



Full Length Article

Hydrogenation of biomass-derived ethyl levulinate into γ -valerolactone by activated carbon supported bimetallic Ni and Fe catalysts



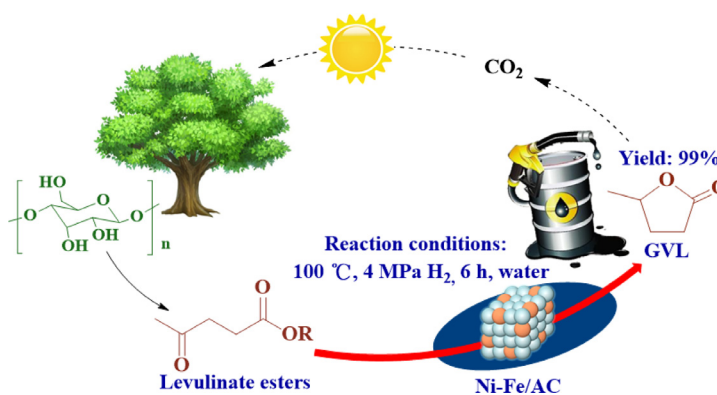
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HIGHLIGHTS

- Bimetallic Ni-Fe/AC catalysts with different Fe/Ni ratios are prepared.
- Ni-Fe/AC catalysts are efficient for catalyzing EL to GVL under mild conditions.
- The catalysts are characterized by XRD, TEM, HRTEM, EDX, XPS, H₂-TPR and NH₃-TPD.
- Ni-Fe alloy and co-presented FeO_x contribute to the high catalytic activity.
- The Ni-Fe/AC catalysts can be easily separated due to their strong magnet.

GRAPHICAL ABSTRACT



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ABSTRACT

Gamma-valerolactone (GVL) has been identified as a sustainable high-value platform molecular for the production of fuels and carbon-based chemicals. In this work, a series of activated carbon supported low-cost bimetallic Ni-Fe catalysts (Ni-Fe/AC) with different molar content of Fe species were prepared by using co-precipitation method for the liquid phase hydrogenation of ethyl levulinate (EL) to produce γ -valerolactone. The Ni-Fe_{0.5}/AC exhibited the highest activity among the bimetallic or monometallic catalysts under mild reaction conditions (100 °C, 4 MPa H₂, 6 h) and achieved 99.3% conversion of EL and 99.0% yield of GVL. Under more mild conditions (60 °C, 2 MPa H₂) and prolonging the reaction time to 24 h, EL could be converted completely and the obtained GVL yield was more than 98%. The catalysts were characterized by various techniques including XRD, TEM, HRTEM, EDX, XPS, H₂-TPR and NH₃-TPD. Based on the structure and activity relationship study, the formation of highly dispersed Ni-Fe alloy structure and the co-presented FeO_x nanoparticles could be responsible for the high catalytic hydrogenation activity.

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1. Introduction

Biomass is the most abundant, inexpensive and renewable organic carbon resource, which is identified as an ideal promising

green feedstock for the production of fuels and chemicals [1–4]. The related study is attracting more and more attention for the environmental and sustainable concerns [5]. So far, biomass has been converted into fuels and diverse value-added chemicals including different alcohols [6,7], formic acid (FA) [8], gluconic acid [9,10], etc. Various downstream products are obtained when glucose monomers are further converted, such as levulinic acid (LA)

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[11,12] or levulinate esters [13,14], 2,5-furandicarboxylic acid (FDCA) [15,16], furfural alcohol (FAL) [17], 2,5-dimethylfuran (DMF) [18,19] and γ -valerolactone (GVL) [20–22], etc. Among these chemicals, levulinic acid or its esters is regarded as one of the ten most important biomass platform molecule compounds [23,24], as it can be obtained by the dehydration of carbohydrates [25] or alcoholysis [26–28], meanwhile, it can be further converted to fuels or various high-value products. Notably, the hydrogenation of levulinic acid or its esters to GVL (as shown in Scheme 1) is one of the key reactions in sustainable biomass conversion [29,30]. GVL is highly stable, low toxic, safe to store and can be widely utilized as liquid fuel, fuel additive, food additive, green solvent for biomass processing and intermediate for the production of fine chemicals [31–33]. Especially, GVL is ready used as the blending agent of gasoline, diesel, or biodiesel fuel due to its heating value and higher energy density. Horvath et al. [34] showed that a mixture of 90% gasoline and 10% GVL has a similar octane value to a mixture of 90% gasoline and 10% ethanol, while GVL improves the burning characteristics of the fuel due to its low vapor pressure.

To date, a considerable amount of work has been done on the hydrogenation of LA or its esters to GVL using homogeneous or heterogeneous catalysts. According to the previous reports, homogeneous catalysts such as RuCl_3 , $\text{Ru}(\text{acac})_3$ ligated with $\text{P}(\text{Oct})_3$, TPPTS or DPPDS have been successfully applied to hydrogenate LA to GVL with excellent yields [35,36]. However, for practical application, homogeneous catalysts suffer from noble metals and complex ligands, and poor recyclability due to the difficulty in the catalyst/product separation [37]. Heterogeneous catalysts reported for the hydrogenation of LA primarily include various metals (e.g. Pd, Pt, Au, Ru, Ir, Rh and Re) supported on activated carbon (AC) or other carriers [38–42] converted LA to GVL with over 95% yield, at 150 °C under 5.52 MPa H_2 for 2 h. However, the noble metal-based catalysts suffer from low abundance in earth, which limited their large-scale industrial application to produce GVL [43].

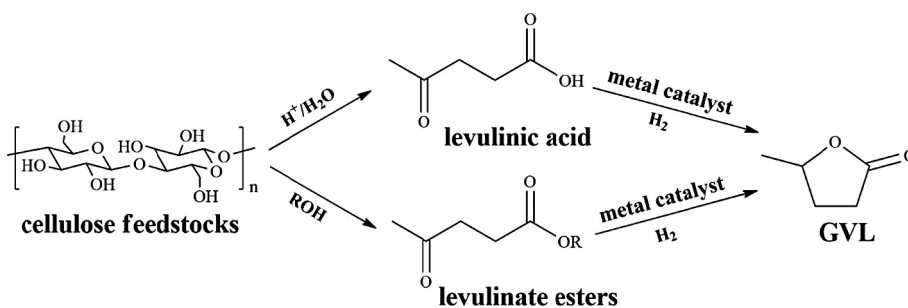
It is highly desirable to develop economically feasible, abundant and recyclable catalysts for GVL production [44]. Pravin et al. [45] reported nanocomposite catalysts of Cu/SiO_2 with tunable Cu loadings for almost full conversion of LA to GVL in vapor-phase conditions (265 °C, 2.5 MPa H_2). Mohan et al. [46] examined the Ni/HZSM-5 catalyst at 250 °C and 1 bar H_2 and achieved 100% LA conversion and 92.2% selectivity to GVL. Velisoju et al. [47] screened Ni (20 wt%) supported on SiO_2 , $\gamma\text{-Al}_2\text{O}_3$ and ZrO_2 catalysts for hydrogenation of aqueous LA or esters to GVL at 270 °C and ambient pressure. Up to now, most of the reported transition metal based catalysts required relatively high reaction temperatures with H_2 gas as H-donor, such as 265 °C for Cu/SiO_2 catalysts and 250–270 °C for Ni-based catalysts.

Currently, various multifunctional bimetallic catalysts including Ru-Sn [48], Pd-Au [49], Ni-MoOx/C [37], Cu-Cr [50] and Cu-Fe [51]

were also employed in the hydrogenation of LA or its esters to GVL. Thereinto, Li [50] synthesized stable and efficient CuCr catalyst and it showed rather high catalytic capacity for the solvent-free hydrogenation of ethyl levulinate (EL) to GVL in a yield up to 95%. Yan [51] reported Cu-Fe catalyst, which exhibited highly efficient performance in the hydrogenation of biomass-derived levulinic acid with 90.1% GVL yield under mild vapor phase temperature (200 °C). Recently, studies have shown that Fe species can act as an electronic/chemical promoter to modify metal catalysts and result in enhanced catalytic activity and selectivity because it increases the surface area and dispersion of host metal elements [52]. The multifunctional catalysts are becoming a hot research topic owing to their tunable composition and size, excellent dispersion and electronic properties, which closely link to various applications including magnetism, electronics and especially catalytic activity [53–55]

Given the hydrogenation activity of Ni and the synergistic effect of Fe as well as their low cost, herein, we developed an activated carbon supported non-noble bimetallic Ni and Fe heterogeneous catalyst (Ni-Fe/AC) for liquid phase hydrogenation of EL to GVL. Using EL instead of LA as the feedstock is based on the following consideration. LA is generally produced by the dehydration of carbohydrates lignocellulose by hydrolysis in strong acidic medium, wherein during this process, it is inevitably generating polymeric humin due to the thermal decomposition of intermediates and leading to a low yield of LA [56,57]. However, the formation of humin can be significantly inhibited (up to 70%) by alcoholysis in various alcoholic medium owing to the formation of the corresponding levulinic esters in high yield (95%) compared with LA (25%) from C6 sugars [58]. What's more, levulinate esters are more easily separated from the reaction system and the efficient recycling advantage of alcohols during the sustainable synthesis will greatly reduce the costs [59]. Furthermore, the catalytic hydrogenation of levulinic esters to GVL route can effectively inhibit the active metal leaching from the hydrogenation catalysts caused by the free carboxyl of LA [28].

In this study, a series of activated carbon supported bimetallic Ni-Fe catalyst were prepared by using co-precipitation method to catalyze biomass-derived EL for the production of GVL. The various effects including molar content of Fe species, reaction temperature, H_2 pressure and reaction time on the reaction were studied. Furthermore, the relationship of the structure and activity was studied systematically by various characterization techniques of X-ray power diffraction (XRD), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), H_2 temperature-programmed reduction (H_2 -TPR) and the temperature-programmed desorption of ammonia (NH_3 -TPD).



Scheme 1. The transformation of cellulose to γ -valerolactone.

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