Recent advances in the production of γ-valerolactone with liquid hydrogen source

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Abstract. Gamma(γ)-valerolactone (GVL) which can be produced from carbohydrate biomass has been regarded as one of the most promising platform chemicals because it can be converted to liquid alkenes adapted for transportation fuels. In the producing process, GVL was synthesized via hydrogenation of levulinic acid, which was obtained from acidic hydrolysis of carbohydrate biomass. Generally, gaseous hydrogen was employed as hydrogen source in the hydrogenation reaction. However, highly pure and high-pressure gaseous hydrogen faces high risk of hydrogen storage, transportation and operation. Moreover, due to the need for activating the gaseous hydrogen, noble metal catalysts were commonly used, limited the large-scale application. Some liquids, such as formic acid, alcohol and water, can act as hydrogen donor under certain conditions. Liquid hydrogen source possesses safe and high efficiency advantages in the hydrogenation process. This paper highlights the recent progress in the production of GVL with liquid hydrogen source.

1. Introduction
Excessive exploitation and heavy rely on fossil resources have not only caused energy depletion, but also brought critical environment issues such as acid rain and global warming. One of the feasible solution to reduce the dependence on fossil fuels is to utilize biomass, the most abundant renewable carbon-neutral resource on Earth, as feedstock for chemicals and fuels production[1, 2].

GVL has attracted significant attention in the last decade as a promising energy molecule which can be produced from carbohydrate biomass. This chemical has excel physicochemical properties for various application in industry and daily life. It was commonly used as advanced fuels, green solvents, and additives. Moreover, it can be used as a raw material for fine chemical production. GVL was synthesized via hydrogenation of levulinic acid (LA) obtained from acidic hydrolysis of carbohydrate biomass.

According to hydrogen source in the hydrogenation of carbohydrate biomass to GVL, two typical approaches have been used for the GVL synthesis, including gaseous hydrogen and non-gaseous hydrogen as hydrogenation reagents. The synthesis with gaseous hydrogen needs high-pressure and highly pure hydrogen pump into the cylinder, facing high risk of hydrogen storage, transportation and operation. Due to the need for activating the gaseous hydrogen, noble metal catalysts such as [Ru(CO)₃I₃], CuAg/Al₂O₃, Ru/C were commonly employed for promoting the synthesis of GVL[3-6].
Developing cost effective and activity stable catalysts remains a significant challenge. The non-gaseous hydrogen sources mainly include formic acid, alcohols and water as hydrogen donors in the previous reports[7-15]. In this paper, we reviewed recent advances in the GVL production from carbohydrate biomass with liquid hydrogen source. Importantly, water as hydrogen source instead of traditional gaseous hydrogen was highlighted.

2. Characteristics and Application
GVL is a safe and biodegradable chemical, even can be used as food additive. It has low melting, high boiling and open cup flash points (Table 1), and thus is suitable for storage and transportation. Meanwhile, GVL is miscible with water and most of organic solvents, so it was employed as solvent instead of toxic organic solvents.

| Issue                  | Value   |
|------------------------|---------|
| Carbon (wt%)           | 60      |
| Hydrogen (wt%)         | 8       |
| Oxygen (wt%)           | 32      |
| Boiling point (°C)     | 207-208 |
| Melting point (°C)     | -31     |
| Density (g/cm³)        | 1.05    |
| Flash point (°C)       | 96      |

GVL can be produced by hydrogenation of LA and its eaters with satisfied selectivity and yield (Figure 1) [16-18]. The detail mechanism was reviewed in the previous report[19]. Tang[20] reported metal hydroxides catalyzed GVL synthesis from ethyl levulinate (EL). ZrO(OH)2‧xH2O was examined to be active and 93.6% yield of EI conversion and 94.5% yield of GVL selectivity were reached with 2-propanol as hydrogen donor at 200 °C for 1 h.

Figure 1. Synthesis Routes of GVL from LA and Its Eaters.

As to fine chemicals production from GVL as raw material, many value-added chemicals such as furan carboxylic acid, pentatonic acid and pentanediol, were easily synthesized. Msanzer[21] reported
solid base catalyzed GVL to produce α-dimethyl-GVL with 60%, conversion and 25% yield respectively (Figure 2). Dumesic[22] reported the conversion of GVL to liquid alkenes for transportation fuels in an integrated system with more than 75% overall yield of C₈+ alkenes. The catalytic system provides an efficient and cheap processing strategy for GVL.

Figure 2. Preparation of valued-added Chemicals from GVL.

3. Production of GVL with Liquid Hydrogen Source
In the general process of GVL production from LA, gaseous hydrogen often employed as hydrogen source. However, highly pure and high-pressure hydrogen bring transportation and operation risk due to the flammable and combustible nature of gaseous hydrogen. Recently, some studies showed liquid source such as formic acid, alcohol and water displayed excellent hydrogenation activity for LA and its esters[10, 16]. These liquid hydrogen source possesses safe and high efficiency advantages in the hydrogenation process.

3.1. Formic acid/formate as Hydrogen donor
Recent research showed formic acid or formate can be used as a good hydrogen carrier and as clean fuel cell material because it is easily decomposed to release hydrogen with cheap catalysts (e.g. Ni) under mild conditions[23]. We studied conversion of biomass wastes into value-added chemicals and fuels and found formic acid/formate can be selectively obtained with high yields (> 75%) under mild alkali hydrothermal conditions only with some minutes[24, 25]. Hence, formic acid which can be obtained from biomass is regarded as a safe, renewable and facile hydrogen donor in the hydrogenation process.

Fu[26] reported the conversion of LA and formic acid to GVL with heterogeneous Ru-P/SiO₂ catalysis. A 96 % yield of GVL was reached via a two-step process. Furthermore, no hazardous 2-Me-THF produced during the process. Reduction of biomass-derived EL to GVL with formic acid as hydrogen donor over iron catalyst was proposed in this group[29]. Ruppert[27] reported hydrogenation of LA to GVL over Ru/C catalyst. Formic acid can be decomposed rapidly and an 75% yield of GVL was obtained. To understand the mechanism of the transformation, the DFT calculations combined experiments were conducted and the result showed surface formate partially inhibits the LA reduction. Varkolu[28] reported vapor phase Ni-catalyzed hydrogenation of LA to GVL at 250 °C. The Ni/Al₂O₃ catalyst displayed excellent catalytic activity for GVL production. The significant decrease of GVL formation over Ni/MgO and Ni/hydrotalcite could be attributed to water generation.

3.2. Alcohols as Hydrogen Source
The low toxicity and inexpensive alcohol is one choice of hydrogen donor. Alcohol can proceed via hydrogen transfer catalytic (HTC) reaction during the GVL conversion. Mu[29] prepared a porous nano
Zr-CA polymer catalyst (ID ~ 3.5 nm) for conversion of LA and its eaters to GVL. The test results showed both the acidic and basic sites of the catalyst contribute to GVL formation and the yield was up to 97%. Huo[30] reported a ternary Cu/ZnO/Al₂O₃ catalyst was prepared by co-precipitation way and isopropanol was employed as hydrogen donor for hydrogenation of EL. A 99% yield of GVL was achieved and the catalyst was stable after four times recycles.

3.3. Water as Hydrogen Source

Water is the most abundant hydrogen source and eco-friendly reagent. Jin’s group studied[31, 32] hydrogen production via water dissociation with metals (Zn, Fe, Al, Mn, Co) under mild hydrothermal conditions. Furthermore, hydrogenation of LA to GVL with water splitting by Zn was studied with non-noble metal catalyst. The results showed commercial metal powder such as Fe, Cu, Ni, Mo and Cr displayed obvious catalytic activity for LA hydrogenation and more than 90% yield of GVL was achieved at 180 °C. Further research indicated Fe catalyst facilitates GVL formation and a 98% yield of GVL was obtained at 250°C (Figure 3). Moreover, Fe remains stable activity after four recycles. Interestingly, a synergistic effect of the Fe and ZnO obtained by Zn oxidation with water was observed. In addition, common SUS316 material used in the reactor wall has catalytic role for LA conversion and a 56% yield of GVL was reached. This study indicates water can be used as a hydrogen donor via simple splitting with metal under mild hydrothermal conditions. It provides a better choice for GVL synthesis from biomass with liquid hydrogen source.

![Figure 3. Production of GVL from Biomass with Water as Hydrogen Source][31].

4. Conclusion

Many approaches for efficient and economical synthesis of GVL from biomass and their derivatives have been proposed in the last decade. Liquid hydrogen sources possess safe transportation and facile operation for GVL conversion during the hydrogenation process. Eco-friendly and abundant water and biomass-derived formic acid show great potential in the hydrogenation synthesis. Especially for water, the role of metal and its oxide during the water splitting and LA hydrogenation needs further investigation.

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