts are too expensive for the industrial synthesis of GVL. Compared to noble metal catalysts, transition metal catalysts are more economical and practical, especially for nickel-based catalysts, such as Ni/Al₂O₃, Ni-Cu/Al₂O₃, Ni/MgAlO₂, Ni/MgO [23-25]. Lv et al. [23] obtained 69.9 % GVL yield and 74.9 % LA conversion with Ni/ MgO catalyst under optimal reaction conditions of 150 °C, 1.0 MPa H₂ for 2 h. In recent years, Raney Ni, Ni@NCMs, also had been proved to be effective for the hydrogenation of LA and its esters to GVL [26, 27]. However, for the traditional preparation process such as co-precipitation and impregnation, the active site cannot be dispersed uniformly on the catalyst. Moreover, the utilization of nickel was relative low, and the solvents might block the inner surface and pores of the supports which leading to a low loading. Fortunately, MOCVD is considered as a potential alternative to obtain the catalyst with the Ni nanoparticles well-dispersed [28]. To our knowledge, the nickel-based catalysts prepared by MOCVD method for the hydrogenation of LA and its esters to GVL was reported minimally. Thus, considerable interest has been paid on MOCVD synthesis of supported Ni catalyst. The key issue for the MOCVD located on the selection of suitable Ni-based metal-organic precursors, which should be adequately volatile and sufficiently stable at room temperature as well as non-toxic. Highly and homogeneously nickel-supported catalysts has been synthesized by using Ni(COD)₂ as the MOCVD precursor [28]. However, the toxicity and instability limited its wide application. We found that Ni(acac)₂ shoud be a good choice for the replacement of Ni(COD)₂, owing to its appropriate sublimation and thermal decomposition temperature. Additional, it is relative cheaper, less toxic and more stable than Ni(COD)₂. Based on the above, supported Ni catalysts prepared by MOCVD method with Ni (acac)₂ as the metal-organic precursor were applied to the hydrogenation of EL to GVL.

In this work, Ni(acac)₂ (Nickel(II) acetylacetonate) was used as the metal-organic precursor to synthesize a series of supported Ni catalysts via MOCVD method, and the as-synthesized catalysts were manifested to be efficient for the hydrogenation of EL to produce GVL under mild conditions. N2-adsorption/desorption, XRD, FT-IR, ICP, and TEM were further taken to characterize the catalysts. The results showed that the 2 wt.% Ni/AC(MOCVD) presented superior catalytic activity when compared with the catalyst prepared by impregnation method. This behavior is explained in terms of the smaller Ni nanoparticles (4.28 nm) and higher dispersion on 2 wt.% Ni/AC(MOCVD). Among the catalysts, the 2 wt.% Ni/AC catalyst exhibited the best catalytic performance with 99.7 % EL conversion and 79.8 % GVL yield under 1 MPa initial H₂ pressure (measured at room temperature) at 250 °C for 2 h. In addition, the reaction conditions and pathways were also investigated. This paper successfully synthesized the Ni-based catalysts with high dispersion and relatively small particle size via MOCVD method, which presented excellent catalytic activity and will promote the further commercial application of Ni-based catalysts.

2. Experimental

2.1. Materials

The organic metal precursor nickel acetylacetonate (Ni(acac)₂), Ni $(NO_3)_2$ ·6H₂O, Dodecane (internal standard) were purchased from Shanghai Dibai Biotechnology Co., Ltd., Tianjin Kemiou Chemical Reagent Co. and Aladdin. Catalyst support included activated carbon (AC), SiO₂, Al₂O₃ and H-ZSM5 were purchased from NORIT, Tianjin Kemiou Chemical Reagent Co., Ltd., Aladdin, Aladdin and Shen Shi Mining Co., Ltd., respectively. EL was purchased from Beijing Bellingway Technology Co., Ltd. (99 %), and GVL was purchased from

Aladdin (99 %). All the chemicals were directly used without pretreatment after purchase.

2.2. Catalyst preparation

MOCVD method: The deposition of Ni particles on the support was conducted in a schlenk bottle. Specifically, a certain amount of Ni (acac)₂ precursor was mechanically mixed with the support, then the mixture was transferred into the schlenk bottle. After vacuuming, the schlenk bottle was put into the drying oven at 200 °C for 12 h, which resulted in a complete deposition of the precursor onto the support. Finally, the thermal decomposition and reduction progress were carried out at 460 °C for 4 h in the flow of H₂/N₂ (40 mL min⁻¹, volume flow ratio was 1:1), with a heating rate of 5 °C/min. The obtained catalysts were recorded as x wt.% Ni/support, where x was the theoretical loading amount of Ni.

Impregnation method (IM): The catalyst prepared by classical impregnation method was using an aqueous solution of Ni(NO₃)₂·6H₂O and activated carbon. Firstly, the activated carbon was dried at 120 °C for 12 h. Secondly, AC was adequately dispersed in an aqueous solution of Ni(NO₃)₂·6H₂O at room temperature for 24 h. Then the mixture was dried at 120 °C for 12 h. Subsequently, the dried sample was then subjected to H₂/N₂ (40 mL min⁻¹, volume flow ratio was 1:1) reduction at 460 °C for 4 h. The obtained catalysts were recorded as 2 wt.% Ni/AC (IM).

2.3. Catalyst characterization

Thermogravimetric (TG) and differential thermal analysis (DTA) experiments were carried out using a QMA200 M instrument. An appropriate amount of samples were taken in the ceramic frame and the temperature changed from room temperature to 800 °C in the atmosphere of N₂ with the heating rate of 10 °C min⁻¹. The weight changes of samples that underwent temperature change were recorded.

Fourier transform infrared (FT-IR) spectra were recorded at 298 K on powder samples using the KBr wafer technique on a Nicolet Impact 410 with a resolution of 4 cm⁻¹.

X-ray diffraction (XRD) was measured on an ESCALAB250 (ThermoScientific) diffractometer with monochromatic Cu-K α as the radiation source ($\lambda = 1.54056$ Å) and operated at 40 kV and 200 mA. The scan speed was 3° min⁻¹ with a scanning angle of 5–80°.

Nitrogen adsorption/desorption measurements were performed on Quantachrome Autosorb iQ2 automated gas sorption system. The specific surface area of the sample was calculated by the Brunauer-Emmett-Teller (BET) method and the total pore size distributions were determined by Barrett-Joyner-Halenda (BJH) method from the isotherms. Before measurements, the samples were deaerated at 100 °C for 1 h and then outgassed at 300 °C for 3 h.

To determine the composition of the catalyst, Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-OES) was conducted on a thermal 7000 series analyzer. Initially, the samples were pretreated with aqua regia dissolving solid samples. Subsequently, the microwave digestion took place in a microwave digestion apparatus for 30 min to completely dissolve the metal. After cooling and filtration, the sample was then submitted to metal analysis.

Transition metal catalysts were analyzed using a Tecnai G^2 F30 (FEI) transmission electron microscope. The samples were sonicated for 5 min in ethanol to make them highly suspended, then dripped in a carbon film supported on a copper grid.

2.4. Ethyl levulinate hydrogenation

The catalytic conversion of EL was performed in a 50 mL batch reactor (Parr 4597). For each reaction, 0.2883 g (2 mmol) of EL and 0.4258 g (2.5 mmol) of dodecane (internal standard) were dissolved in 20 mL of isopropanol, together with 0.1 g of catalyst. Thenceforth, the reaction was carried out at a certain temperature, H_2 pressure and reaction time with the mechanical stirring speed of 1000 rpm. After the reaction, the liquid products were analyzed by GC–MS (Agilent 6890A-5975C) and GC (SP-7890). The conversion of EL and the yield of GVL were calculated according to the following equations:

$$Conversion = \left(1 - \frac{c(residual ethyl levulinate)}{c(initial ethyl levulinate)}\right) \times 100\%$$
(1)

$$\frac{\text{Product}}{\text{c(initial ethyl levulinate)}} \times 100\%$$
(2)

3. Results and discussion

3.1. Catalyst characterization results

Ni(acac)₂ was used as the precursor for nickel-based catalyst because of its adequate volatility nature and relatively wide temperature "gap" between evaporation and decomposition. In addition, it is commercially available and sufficiently stable at room temperature, compared to other precursors such as Ni (COD)₂, Ni(hfac)₂ and so on.

Thermogravimetric analysis was applied to verify the volatile characteristics of Ni(acac)₂ (Fig. 1). The precursor showed excellent stability up to 210 °C and illustrated a gradual weight loss before 150 °C due to the removal of water. Moreover, the melting point (226 - 238 °C) and boiling point $(220 - 235 °C \ 14.67 \ kPa^{-1})$ of Ni(acac)₂ are very close, which indicated that Ni(acac)₂ was easy to sublimate. Thus, the sublimation temperature could be set as 200 °C under vacuum in this study. DTA of the TG profiles of Ni(acac)₂ showed 76.6 % weight loss around 220 - 460 °C, due to the loss of organic ligands. The result was in a good agreement with the calculated weight percent loss to produce pure Ni (22.8 % calculated), which confirmed the precursor could be totally decomposed. Therefore, in this work, the thermal decomposition temperature was set at 460 °C.

In order to investigate the possible formation mechanism of small Ni particles, FT-IR spectra of catalysts were performed and the results were shown in Fig. 2. The spectrum of 10 wt.% Ni(acac)₂/AC (meant that the mass fraction of Ni atom was 10 %) exhibited the typical broad-band at 1641 cm⁻¹ and 1530 cm⁻¹, which could be assigned to telescopic vibration of C=O and the stretching vibration of C=C. It was mainly attributed to the fact that the C=O double bond of nickel metal and acetylacetone formed a large π bond resulting in C=C and C=O stretching vibration peak shifted to the low-frequency direction. Besides, the spectrum of 10 wt.% Ni(acac)₂/AC exhibited a typical broad-



Fig. 1. TG/DTA curve of Ni(acac)₂ precursor.



Fig. 2. FT-IR spectra of Ni-based catalysts.

band at 1430 cm⁻¹ and 1378 cm⁻¹, which could be attributed to the stretching vibrations and flexural vibrations of C–H bond. Significantly, this typical spectrum disappeared in 10 wt.% Ni/AC due to thermal decomposition of Ni(acac)₂. The spectrum of 10 wt.% Ni/AC was similar to AC, indicating the purity of the as-synthesized catalyst was high. When mixing Ni(acac)₂ with AC, the large π bond resulted in Ni²⁺ strongly bonded to the functional group of the AC. It was clear that NiO species was successfully converted to metallic nickel.

XRD analysis was carried out to investigate the crystal structure of the catalysts (as shown in Fig. 3). The broad peak at $2\theta = 14.6^{\circ}$ was the characteristic peak of AC support. The three sharp diffraction peaks observed at $2\theta = 45.5^{\circ}$, 51.9° , and 76.5° are corresponding to the (111), (200), and (220) lattice planes of Ni° (ICDS 98-064-6090), respectively [21,24,29]. No diffraction peak of NiO was found in the XRD patterns, further confirmed that the Ni(acac)₂ precursors were completely reduced to Ni° particles. This result was consistent with the TG/DTA results. Furthermore, the intensity of the diffraction peaks of Ni° increased with the increasing of Ni loadings from 2 wt.% to 10 wt.%.

To determine the textural parameters and actual loading amount of the synthesized Ni/AC catalysts, N₂ adsorption/desorption and ICP analysis were carried out separately. As shown in Table 1, with the increase of Ni content from 0 to 10 wt.%, the BET surface area (S_{BET})



Fig. 3. XRD patterns of Ni/AC catalysts with different Ni loadings.

 Table 1

 Textural properties of Ni/AC catalysts with different Ni loadings.

| Catalyst | S_{BET} (m ² g ⁻¹) | Pore size ^a (nm) | Pore volume $(cm^3 g^{-1})$ | Ni content ^b (wt.%) |
|---------------|--|--------------------------------|-----------------------------|-----------------------------------|
| AC | 980 | 2.78 | 0.56 | - |
| 2 wt.% Ni/AC | 965 | 2.35 | 0.56 | 2.10 |
| 5 wt.% Ni/AC | 887 | 2.34 | 0.52 | 5.21 |
| 10 wt.% Ni/AC | 795 | 2.32 | 0.47 | 10.49 |
| 2 wt.% Ni/ | 958 | 2.36 | 0.56 | 1.88 |
| AC(IM) | | | | |

^a Average pore diameter was calculated from the desorption branches by the BJH model.

^b Determined by ICP analysis.

and the pore volume (V) reduced slowly (S_{BET}: from 980 to 795 m² g⁻¹, Pore volume: from 0.56 to 0.47 cm³ g⁻¹). Simultaneously, the pore size also showed a minimal drop due to the obstruction of the channel by the Ni particles²⁷. For the catalyst prepared by MOCVD method, the ICP results demonstrated that the actual loading of Ni was slightly higher than the theoretical loadings. The difference between actual metal loadings and the theoretical loadings could contribute to the loss of bound water and impurities in AC. Compared with the catalyst prepared by MOCVD method, the loss of Ni was inevitable. As a result, we chose the MOCVD method.

TEM was conducted to investigate the morphologies and metal dispersions of the Ni/AC catalysts. As depicted in Fig. 4, the average diameter of 2 wt.% Ni/AC (MOCVD) was around 4.28 nm, while the average diameter of 2 wt.% Ni/AC (IM) was around 7.58 nm. Additional, as determined from XRD analysis, the crystal size of 2 wt.% Ni/AC (MOCVD) calculated by using Scherrier equation through the Ni (111) diffraction peak was around 4.52 nm, which was consistent with the TEM results. It was also reported that the mean size of Ni/AC prepared by impregnation method was about 8.0 nm, which was closed

| Table 2 | |
|---|--|
| Hydrogenation results of EL over different catalysts ^a . | |

| Entry | Catalyst | Solvent | Conv. (EL)/% | Yield/% | | |
|-------|---|-------------|--------------|---------|------|-----|
| | | | | GVL | А | В |
| 1 | Without | Isopropanol | 10.0 | 7.8 | 1.3 | 0.8 |
| 2 | AC | Isopropanol | 14.0 | 10.2 | 2.9 | 0.8 |
| 3 | 10 wt.% Ni/AC | Isopropanol | 97.6 | 67.0 | 27.3 | 1.8 |
| 4 | 10 wt.% Ni/Al ₂ O ₃ | Isopropanol | 79.4 | 47.3 | 4.3 | 5.1 |
| 5 | 10 wt.% Ni/SiO ₂ | Isopropanol | 26.3 | 16.9 | 8.2 | 0.6 |
| 6 | 10 wt.% Ni/HZSM-5 | Isopropanol | 14.8 | 14.4 | 0.2 | 0.2 |
| 7 | 10 wt.% Ni/AC | Ethanol | 39.9 | 33.8 | - | 0.0 |
| 8 | 10 wt.% Ni/AC | 2-butanol | 78.3 | 38.3 | 39.2 | 0.0 |
| 9 | 10 wt.% Ni/AC | Methanol | 97.4 | 12.3 | 82.4 | 0.0 |
| 10 | 2 wt.% Ni/AC | Isopropanol | 99.7 | 79.8 | 1.3 | 2.2 |
| 11 | 2 wt.% Ni/AC(IM) ^b | Isopropanol | 90.2 | 62.5 | 9.3 | 2.4 |
| 12 | 5 wt.% Ni/AC | Isopropanol | 97.4 | 67.7 | 26.4 | 1.9 |

 $^{\rm a}$ Reaction conditions: EL (2 mmol), dodecane (2.5 mmol, internal standard for GC), solvent (20 mL), catalyst (0.1 g) and initial H₂ pressure (1 MPa), reaction time (2 h), reaction temperature (250 °C).

to our result [30]. Therefore, the Ni nonoparticles obtained from MOCVD method exhibited narrower size distribution with high dispersion when compared to the impregnation method.

3.2. Activity and stability of synthesized catalysts

As shown in Table 2, the catalytic performance of the as-prepared catalysts was examined under different conditions, including different supports, solvents and Ni loadings. The main product was GVL, accompanied by the formation of levulinic esters (A) and valerate esters (B) due to side reaction (Scheme 1). For the 2 wt.% Ni/AC catalyst prepared by MOCVD method (as shown in entry 10), the EL was almost completely converted with the conversion of 99.7 % and GVL yield of 79.8 %. Apparently, the Ni active sites simultaneously promoted the



Fig. 4. TEM images of (a, b, c) 2 wt.% Ni/AC, (d, e, f) 2 wt.% Ni/AC (IM).



Scheme 1. Main products from hydrogenation of EL to GVL.

R=methyl, ethyl, Isopropyl, sec-butyl

fracture of the C–O bond to form γ -hydroxyl acid or esters. At last, GVL was formed from the γ -hydroxyl acid or its esters through the process of dealcoholization and cyclization.

To optimize the best reaction conditions for the hydrogenation of EL catalyzed by the Ni-based catalyst, the effect of different supports was investigated. For entry 1 and 2, it demonstrated that the EL conversion only reached 10.0 % without catalyst and slightly increased to 14.0 % on the AC support. Interestingly, Ni/SiO₂ exhibited low conversion and yield, owing to the low acidity of the supports. When using the moderately strong acidity oxides, such as Al₂O₃, the result showed that the conversion and yield could reach to 79.4 % and 47.3 %, respectively. The diameter of Ni(acac)₂ was around 12 Å, which is bigger than the micropore of the HZSM-5 (d = $5 \sim 6$ Å) [31,32]. Therefore, during the MOCVD progress, the Ni(acac)₂ can hardly deposit into the micropore of the HZSM-5 which probably leading the surface aggregation of Ni particles with lower activity. As shown in Table 2 (entry 3, 4, 5 and 6), it was noteworthy that the activity of Ni/AC was higher than any other catalysts, which was probably correlated with the large specific surface area and pore diameter of activated carbon. Furthermore, acid sites on the surface of the activated carbon also promoted the reaction [33] Therefore, Ni/AC was selected for further studies.

Moreover, the effect of the solvent on the hydrogenation activity of the catalyst was investigated. According to entries 3, 7, 8, and 9 in Table 2, solvents significantly affected the hydrogenation of EL to GVL over Ni/AC catalyst under optimum conditions. Generally, CTH (catalytic transfer hydrogenation) reaction with second alcohol provided much higher EL conversion and GVL yield than primary alcohol. The reducing potential of various alcohols was IPA < 2-butanol < ethanol < methanol [34]. The yield of GVL was in line with this order. The highest reduction of Methanol resulted in relatively poor H-donor abilities. When using methanol as a solvent, the conversion was 97.4 % whereas little GVL was obtained. As depicted in Table 2 entry 9, it was clearly that most of EL converted to methyl levulinate (intermediate). Primary alcohol provided little GVL because of difficult β -H removement in the CTH reaction. Among all the alcohols, isopropanol showed better performance, and was chose for further researches.

The catalytic performance of different Ni loadings catalysts was also listed in Table 2. When a small amount of Ni deposited on the AC, the conversion and yield both rose obviously. However, the selectivity of EL further decreased with the increase of Ni loadings. Previous studies revealed that the hydrogenation and lactonization were two intermediate steps for the transformation of EL to GVL [[23]]]]. The excessive amount of nickel affected the process of lactonization, which tended to produce by-product A [[34]]]]. For the 2 wt.% Ni/AC (IM) shown in entry 11, the catalytic performance was inferior to the Ni/AC with EL conversion of 90.2 % and GVL yield of 62.5 %. Compared with the results, it was obviously that the Ni/AC prepared by MOCVD method had better catalytic performance, which was due to the smaller particle size and the higher dispersion of Ni/AC [[26]]]].

Thereafter, the effect of reaction temperature on the catalytic activity of 2 wt.% Ni/AC was studied. As shown in Fig. 5 (a), the conversion of EL increased stably and the yield of GVL rose rapidly with temperature increased from 200 to 250 °C. The highest yield of GVL could reach 79.8 % within 2 h at 250 °C. In the meantime, A1 (isopropyl levulinate) decreased. Moreover, B1 (isopropyl valerate) increased. This phenomenon reflected that the C–O bond fractured easier at high temperature [35,36]. In order to shorten the reaction time and obtain higher GVL yield, the temperature of 250 $^\circ C$ was selected for the next research.

And then, the effect of H₂ pressure was shown in Fig. 5 (b). It can be seen that the H₂ pressure had a slight influence on the transformation of EL into GVL. This phenomenon may be ascribed to the reason that the isopropanol could also be the hydrogen donor on the CTH of EL to GVL. When the H₂ pressure was 1 MPa, the conversion and yield achieved 97.6 % and 79.8 %, respectively. Further enhancing the H₂ pressure led to the decline of GVL yield, implying more undesirable by-products generated, such as 1, 4-pentanediol (1, 4-PDO), 2-MTHF and so on, which was in accordance with previous reports [37,38].

For the sake of higher GVL yield, we investigated the effect of reaction time. As shown in Fig. 5(c), the result exhibited that the reaction rate was rapid within the first 2 h and the GVL yield reached 79.8 % with almost complete conversion of EL. Although the conversion of EL to GVL could be promoted with further prolonging the time, the selectivity of the GVL displayed a downward trend at the meantime. Above all, the optimized condition for efficient catalytic hydrogenation of EL to GVL was: 250 °C, 1 Mpa initial H₂ and 2 h.

The stability is significant for the commercial industrial production, so we studied the reusability of 2 wt.% Ni/AC under optimum conditions (Fig. 6). After each cycle, the catalyst was collected by filtration, washed with fresh isopropanol, and then dried for the next run. After the second run, both the conversion of EL and the yield of GVL decreased obviously. After four cycle, the conversion of EL and yield of GVL was 85.3 % and 68.2 %, respectively.

XRD diffraction peaks of the fresh and spent Ni/AC catalyst were shown in the Fig. 7. Apparently, for the spent 2 wt.% Ni/AC, the characteristic peak of Ni0 at 44.0° and 51.2° became weaker. Moreover, additional peak at 43.2° which belonged to (200) planes of NiO appeared for the spent 2 wt.% Ni/AC. These phenomenon suggested that the Ni species possibly undergo oxidation or leaching loss during the reaction, which was considered as the disadvantage of almost all monoatomic supported catalysts [[39]] The Brunauer-Emmett-Teller (BET) surface area, pore volume and pore size for the spent 2 wt.% Ni/ AC were displayed in Table 3. The surface area declined from $965 \text{ m}^2/\text{g}$ to $886 \text{ m}^2/\text{g}$ after the reaction. Simultaneously, the pore size of the catalyst slightly declined and the pore volume decreased from $0.56 \text{ cm}^3 \text{g}^{-1}$ to $0.41 \text{ cm}^3 \text{g}^{-1}$. According to the previous literature, it should be caused by the coke deposition on the surface and in the pores of the catalyst. ICP-OES was performed to determine the Ni content of the spent catalyst. The result exhibited that the Ni content decreased from 2.1 wt.% to 1.86 wt.% after recycling, which further confirm the leaching loss of Ni species during the reaction. It is reported that aggregation and sintering of Ni particles could also result in the deactivation of the catalyst. Thus, TEM was carried out to observe the morphology change of Ni on the surface of the catalyst. As depicted in Fig. 8, the Ni particles still distributed uniformly on the surface of AC, but the particle size has increased from 4.28 nm to 5.07 nm for the spent catalyst. In summary, we concluded that it is the oxidation, aggregation and leaching loss of the Ni species, together with the coke deposition during the reaction which leading the deactivation of the Ni/ AC catalyst.

3.3. Proposed mechanism

Based on the previous study [40-43], the possible mechanism of Ni/



Fig. 5. The effect of the reaction conditions in the conversion of EL in the presence of 2 wt.% Ni/AC catalyst. EL (2 mmol), dodecane (2.5 mmol, internal standard for GC), catalyst (0.1 g); A1 (isopropyl levulinate); B1 (isopropyl valerate); (a) Reaction temperature (1 MPa H₂, 2 h); (b) Reaction pressure (250 °C, 2 h); (c) Reaction time (250 °C, 1 MPa H₂).



Fig. 6. The recycling experiments of 2 wt.% Ni/AC (250 °C, 1 MPa H₂, 2 h).



Fig. 7. XRD patterns of fresh and spent 2 wt.% Ni/AC catalyst.

AC catalyzed hydrogenation of EL to GVL was proposed above. As depicted in Scheme 2, GVL could be generated in two pathways. The first route showed that γ -hydroxy pentanoic was produced from EL through the hydrogenation of the ketone group. γ -hydroxy pentanoic, as the intermediate, was unstable under the reaction condition, therefore, it could be converted into GVL via the intramolecular transesterification. The other route involved the ketone group of EL hydrogenated to form ethyl 4-hydroxyvalerate (4-HPE), which generated GVL upon dealcoholization and cyclization. As we know, the reaction was driven by the thermodynamic properties of the intermediates and the products. Besides this, it was apparently that the reaction was irreversible. According to the GC-MS result, no 4-HPE was detected, which demonstrated that the 4-HPE were unstable and can quickly be transferred to

Table 3

Textural properties of fresh and spent 2 wt.% Ni/AC catalyst.



Fig. 8. TEM images of (a, b, c) fresh 2 wt.% Ni/AC and (d, e, f) spent 2 wt.% Ni/AC.

the GVL. Because the rate of transformation from EL to 4-HPE was rapid, equilibrium of reaction was up to the generation of 4-HPE. Then GVL was further hydrogenated to form 1, 4-PDO, 2-MTHF and valerate esters. In addition, EL could produce levulinic esters due to the substitution reaction at low temperature or pressure.

4. Conclusions

Overall, this study clearly demonstrated that the high dispersed Ni/ AC catalyst prepared by MOCVD method with Ni(acac)₂ as the precursor was successfully applied in efficient catalytic hydrogenation of EL to GVL. Results revealed that the Ni particles obtained from MOCVD method exhibited narrower size distribution with high dispersion, which presented superior catalytic activity in hydrogenation of EL to GVL when compared to the impregnation method. Therefore, the design of high dispersed Ni particles with smaller particle size via MOCVD method will facilitate the metal-catalyzed hydrogenation of EL to GVL. In addition, the 2 wt.% Ni/AC catalyst was proved to have the best catalytic performance for the hydrogenation of EL to GVL. The results showed that the conversion of EL achieved 99.7 % and the yield of GVL reached 79.8 % via IPA as solvent under the conditions of 250 °C and 1 MPa H2 for 2 h. This novel Ni/AC catalysts possessed excellent catalytic performance was proved to be a promising catalyst in the hydrogenation of EL to GVL in biomass utilization. Preparation of the catalysts using other non-precious metals and the study of their catalytic performances are in progress.

CRediT authorship contribution statement

Na Ji: Conceptualization, Methodology, Writing - review & editing. Zhenyu Liu: Writing - original draft. Xinyong Diao: Writing - review & editing. Jinrong Bao: Visualization, Investigation. Zhihao Yu: Software. Chunfeng Song: Writing - review & editing. Qingling Liu:

| Catalyst | $S_{BET} (m^2 g^{-1})$ | Pore size ^a (nm) | Pore volume (cm 3 g $^{-1}$) | Ni content ^b (wt.%) | | | |
|--|------------------------|-----------------------------|----------------------------------|--------------------------------|--|--|--|
| 2 wt.% Ni/AC (fresh) 2 wt.% Ni/AC (spent) | 965 886 | 2.35 2.33 | 0.56 0.41 | 2.10 1.86 | | | |

^a Average pore diameter was calculated from the desorption branches by the BJH model.

^b Determined by ICP analysis.



Scheme 2. Proposed reaction pathways of EL to GVL.

Writing - review & editing. **Degang Ma:** . **Xuebin Lu:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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