Study on Preparation of Levulinic Acid from Biomass and its Prospects

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Abstract—As a multifunctional platform compound, levulinic acid has drawn significant attention throughout the world for its active groups such as carbonyl and carboxyl groups. There are a lot of papers on the preparation technology of the levulinic acid, but few on the catalysts preparation and its applications. The preparation of the solid acid catalysts and its applications on preparation of levulinic acid from biomass were summarized in the paper, the further processing products as green polymer precursors were reviewed, and the prospects for development of levulinic acid from biomass were also forecasted.

Index Terms—biomass; Solid acid; Levulinic acid; Derivatives

I. INTRODUCTION

As the demand for non-renewable fossil resources increases, the reserves of fossil resources throughout the world have dropped dramatically. As a renewable energy and environment-friendly resource, biomass has drawn extensive attention. And preparing the fossil material from biomass resources instead of fossil resources has become a primary subject [1-3].

Levulinic acid is considered to be promising organic intermediates with high reactive carbonyl and carboxyl groups that can take the reactions of esterification, hydrogenation, condensation, oxidation and halogenation into value-added chemicals [4], which can be used for fragrances, solvents, oil additives, pharmaceuticals, and plasticizer [5-11]. Just because of their wide applications, the preparation of the levulinic acid from biomass has been a hot topic. Traditionally, the reaction of producing levulinic acid was carried out in the liquid phase using the mineral acids as the catalysts, which caused the catalysts being difficulty be separated from the reaction system, resulting in environment pollution. However, solid super acid can be a viable alternative to homogeneous catalysts because they were easy to separate and recycle [12-14].

II. Catalysts for the preparation of levulinic acid

Traditionally, the mineral acids such as HCl, H₂SO₄ and H₃PO₄ were the most common catalysts for preparation of levulinic acid with their high catalytic activity [15]. But for their shortage of pollution to environment and corrosion to equipment, the mineral acids would endly be replaced by more environmentally beneficial solid acids.

Solid super acids have become more attractive around the world for their environmental benefits and no corrosion to equipment, it was found that the solid acid catalysts can also reduce the production cost by being reused for several times and had less loss on catalytic activity. There are many papers reporting the preparation of levulinic acid with solid acids as catalysts. Chen et al. [16] reported the formation of levulinic acid from steam exploded rice straw with solid acid S₂O₅²⁻/ZrO₂-SiO₂-Sm₂O₃ as catalyst, the highest yields of 58% was obtained at the optimal conditions of the temperature 200°C, reaction time 10min, solid-liquid ratio 1:15(w/v) and the solid acid concentration 13.3 wt%. When the catalyst was reused for the third time, the activity had a little loss because of the reduction of acidity. Liu et al. [17] revealed the preparation of levulinic acid at yield of 72.28% from sucrose with S₂O₅²⁻/ZrO₂-TiO₂-Al₂O₃ as catalyst at the optimal conditions of sucrose concentration 15 g/L, catalyst dosage 15 wt% (to sucrose), reaction temperature 200°C and the reaction time 60 min. The experiment also showed that the catalytic activity remained more than 70% when it was reused for the fifth time.

III. The preparation of levulinic acid from Biomass feedstocks

Biomass, alternative fossil resources, can be converted into various value-added chemicals. The most important chemical is levulinic acid, a chemical precursor, prepared by glucose, sucrose, cellulose, residues of crops and forestry from biomass. Glucose is the most ideal hexose sugar for synthesizing levulinic acid [18]. Zeng studied the preparation of levulinic acid from glucose with solid heteropolyacid salts Ag₃PW₁₂O₄₀ as catalyst at the highest yield of 81.61% under the optimal conditions of reaction temperature 200°C, reaction time 2h, catalyst dosage 0.9g and glucose concentration 40g/L [19]. Nazlina and co-workers prepared levulinic acid from glucose with CrCl₃ and HY zeolite as the catalysts. The yield of 55.2% was obtained at the conditions of the reaction temperature 145.2°C, the reaction time 146.7 min and the...
catalyst concentration 12 % (w/v) [20]. While Nazlina et al. performed further study in 2013, the yield of 60% was obtained after the reaction condition was optimized [21]. Heeres et al. used the ruthenium catalysts to prepare the levulinic acid from C₆ sugar and the yield of above 60% was obtained at the conditions of reaction temperature 140°C and the reaction time 2 h [22].

Sucrose is another promising raw material for preparing levulinic acid. Zeng et al. [23] did experiment on the preparation of levulinic acid from sucrose with SO₃/TiO₂-ZrO₂ as catalyst in water, the yield of 50.0% was obtained at the optimal conditions of reaction temperature 180°C, reaction time 1 h and catalyst dosage 1 g. Jiang et al. [24] prepared levulinic acid by catalytic hydrolysis of sucrose with SO₃/Fe₂O₃-Al₂O₃-SiO₂ as catalyst, the yield of 33.05% was obtained at the reaction temperature 200°C, reaction time 24 h and catalyst concentration 3 wt%(to the sucrose). Li et al. [25] studied catalytic preparation of levulinic acid with H₂SO₄ as catalyst, the yield of 43.31% was obtained at the conditions of reaction temperature 110°C, reaction time 60 min, sucrose concentration 0.4 mol/L and catalyst concentration 3.5 mol/L.

Cellulose, the widely distributed polysaccharide in nature, has the potential to replace the fossil resources for the preparation of levulinic acid [26-27]. Sun et al. [28] reported the one-pot synthesis of levulinic acid from cellulose using HPA ionic liquid catalysts in a water-methyl ketone biphasic system with the highest yield of 63.1% obtained. The experiment also showed that the catalysts [MIMPSH]H₃₆PW were easily separated and reused with high activity. Amberlyst 70 was another kind of solid acid catalyst for conversion from cellulose to HMF and levulinic acid in two reaction steps: (1) non-catalytic hydrothermal decomposition of cellulose at moderate temperatures to produce glucose and HMF; (2) further reacted at relatively low temperatures to produce levulinic acid [29].

Additionally, the residues of the agriculture and forestry were also raw materials for the preparation of levulinic acid [30-32]. Although the raw materials for the production of levulinic acid were different, the progress route remains the same. Fig.1 depicted the progress route in three steps: (1) The first step was to separate the cellulose from raw materials. (2) Cellulose was hydrolyzed to glucose. (3) Glucose was converted into levulinic acid through an intermediate of 5-HMF.

**Fig. 1.** The progress route of preparing levulinic acid from biomass

**IV. The derivatives of levulinic acid and its applications**

γ-valerolactone is the most important derivatives of levulinic acid because of its wide use such as fuel additive, food ingredient and solvent. At the same time, it was also an intermediate for the preparation of chemicals that included nylon and high-grade alkene fuels [33]. It was just because of the wide use that many papers had reported the preparation of γ-valerolactone from levulinic acid. Rajeev revealed the conversion from levulinic acid to GVL through a 2-hydroxypentanoic acid intermediate using the bifunctional catalyst Shvo. However, they tried to replace the Shvo catalyst of an iron-based congener that was easily prepared with high activity [34]. Amol prepared the nanocomposites catalysts of Cu–ZrO₂ and Cu–Al₂O₃ by the co-precipitation method to catalyze the esterification of levulinic acid to γ-valerolactone. Both of the catalysts showed the esterification of LA with >90% selectivity to GVL in methanol and water respectively [35]. Additionally, other catalysts can be also used for the hydrogenation of levulinic acid to γ-valerolactone in order to improve the selectivity such as iridium pincer complexes catalyst [36], RuSn bimetallic catalyst [37] and a commercial ruthenium supported catalyst in combination with a heterogeneous acid co-catalyst [38].

Methyltetrahydrofuran (MTHF), synthetized from levulinic acid via a single stage catalytic hydrogenation process, can be used as solvent and fuel extender. And the paper also reported another two products prepared from levulinic acid such as δ-aminolevulinic acid and diphenolic acid [39]. δ-aminolevulinic acid can be used as a broad spectrum herbicide with environmental benefit, high selectivity and biodegradability. And diphenolic acid can replace the bisphenol A as the raw materials of phenol resins, epoxy resins and polyester resins [40].

Calcium levulinate prepared from levulinic acid was new filling calcium preparations and food nutritive fortifier. In addition, some derivatives of levulinic acid also can be used as antifreeze, surfactants, softeners, emulsifiers, preservatives, detergents, synthetic resin modifier and so on.

**V. CONCLUSION**

As a multifunctional platform compound, levulinic acid can be used for the synthesis of high-value organic chemicals as what have been discussed above. It is just because of the wide range of applications that the preparation of levulinic acid became the hot topic. Biomass represents the promising source for the production of levulinic acid due to the affordability and renewability. During the preparation process of levulinic acid from biomass, the selection and preparation of catalysts remained a key technical barrier to improve overall process yield and efficiency. The ideal catalysts for the preparation of levulinic acid were Heterogeneous catalysts, which were easy to separate from the reaction system and to be recycled for several times in order to reduce the costs. The most important thing was that heterogeneous catalysts were no pollution to the environment and no
corrosion to equipment. But all we needed to do was to prepare high active heterogeneous catalysts to improve the yield and selectivity with expectation to realize the industrial production.

REFERENCES


