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Conversion of Levoglucosenone to Platform Chemicals in Aqueous Phase over Solid Acid Catalysts

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Abstract: *The main pathways by which homogenous catalyst carry out the levoglucosenone (LGO) isomerization to 5-hydroxymethylfurfural (HMF) and dehydration to levulinic acid (LA) in aqueous phase are elucidated by using an HZSM-5 and Amberlyst 70 as representative solid acid catalysts. HMF is the primary product during LGO degradation and can be further dehydrated to LA in the presence of solid acid catalysts. Similar trends with a similar maximum yield of HMF (44% carbon yield) and LA (33% carbon yield) were obtained in relatively high temperatures over HZSM-5. The maximum yield of LA was obtained in 57.7% carbon yield (69.1% mole yield) by using Amberlyst 70. This result suggests that strong Brønsted acid sites are necessary for high LA yields. In addition, HZSM-5 with both Brønsted and Lewis acid sites promotes the side reactions of LGO to furfural and formation of humins in contrast to Amberlyst 70 with strong Brønsted acid sites. Thus, to design more efficient of LGO isomerization and dehydration reactions, it is desirable to have a high ratio of Brønsted to Lewis acid sites.*

Keywords: Biomass conversion; Solid acid catalysts; Levoglucosenone, Platform chemicals.

1. Introduction

In recent years, lignocellulosic biomass has attracted extensively interest as a renewable source for the production of biofuels and biochemicals to decrease the influence of the dwindling fossil energy reserves.[1] Among the three main components (lignin, hemicellulose, and cellulose) of lignocellulosic biomass, cellulose, which accounts for 35-50%-*wt* of dry biomass, is the most abundant bio-renewable resource in nature. Recent research reported that cellulose-derived levoglucosenone (LGO) showed a promising intermediate for the production of sustainable chemicals. Our previous study revealed 38%-C LGO yield by pyrolysis of cellulose with an equivalent mass of high stability and strong acidity ionic liquids.[2] Owing to these high yields production of LGO from cellulose, it provides more reaction routes to selectively convert cellulose to biofuels and biochemicals.

5-Hydroxymethylfurfural (HMF), usually derived from C5 and C6 carbohydrates, respectively, present prospect properties as a key platform chemical.[3-5] A number of furan derivatives, namely alkoxymethylfurfurals, bishydroxymethylfuran, 2,5-furandicarboxylic acid, 5-hydroxymethylfuroic acid, and 2,5-dimethylfuran, with a promising potential in fuel or polymer applications, and some other important nonfuranic compounds such as levulinic acid (LA), adipic acid, 1,6-hexanediol, caprolactam, and caprolactone can be synthesized from HMF.[4] LA, one of the twelve most promising value added chemicals from biomass by the Biomass Program of the US Department of Energy in 2004,[6] is a member of the gamma-keto acids that itself is a promising chemical intermediate to produce a number of bio-chemicals including succinic acid, resins, polymers, herbicides, pharmaceuticals and flavoring agents, solvents, plasticisers, anti-freeze agents and biofuels/oxygenated fuel additives.[7-9] Recently, Krishna et al.[10] successfully converted LGO to HMF and LA in aqueous phase over sulfuric acid. However, homogeneous acid-catalyzed processes need more capital and operating costs because of rigorous reaction conditions requiring special materials for reactor construction and chemical recovery systems.[11] Furthermore, the recovery process produces significant amounts of waste and cause environmental pollution. Considering these drawbacks, heterogeneous catalysts represent a viable alternative to homogeneous catalysts and may offer an environmental advantage due to their selective and easy to handle nature, reducing equipment corrosion issues and relatively low cost if the catalyst can be easily separated and recycled.[8] As a typical representative of solid acid catalyst, zeolites, which are highly structured crystalline microporous inorganic aluminosilicates containing channels with very well-defined pores in the range of 5–13 Å, where the catalytic groups are located,[12, 13] may offer much more advantages than other acidic catalysts in sugar dehydration, including simple catalyst separation and regeneration comparing to homogenous acid catalysts, high stability in relatively high temperature system in contrast to other materials, such as Amberlyst resins.[14]

In this work, a methodology of simple yet robust experiments are developed to delineate the pathways by which solid acid catalysts effect on LGO isomerization and dehydration chemistry in an aqueous phase system. LGO firstly undergoes hydration reactions followed by isomerization to HMF and further dehydration to form LA. We compare the selectivity trends of HZSM-5. In addition, LGO conversion catalyzed by strong Brønsted acid sites (Amberlyst 70) is used to compare the role of Brønsted and Lewis acid sites of solid acid catalysts on products selectivity. This study provides a substitutable design of heterogeneous catalysts to homogeneous catalysts for LGO degradation reactions.

2. Experimental

2.1 Materials and catalyst preparation

LGO ($\geqslant$99%) was purchase from the CIRCA Group (Knoxfield Victoria, Australia), LA was purchased from TCI company (Tokyo, Japan), while HMF, furfural, formic acid (FA) was purchased from Wako Pure Chemical Industries (Osaka, Japan), respectively. All the chemicals were directly used as received without further purification. ZSM-5 (CBV 3024E, ammonium form), mordenite (CBV 21A, ammonium form), beta zeolite (HSZ 980HOA, β-1, proton form; CP814N, β-2), and Y zeolite (HSZ 390HUA, Y-1, proton form; CBV 400, Y-2, proton form; CBV 100, Y-3, sodium form) were purchased from Zeolyst International and Tosoh. To generate the acidic form of the zeolite, all the zeolites were calcinated in ambient atmosphere for 4 h at 550 ºC. Amberlyst 70 was purchased from Organo Corporation, and it was prewashed with deionized water and ethanol followed by drying overnight before use.

2.2 Reaction procedure

Experiments were performed using 5 mL aqueous solutions of 50 mg reagents with appropriate amounts of catalysts. The reactors were placed into an oil bath at the desired reaction temperature and stirred at 600 rpm. After specific reaction times, the reactors were quickly removed from the oil bath and cooled by quenching in an ice-water bath at the appropriate time, followed by filtering through a 0.45μm PTFE membrane filter to separate catalysts.

2.3 Analytical Methods

The reaction products were analyzed by HPLC on a Shimadzu LC-20 prominence series equipped with a photo diode array (UV, Shimadzu SPD-M20A) and a refractive index (RI) detector. Analytes were separated on a BioRad Aminex 87H column with a temperature of 35 oC and 5 mM sulfuric acid mobile phase at a flow rate of 0.6 mL/min.

3 Results and Discussion

3.1 Zeolites selection

Table 1 Effect of zeolite types on LGO degradation in aqueous phase.

Zeolites	Conv.* (%-C)	Yields (%-C)			Carbon balance (%)
		DH	HMF	FF	
HZSM-5	56.6	16.6	29.2	6.7	79.2
Mordenite	16.1	34.5	4.2	1.1	89.1
β−1	29.3	30.7	5.5	1.6	77.9
β−2	23.2	32.3	5.9	1.1	83.8
Y−1	25.2	34.2	0.5	0.1	75.4
Y−2	19.5	33.7	0.1	0.1	80.6
Y−3	37.0	32.1	0.0	0.1	63.1

* Conversion = 100−$Y_{(LGO+DH)}$.

Table 1 displays that seven different types of zeolites were screened for the conversion of LGO in aqueous phase at 150 ºC. The maximum HMF yield was obtained in 29.2% by using HZSM-5 catalyst, compared to HMF yields of 4.2% and 5.9% when mordenite and β−2 zeolite were respectively used at the same conditions, suggesting that only HZSM-5 is effective to isomerize LGO to a high HMF yield. It is notable that Y zeolite did not promote the generation of HMF and FF, indicating the pore/cage diameter of zeolite may also have an influence on LGO isomerization. Jae et al.[15] tested the pore size and sharp of zeolites for the conversion of glucose to aromatics in a pyroprobe reactor, they concluded that large pores facilitated the formation of coke while medium pore zeolites with pore sizes in the range of 5.2–5.9 Å showed the highest aromatic yields. LGO is supposed to have a similar molecular dimension with levoglucosan whose critical diameter is around 5.7–6.7 Å.[15] Y zeolites, pore size of 7.4 Å,[16] led to the lowest HMF yield due to its low acid site density. The beta zeolites (~7 Å),[15] which have 1- and 3-dimensional channel systems, gave much higher HMF yields compared to Y zeolites. HZSM-5, containing a 3-dimensional channel system with medium pore size diameter of ~5.5 Å, led to significantly higher yields of HMF and FF in contrast to beta zeolites and mordenite, demonstrating that the pore and cage diameter of HZSM-5 are large enough to allow LGO to diffuse and convert. However, the carbon balance is about 20% short, illustrating that in addition to converting LGO to identified compounds, HZSM-5 also catalyzed side reactions of these products such as polymerization to humins, causing unidentified species that cannot be detected by HPLC.

3.2 Product distributions with HZSM-5

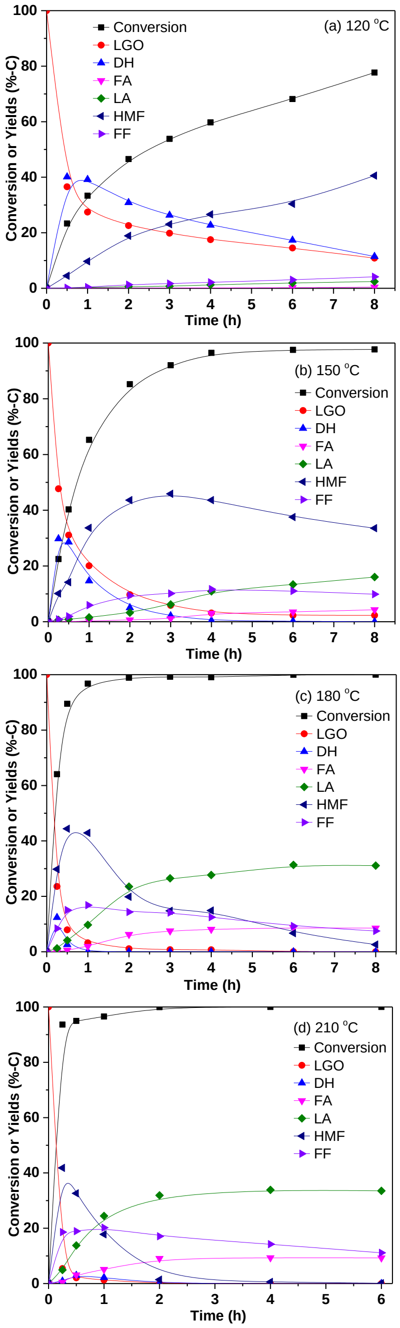


Fig. 1 Effect of time and temperature on product yields by HZSM-5 catalyzing LGO degradation in aqueous phase. Conversion = 100−$Y_{(LGO+DH)}$.

Fig. 1 depicts the carbon yields of major products as a function of time with HZSM-5. As shown in Fig. 1, increasing reaction temperature would significantly shorten the maximum conversion time while inhibit the generation of DH. HMF and FF are the initial products of LGO isomerization. HMF showed similar trends in which a similar maximum yield around 44% was obtained in relatively short reaction times. Nevertheless, FF yields increased with ramping temperatures, suggesting high temperatures favor to form FF. LA yield production increased with reaction time, reaching a plateau at 31% carbon yield at 180 ºC. A closer look showed in Fig. 1(c) and (d) only a 2% increase in LA yield when temperature was elevated from 180 ºC to 210 ºC, indicating 180 ºC is high enough for this experiment. Accordingly, additional solid acid-catalyzed LGO reactions in aqueous phase were performed at 180 ºC with modified ZSM-5.

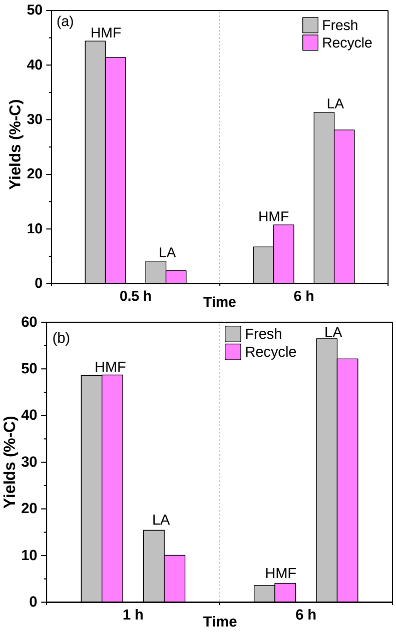


Fig. 2 HZSM-5 (a) and Amberlyst 70 (b) recycling study.

Due to the high thermal and chemical stability, used zeolites can be allowed for high temperature calcination treatments to regenerate acid sites. The stability of HZSM-5 has also been investigated for the isomerization of LGO to HMF and then dehydration to LA by conducting a cycle of reaction at 180 ºC for 6 h, followed by reutilization of HZSM-5 at the same conditions for 0.5 h and 6 h, respectively. The results are depicted in Fig. 2. After HZSM-5 was recalcined at 550 ºC for 2 h to remove the surface carbonaceous residues, which were formed as a result of intrinsic adsorbability of zeolite, a HMF yield of 41.4% and a LA yield of 28.1% were obtained, respectively, revealing that the original HMF and LA yields with slightly decreases can be recovered upon calcination.

3.3 LGO conversion with Amberlyst 70 catalyst

An acidic ion exchange polymer resin was chosen to investigate the significance of Brønsted acid sites on LGO degradation reactions. As a typically pure solid Brønsted acid catalyst, Amberlyst 70 has been proved to be an effective solid acid catalyst for a wide range of acid-catalyzed reactions, such as carbohydrates dehydration.[17]

Product yields during LGO degradation were measured as a function of time over Amberlyst 70 as shown in Fig. 3. The trends of product yields catalyzed by Amberlyst 70 were similar to HZSM-5 whereas the catalytic activity of Amberlyst 70 was more effective than HZSM-5. Amberlyst 70 tremendously restrained the formation of FF, less than 3% carbon yield of FF was formed compared to the maximum yield of 16.8% by using HZSM-5 at 180 ºC. This may reveal that Lewis acid sites can significantly promote the C–C bond cleavage of LGO. LA yields increased with LGO conversion and reached a plateau after 6 h at 180 ºC, the maximum yield of LA was obtained in 57.7% carbon yield (69.1% mole yield) by using Amberlyst 70 compared to 31.4% by using HZSM-5 at 180 ºC, indicating that strong Brønsted acid catalysts are necessary for high LA yields. It is noteworthy that LA yield obtained by Amberlyst 70 (69.1% mole yield) in this study was similar to a previous study catalyzed by sulfuric acid,[10] suggesting heterogeneous catalysts may be superior to homogeneous catalysts due to its simple recyclability and low investment. However, the thermal stability of Amberlyst 70 in relatively high temperature may restrict its utilization.

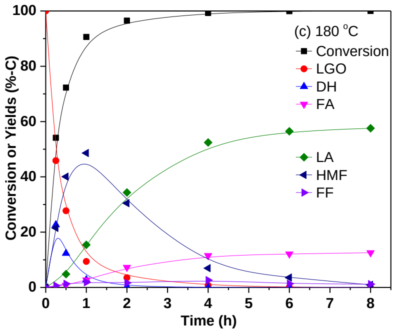
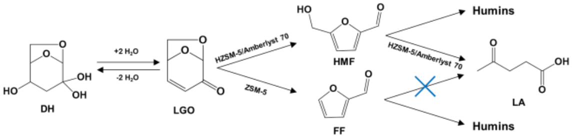


Fig. 3 Effect of temperature and time on product yields by Amberlyst 70 catalyzing LGO degradation in aqueous phase. Conversion = 100–$Y_{(LGO+DH)}$.

Further studies were also carried out to test for the recyclability and regeneration of Amberlyst 70. The used Amberlyst 70 at 180 ºC for 6 h was recovered with filtration and then washed with consecutive acetone and deionized water, followed by drying at 60 ºC in vacuum overnight before use. The results are shown in Fig. 2(b), almost same HMF yield was obtained after 0.5 h compared to fresh Amberlyst 70. Further increasing the time to 6 h, a 56.5% LA yield with a 4.3% decrease was obtained, the reason can be explained that the humins on the surface of Amberlyst 70 was not fully washed off with the above method, which inhibited the contact of reagents and catalysts.

3.4 Reaction pathways



Scheme 1 LGO degradation in aqueous phase over solid acid catalysts.

The reaction pathways of LGO degradation in aqueous phase over solid acid catalysts are shown in Scheme 1. LGO undergoes hydration reactions to add two water molecules to form DH. Briefly, a water molecule is added to the C=C bond to form a hydroxyl group while a water molecule is added to the ketone functionality to form a germinal diol, respectively, which is reversible. Both Brønsted and Lewis acid sites can catalyze the isomerization of LGO to form HMF, while FF is particularly prone to be formed in the presence of Lewis acid sites. Consequently, Amberlyst 70 produces higher yields of HMF comparing to HZSM-5, suggesting HMF production is predominantly catalyzed by Brønsted acid sites. HMF can further effectively dehydrate to form LA or undergo degradation reactions to produce humins in the presence of both Brønsted and Lewis acid sites, while FF only undergoes degradation reactions to produce humins. Moreover, it is notable that HZSM-5 produces higher humin yields than Amberlyst 70, indicating Lewis acid sites are more accountable for the formation of humins than Brønsted acid sites. Similar conclusions have been deduced by Huber and co-workers.[18] They investigated the role of Brønsted and Lewis acid sites on the influence of xylose dehydration to FF in aqueous phase, and concluded that Lewis acid sites were dominantly responsible for the decrease in FF selectivity because it catalyzed the reactions between xylose and FF to form humic compounds.

4. Conclusions

In summary, we have demonstrated a process to produce a 57.7% carbon yield (69.1% mole yield) of LA from LGO in aqueous phase with the use of homogenous acid catalysts. Amberlyst 70 shows a rather promising prospect for the LGO isomerazation to HMF and dehydration to LA as a result of its inherent Brønsted acid sites. Amberlyst 70 significantly inhibits the side reaction of LGO to FF while HZSM-5 obviously promotes the formation of FF and humins by reason of the presence of Lewis acid site. In addition, through comparison of different types of zeolites (e.g. HZSM-5, Y, beta, and mordenite), we conclude that HZSM-5 zeolite containing relatively strong acid sites and medium pore sizes is effective for LGO degradation.

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