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Conversion of levulinic acid and cellulose to γ-valerolactone over Raney-Ni catalyst using formic acid as a hydrogen donor

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ABSTRACT

The present study aimed to investigate the conversion of levulinic acid (LA) and cellulose (DP∼450) to γ-valerolactone (GVL) over Raney-Ni catalyst. In this process, hydrogenation was fulfilled using formic acid (FA) as the hydrogen donor. The highest LA conversion (100%) and GVL yield (68.5%) were obtained using LA:FA 1:4 ratio, Raney-Ni catalyst (20 mg/mmol of LA) and heating at 200 °C for 48 h. Under similar reaction conditions cellulose (DP∼450) was converted into GVL in 23.3% yield in a single reactor process. The addition of acidic co-catalysts such as Brönsted acids: H_2SO_4, Amberlyst-15 (H^+) or Dowex 50WX8 to the reaction mixture did not improve the GVL yield. The SEM analysis of the Raney Ni-catalyst used in transformation of cellulose to GVL showed that catalyst surface gets contaminated with carbon deposits in the single reactor process.

ARTICLE HISTORY
Received 20 December 2017
Accepted 10 May 2018

KEYWORDS
levulinic acid;
γ-valerolactone; formic acid;
Raney-Ni; cellulose

Introduction

The development of efficient methods for the conversion of lignocellulosic biomass into platform-chemicals is one of the major thrust areas in the current biofuel research. The platform chemicals such as furfural, 5-hydroxymethylfurfural (HMF), levulinic acid (LA) and its hydrogenation product γ-valerolactone (GVL) envisaged in future bio-refinery schemes [1] and as sustainable alternatives to crude-oil based feedstocks [2]. Among these, the GVL or 5-methyldihydrofuran-2(3H)-one possesses potential applications as a green fuel additive, excellent solvent and fine chemical intermediate [3]. It can be directly used as a fuel as well as transformed to fuel precursors or monomers in renewable polymer industry [4,5]. Recently, GVL has been identified as a potential octane number boosting fuel additive to gasoline. Horváth et al. have concluded that GVL is a better alternative to ethanol as a fuel additive due to its lower vapor pressure and relatively higher energy content [6]. Furthermore, GVL does not form an azeotrope with water as compared with ethanol, which requires an energy-intensive concentration process to remove water during the ethanol production by fermentation [7]. In addition, GVL can be upgraded to valuable chemicals such as: 2-methyltetrahydrofuran [8], isooctane [9], 5-nonanone, 1,4-pentanediol, methyl-THF, methylpentenoate, butenes, α-methylene-γ-valerolactone, aromatic hydrocarbons [6,10–13], pentylvalerate and pentane [14].

Generally, GVL is directly produced by selective hydrogenation of commercial biomass-derived LA and its esters under external hydrogen sources using various homogenous or heterogeneous catalysts [15]. Ruthenium-based homogenous catalysts were widely used in the hydrogenation process of LA into GVL; however, poor stability, weak resistance to water and mineral acids restricted their application [1]. A number of other noble metal heterogeneous catalysts including Pd [16,17], Ru [18], Ir nanoparticles [19], Ru on hydroxyapatite [20], and Ru on polyethersulfone [21] have been widely used for this process. To date, Ru/Ir-based supported catalysts have shown the highest activity among the heterogeneous catalytic systems for the reduction of LA to GVL [7,22]. However, the use of expensive metal catalysts is unfavorable for a cost-effective industrial process [23]. On the other hand, use of non-noble metals has also been explored for the conversion of LA to GVL [24]. Nevertheless, only a few examples are known in the use of inexpensive metal catalysts such as Ni for the hydrogenation of LA; in one example, Raney-Ni was used as the catalyst under elevated temperature and H_2 pressure, giving GVL in 90% yield [25,26]. In another example, Mohan et al. has used a series of Ni catalysts with 30 wt% Ni content prepared by a conventional wet impregnation method using different supports such as Al_2O_3, SiO_2, ZnO, ZrO_2, TiO_2 and MgO. The best activity was found in the 30 wt% Ni/SiO_2 catalyst (0.8506 kg GVL kg catalyst^{-1} h^{-1} at 250 °C), which is probably due to the presence of a greater number of surface Ni species in this preparation [27]. The use of a mixed catalyst with formula: Ni(20)Cu(60)-SiO_2 (3:1 weight ratio of Cu to Ni, 80% metal content) is also known for this reduction process [27]. The use of acidic co-catalysts and catalyst supports are known to promote the catalytic activity of the metal in LA to GVL conversion reaction [28]. For example, a 99.9% yield of GVL was reported in using Ru/C catalyst with Amberlyst 70 as a co-catalyst in water; whereas the absence of acid co-catalyst under the same reaction conditions resulted only 13% conversion of LA [28]. Furthermore, some acidic supports are known to catalyze ring opening of the resulting GVL to form over-reduced compounds as well [29].

External molecular H_2 under high pressure conditions is the most common hydrogen source used in catalytic hydrogenation systems for GVL production [30], which requires special equipment for the safe handling of H_2 at

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high pressure [24]. The catalytic transfer of hydrogenation (CTH) has been attempted using various internal H-donors like alcohols [31] and formic acid [32] for safe handling and an environment friendly process. In the CTH method, Raney-Ni has shown catalytic performance for the conversion of ethyl levulinate to GVL using 2-propanaol as the H-donor [33]. The nickel catalysts have shown activity in vapor-phase reduction of LA to GVL as well, while using formic acid as the hydrogen source [34]. In a more recent example Ni/SiO_2 catalysts with NiO nanoparticles prepared by a variety of methods including impregnation, co-precipitation, deposition precipitation and citric acid assisted impregnation are shown as effective catalysts for the reduction of LA using formic acid as the hydrogen source [35]. In a mechanistic study, Feng et al. has suggested that formic acid decomposes into molecular H_2 and CO_2 in these metal catalyzed transfer hydrogenation reactions [32]. To the best of our knowledge, there is no report on the conversion of LA to GVL over Raney-Ni using formic acid as a hydrogen donor.

We report here the Raney-Ni catalyzed reduction of LA to GVL in the presence of FA as sole source of hydrogen under mild conditions as shown in Figure 1. In addition we have studied the possibility of *in situ* generation of LA using cellulose as the feedstock and development of a single reactor transformation of cellulose to GVL in acidic mediums using inexpensive Raney-Ni as the catalyst (Figure 2).

Experimental

Materials and methods

W.R. Grace and Co. Raney®-Ni 2400, slurry, in water, active catalyst (No. 510033) from Aldrich Chemical Co. Milwaukee, USA was used as received without any modification. The physical and chemical analysis data for the catalyst are available at the supplier's website. LA (99.9%), H_2SO_4 (99.9%), Amberlyst-15 hydrogen form dry, Dowex 50WX8 and Sigmacell cellulose—type 101 (DP$\sim$450, from cotton linters) were also purchased from Aldrich Chemical Co. All heating experiments were carried out in 25 mL stainless steel solvothermal reaction kettles with Teflon inner sleeves, purchased from Lonsino Medical Products Co. Ltd., Jingsu, China. These reaction kettles were heated in a preheated Cole-Palmer WU-52402-91 microprocessor controlled convention oven with ±1 °C accuracy. The products were identified using Varian Saturn 2100T GC-MS and confirmed by co-injection of authentic samples. The quantitative analysis was carried out on a Varian 3900 GC, with a WCOT fused silica capillary column (15 m × 0.25 mm), VF-1ms stationary phase and FID detector, injector 250 °C, detector 300 °C. The oven temperature was set at 200 °C with a flow rate 2.0 mL/minute. In the quantitative analysis, a standard curve was generated for each compound using Varian Star 6.2 Chromatographic Workstation software with the total ion current (TIC) peak area being correlated to the concentration of the compound in solution. Scanning electron microscopy (SEM) analysis was carried out using JEOL 6010A SEM instrument at 10 kV.

General procedure for the Raney-Ni catalyzed reduction of LA to GVL

A mixture of LA (116 mg, 1.0 mmol), formic acid (1.0–4.0 mmol) and Raney-Ni (20 mg) was prepared in a 25-mL stainless steel solvothermal reaction kettle with a Teflon inner sleeve and then 2.0 mL of de-ionized water was added. The reaction kettle was firmly closed and heated in a thermostated convection oven maintained at 200 °C for 24–48 h. At the end of the heating period, the kettle was removed from the oven and cooled to room temperature. The resulting product was diluted with 10 mL of de-ionized water and transferred into a glass centrifuge tube. The liquid fraction was separated from the solid residues by centrifuging at 1700X *g* for 5 min. Then liquid fraction was transferred into a vial and analyzed for products by injecting 2 μL samples to the gas chromatograph. The amounts of products formed were calculated using a standard curve generated for GVL using Varian Star 6.2 Chromatographic Workstation software. All the experiments were carried out in duplicate and average percent yields of GVL in reactions carried out for 24–48 h are shown in Table 1.

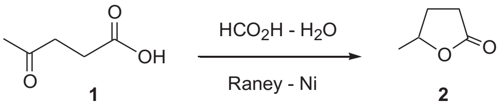


Figure 1. Raney-Ni catalyzed transfer hydrogenation of levulinic acid (1) to γ-valerolactone (2).

General procedure for the one-pot conversion of cellulose to GVL

A mixture of Sigmacell cellulose—type 101 (50 mg, 0.31 mmol glucose equivalent), formic acid (71 mg, 1.54 mmol), Raney-Ni (20 mg) with or without additional acid catalyst (0.20 mmol H^+) was prepared in a 25-mL stainless steel solvothermal reaction kettle with a Teflon inner sleeve and then 2.0 mL of distilled water was added. The reaction kettle was firmly closed and heated in a thermostated convection oven maintained at 200 °C for 24–48 h. At the end of the heating period, the kettle was removed from the oven and cooled to room temperature. The resulting product was diluted with 10 mL of de-ionized water and transferred into a glass centrifuge tube. The liquid fraction was separated from the solid residues by centrifuging at 1700X *g* for 5 min and the liquid fraction was analyzed for products as in 'General procedure for the Raney-Ni catalyzed reduction of LA to GVL' section. These experiments were carried out in duplicate and average percent yields of GVL in reactions carried out for 24–48 h are shown in Table 2.

SEM analysis of Raney-Ni catalyst

The Raney-Ni catalyst remained after centrifuging and separation of the product from entry 2 in Table 2 was washed with de-ionized water (10 mL) and dried under vacuum at 90 °C for 3 h, and analyzed using SEM. A fresh Raney-Ni catalyst sample dried under similar conditions was used as the reference sample. The SEM images and surface analysis data of fresh and used Raney-Ni catalyst samples are shown in Figure 3(a,b), respectively.

Results and discussion

Raney-Ni catalyzed reduction of LA to GVL

The initial experiments on Raney-Ni catalyzed reduction of LA to GVL were carried out with LA:formic acid 1:1 ratio

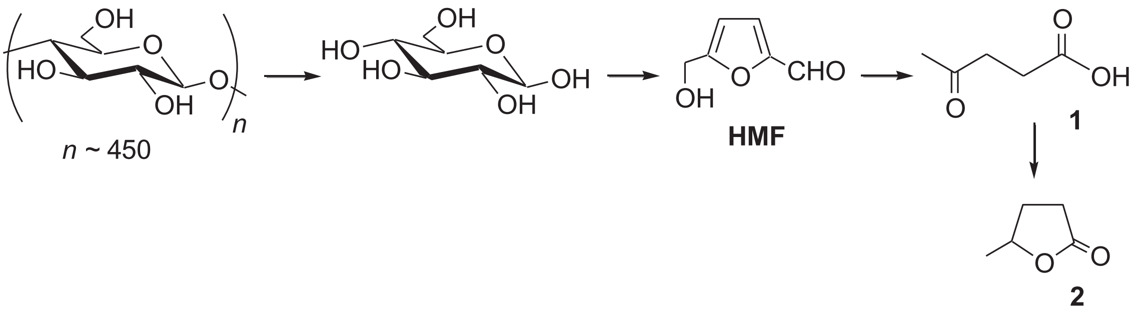


Figure 2. Proposed reaction pathway for the Raney-Ni catalyzed single reactor transformation of cellulose to γ-valerolactone (2) in aqueous formic acid at 200 °C. (a) Fresh Raney-Ni catalyst. (b) Used Raney-Ni catalyst.

Table 1. Raney-Ni catalyzed transfer hydrogenation of levulinic acid (1) to γ-valerolactone (2).

Entry	LA: FA	Heating time (h)	Conversion of LA (%)	γ-Valerolactone Yield (%)
1	1:1	24	52.6	20.4
2	1:1	48	62.6	24.4
3	1:2	24	86.6	56.6
4	1:2	48	90.9	60.5
5	1:4	24	100.00	57.7
6	1:4	48	100.00	68.5

Levulinic acid (116 mg, 1.0 mmol), formic acid (1.0–4.0 mmol), and Raney-Ni (20 mg), in 2.00 mL of water, 200 °C. Averages from duplicate experiments.

Table 2. Raney-Ni catalyzed single reactor transformation of cellulose to γ-valerolactone (2).

Entry	Additional acid co-catalyst	Heating time (h)	γ-Valerolactone yield (%)
1	–	24	22.2
2	–	48	23.3
3	H_2SO_4	24	20.6
4	H_2SO_4	48	23.4
5	Amberlyst-15(H^+)	24	20.9
6	Amberlyst-15(H^+)	48	22.9
7	Dowex 50WX8	24	21.4
8	Dowex 50WX8	48	20.5

Sigmacell cellulose—type 101 (50 mg, 0.31 mmol glucose equivalent), formic acid (71 mg, 1.54 mmol), Raney-Ni (20 mg), with or without additional acid co-catalyst (0.20 mmol H^+) in 2.00 mL of water, 200 °C. Averages from duplicate experiments.

and these experiments showed only 52.6 and 62.6% conversions of levulinic acid after 24 and 48 h, respectively (entry 1 and 2 in Table 1). The increase in the amount of formic acid showed improvements in LA conversions as well as GVL yields, as shown in entries 3 and 4. The 100% conversion of LA and highest GVL yield was achieved with LA:formic acid 1:4 ratio and 48 h reaction (entry 6).

Single reactor conversion of cellulose to GVL

All Raney-Ni catalyzed single reactor cellulose to GVL conversion experiments were carried out using five equivalents of formic acid per glucose unit of cellulose to ensure cellulose depolymerization and conversion to LA as well as transfer reduction to GVL. In the initial experiments, a mixture of cellulose, formic acid and Raney-Ni catalyst in water was heated at 200 °C; these runs produced 22.2 and 23.3% GVL after 24 and 48 h, respectively as shown in entries 1 and 2 in Table 2. The proposed reaction pathway for the Raney-Ni catalyzed single reactor transformation of cellulose to GVL in aqueous formic acid is shown in Figure 2, where cellulose is first depolymerized to glucose and then dehydrated to 5-hydroxymethylfurfural (HMF). Then, rehydration of HMF gives LA, which undergoes the transfer reduction and lactonization, producing GVL. In an attempt to improve the GVL yield, we have tested the addition of homogeneous (H_2SO_4) as well as heterogeneous (Amberlyst-15(H^+)) and Dowex 50WX8) Brönsted acids as co-catalysts to the reaction mixture. However, addition of these strong acids as co-catalysts failed to produce significant improvements in GVL yields as shown in entries 3–8 in Table 2.

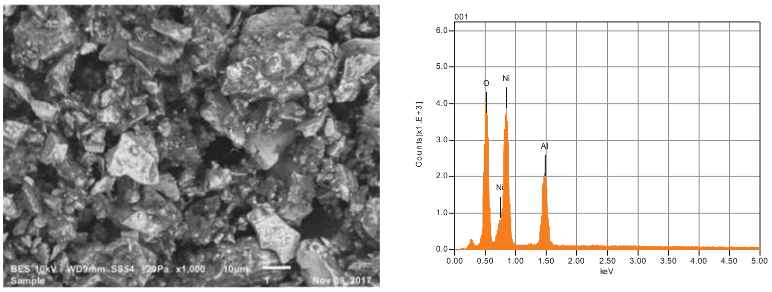
SEM analysis of Raney-Ni catalyst

In an attempt to study the changes on the nickel surface in using Raney-Ni in single reactor conversion of cellulose to GVL in aqueous formic acid medium we have analyzed the used Raney-Ni from experiment in entry 2 of Table 2 and a fresh Raney-Ni sample using SEM. The SEM images and surface analysis data are shown in Figure 3. The SEM image of used Raney-Ni showed a carbon deposited dull surface as in image b in Figure 3, whereas the fresh Raney-Ni sample showed a sharp crystalline surface of Ni particles. The elemental analysis of the surface further supports this conclusion as the used Raney-Ni showed 49.79% carbon and 37.15% oxygen by mass on the surface, whereas the fresh surface showed only nickel, aluminum and oxygen on the catalytic surface (Figure 3(a)).

Conclusion

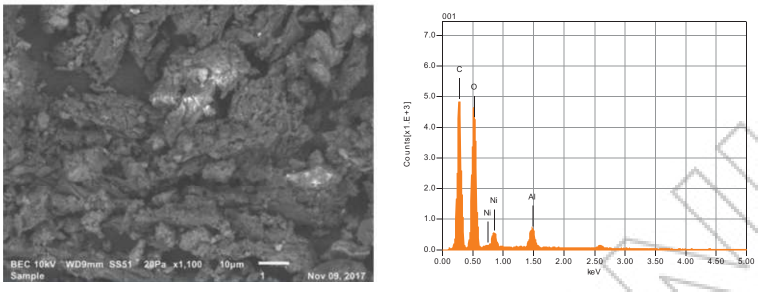
We have shown that LA can be converted to GVL in 57.7–68.5% yield by using four equivalents of formic acid and Raney-Ni as the catalyst in water at 200 °C for 24–48 h. Under similar reaction conditions cellulose (DP$\sim$450) was converted GVL in 22.2–23.3% yield in a single reactor process. The addition of strong Brönsted acids H_2SO_4, Amberlyst or Dowex as co-catalysts to the reaction mixture showed no significant effect on the GVL yield. This technique provides a simple single reactor process to produce GVL from LA and cellulosic biomass without the use of an external hydrogen source. In addition, the current methods for the preparation of GVL require the use of expensive noble metal catalysts such as Pd [16,17], Ru [18,20,21], and Ir [19]; whereas the new method presented uses inexpensive Raney-Ni as the catalyst. However, the Raney-Ni catalyst surface gets contaminated with carbon deposits when cellulose is used as the renewable feedstock. We are currently working on methods for cleaning the Raney-Ni catalyst surface and regeneration of the catalysts, so that the catalyst can be reused in single reactor production of GVL from cellulosic biomass.

(a). Fresh Raney-Ni catalyst



Surface analysis (mass %)
O 23.50; Al 14.27; Ni 62.23%

(b). Used Raney-Ni catalyst



Surface analysis (mass %)
C 49.79; O 37.15; Al 3.21; Ni 9.58%

Figure 3. SEM images and analysis of fresh and used Raney-Ni catalyst from experiment in entry 2, Table 2, in the Raney-Ni catalyzed single reactor transformation of cellulose to γ-valerolactone in aqueous formic acid at 200 °C.

Disclosure statement

Q1 No potential conflict of interest was reported by the authors.

Funding

We thank United States National Science Foundation (NSF) grants CBET-1336469, CBET-1704144, HRD-1036593, and United States Department of Agriculture (USDA) grant CBG-2010-38821-21569 for financial support.

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