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Biomass Conversion

Domino Reaction Catalyzed by Zeolites with Brønsted and Lewis Acid Sites for the Production of γ-Valerolactone from Furfural**

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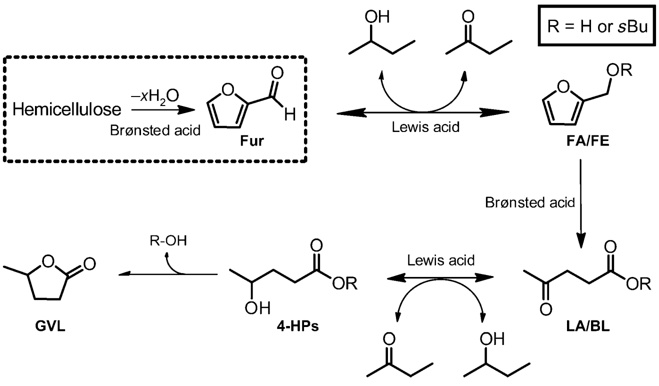
The development of more carbon efficient and economically viable lignocellulosic biomass conversion technologies is critical for the sustainable production of liquid transportation fuels and chemicals.[1] The molecule γ-valerolactone (GVL) has gained attention as a versatile platform chemical for the production of liquid alkenes, as a solvent for biomass processing, as an approved fuel additive, and as a precursor for renewable polymers.[2–4] Biomass-derived GVL is currently produced by the multistep processing of the carbohydrate fractions of lignocelluloses, wherein acid catalysts transform sugars into levulinic acid (LA), and noble-metal catalysts reduce LA to GVL with molecular hydrogen (H_2).[5,6] This strategy suffers from several limitations that hinder the large-scale manufacture of GVL. In particular, the LA-reduction step necessitates precious-metal catalysts (e.g., Ru or Pt) or high H_2 pressures (> 30 bar), which have been shown to negatively impact the economics of GVL-derived transportation fuels.[7] Formic acid has emerged as an alternative to molecular H_2, but noble metals and/or harsh conditions are still required to carry out the hydrogenation step.[8,9] Inexpensive supported transition metals (e.g., Cu/Al_2O_3) are active but suffer from leaching and/or sintering during the reaction.[10] For the large-scale production of GVL, catalytic schemes are required that maximize product yields without the use of precious metals, high H_2 pressure, or an excessive number of unit operations.

Transfer-hydrogenation (TH) reactions, such as the Meerwein–Ponndorf–Verley (MPV) reaction, offer an attractive alternative to molecular H_2 for the reduction of targeted functional groups. The interaction between the catalyst, the hydrogen donor, and the acceptor molecule can be modulated to impact activity and selectivity. Many catalysts are active for TH reactions, including organometallic compounds, transition metals, and metal oxides featuring acid/base properties.[11] Pure-silica zeolites containing a small amount of tetravalent heteroatoms with open coordination sites (e.g., Zr or Sn) have also been used as solid Lewis acids to promote TH reactions. Wise and Williams used homogeneous Ru complexes[12] and Chia and Dumesic[13] used heterogeneous metal oxides to produce GVL from levulinate derivatives by TH reactions with high yields. Corma and co-workers demonstrated the efficacy of Sn-Beta and Zr-Beta zeolites for the intermolecular MPV reaction between alcohols and ketones in organic solvents.[14] Sn-Beta and other tin-containing silicates have also been shown to transform hexoses,[15] pentoses,[16] and trioses[16a,17] through intramolecular hydride and carbon-atom shifts in both organic and aqueous media.

Herein, we report an integrated catalytic process for the efficient production of GVL from furfural (Fur) through sequential TH and hydrolysis reactions catalyzed by zeolites with Brønsted and Lewis acid sites (Scheme 1). In our investigation, we used Fur as a starting material because several well-established methods are available for the production of Fur from hemicellulose.[18] First, Fur was converted into furfuryl alcohol (FA) through a TH promoted by a Lewis acid catalyst and 2-butanol as the hydrogen donor. In the presence of an acid catalyst and 2-butanol, a fraction of FA was converted into butyl furfuryl ether (FE). Next, a Brønsted acid converted FA and FE into a mixture of LA and butyl levulinate (BL) through hydrolytic ring-opening reactions. Finally, both LA and BL underwent a second TH step to produce the corresponding 4-hydroxypentanoates (4-HPs), followed by lactonization to form GVL. In this study, GVL was obtained in a yield of 78 mol % from a starting 5 wt % Fur solution under optimal reaction conditions with Zr-Beta as a Lewis acid catalyst and an aluminosilicate with MFI



Scheme 1. Domino reaction for the production of GVL from hemicellulose by the use of a combination of Lewis and Brønsted acids (Fur, furfural; BL, butyl levulinate; LA, levulinic acid; FA, furfuryl alcohol; FE, furfuryl ether; 4-HPs, 4-hydroxypentanoates; GVL, γ-valerolactone).

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topology and nanosheet morphology (Al-MFI-ns) as a Brønsted acid catalyst. Both TH steps result in the oxidation of the hydrogen donor, which can be readily separated from the products and regenerated under mild gas-phase conditions by the use of inexpensive catalysts (e.g., Ni or Cu) that are not active, selective, or stable for the production of GVL.[19] Importantly, the catalysts, solvents, and mild reaction conditions used in this study are compatible with those required to convert hemicellulose into Fur in high yields.[18a] Therefore, this catalytic system offers an attractive streamlined strategy for the production of GVL from lignocellulosic biomass without the use of precious metals or high pressures of molecular H_2.

The conversion of methyl levulinate (ML) into GVL via methyl/butyl 4-HPs was used to screen the TH activity of various solid Lewis acids in the presence of 2-butanol as the hydrogen donor. Of the two TH steps proposed in Scheme 1, the conversion of ML into methyl 4-HP features a less favorable thermodynamic equilibrium because both methyl 4-HP and 2-butanol are secondary alcohols. However, the spontaneous lactonization of methyl 4-HP to give GVL drives the reaction to completion. Zr-Beta showed the highest activity of all solid Lewis acid zeolites studied, with the formation of GVL in 97% yield at 393 K and an initial GVL production rate of 0.026 mmol GVL (mmol Zr)$^{-1}$ s^{-1} (Table 1, entry 2). In contrast, Sn-Beta showed a reactivity of 0.0014 mmol GVL (mmol Sn)$^{-1}$ s^{-1}; with this catalyst, 26% conversion was observed after 5 h with a selectivity of 95% (Table 1, entry 5). Al-Beta, Ti-Beta, and Al-MFI-ns showed drastically lower reaction rates (Table 1, entries 6–8). The detectable TH activity of Al-based zeolites is attributed to the Lewis acidity of extraframework Al species. ZrO_2 was unreactive under the present reaction conditions (Table 1, entry 9). The conversion of LA into GVL was almost an order of magnitude slower than the conversion of ML (see Table 1 entries 2 and 10), and the low initial selectivity for the formation of GVL (28%) is attributable to the esterification of LA with 2-butanol. Quantitative conversion of LA/BL into GVL occurred during longer reaction times (Table 1, entry 11). Importantly, the catalyst appears to be very stable. It showed no signs of deactivation after 48 h on stream in a packed-bed flow reactor (see Figure S10 in the Supporting Information). Zr-Beta also converted Fur into FA and FE quantitatively with rates exceeding 0.33 mmol GVL (mmol Zr)$^{-1}$ s^{-1} (Table 1, entry 1).

Table 1: Transfer-hydrogenation reactions with solid Lewis acids in 2-butanol.[a]

Entry	Catalyst	Feed[b]	Product[c]	t [h]	Conv.[d] [%]	Sel.[e] [%]	Prod. rate[f]
1	Zr-Beta	Fur	FA + FE	0.08	98	96	327
2	Zr-Beta	ML	GVL	0.25	25	95	26
3	Zr-Beta	ML	GVL	1	60	> 99	17
4	Zr-Beta	ML	GVL	5	97	> 99	5.4
5	Sn-Beta	ML	GVL	5	26	95	1.4
6	Al-Beta	ML	GVL	5	11	98	0.6
7	Ti-Beta	ML	GVL	5	1	94	0.05
8	Al-MFI-ns[g]	ML	GVL	5	5	66	0.02
9	ZrO_2[h]	ML	GVL	5	< 1	–	–
10	Zr-Beta	LA	GVL	0.25	12	28	3.7
11	Zr-Beta	LA	GVL	11	98	> 99	2.5

[a] Reaction conditions: Lewis acid catalyst: 1 mol%, reactant: 6.7 wt% ((mol reactant)/(mol metal) = 100), 393 K. [b] Fur, furfural; ML, methyl levulinate; LA, levulinic acid. [c] FA, furfural alcohol; FE, furfuryl ether; GVL, γ-valerolactone. [d] Conversion: ([mmol (feed converted)]/[mmol (feed initial)]) × 100. [e] Selectivity: ([mmol product]/[mmol (feed converted)]) × 100. [f] Production rate: [(mmol product) (mmol metal)$^{-1}$ s^{-1}] × 10^{-3}. [g] The reaction was carried out with 6.25 mol% Al (i.e., 16:1 ML/Al(tetrahedral)). [h] The reaction was carried out with a 1:5 ZrO_2/ML mass ratio; ZrO_2 had a particle size < 100 nm and a surface area ≥ 25 m^2 g^{-1}.

In a comparative study of several hydrogen donors, Zr-Beta maintained its TH activity and high GVL selectivity for all systems investigated (see Table S1 in the Supporting Information). Such versatility is important because Fur is produced in many different solvents and, to minimize unit operations, the subsequent conversion of Fur into GVL should be performed in the same solvent system. When primary alcohols, secondary alcohols with alkyl chains longer than C_4, or solvent mixtures with lower hydrogen-donor-to-substrate ratios were used (e.g., the use of THF with 4 equivalents of 2-butanol), the reaction rate was slower than when pure 2-butanol or 2-propanol was used. Notably, selectivity for the formation of GVL always remained above 95%, regardless of the solvent used. Recently, it was shown that GVL itself is an excellent solvent for the production of Fur from hemicellulose.[20] Zr-Beta generated quantitative amounts of GVL from ML and LA in a 1:1 (w/w) GVL/2-butanol solvent mixture (see Table S1); thus, the reaction product may also be used as an effective reaction solvent.

Next, the ring opening of FA/FE to LA/BL was coupled with the two TH steps to complete the "one-pot" conversion of Fur into GVL. Ring opening by hydrolytic cleavage of the furanic C−O bond is typically promoted with Brønsted acids, such as aluminosilicates and ion-exchange resins. These catalysts, however, may also promote side reactions that result in the formation of soluble high-molecular-weight species and insoluble humins. Of all acids tested in the initial screening, Al-Beta, Amberlyst-70, and Al-MFI-ns generated GVL in the highest yield (44, 66, and 62%, respectively; Table 2, entries 1, 4, and 10). However, Amberlyst-70 and Al-Beta also converted 8 and 16 wt%, respectively, of the 2-butanol solvent into *sec*-butyl ether, whereas Al-MFI-ns converted less than 2 wt% of the 2-butanol. The crystalline nanosheet morphology of Al-MFI-ns provides larger surface areas and shorter molecular-diffusion lengths as compared to those of micron-sized zeolite crystals, as well as improved hydrothermal stability as compared to that of amorphous mesostructured silicates.[21] The use of Al-MCM-41 and Al-MFI zeolite (crystal size ca. 300 nm) led to the formation of GVL in moderate yields, whereas sulfuric acid produced virtually no GVL. Sulfuric acid fully converted FA/FE mixtures into levulinate derivatives, but GVL yields were low owing to slow rates for the second TH step. Besides FA, FE, LA, and BL, the only other intermediate detected in significant concentrations was 5-methyl-2(5*H*)-furanone (MF), which is the product of LA dehydration.[6] The 4-HPs were never observed, which suggests that the lactonization is very fast under the conditions investigated.

Table 2: Results for the one-pot conversion of Fur into GVL in 2-butanol in the presence of Brønsted acids and Zr-Beta (Si/Zr 127:1).[a]

Entry	Brønsted acid	Fur/Al or Fur/H^+[b]	Water content [wt%]	Yield[c] [mol%] GVL	FE	BL	LA	MF
1	Al-Beta	16:1	–	44	0	2	0	15
2	Al-MCM-41	16:1	–	34	0	0	0	4
3	Al-MFI	16:1	–	8	28	2	0	3
4[d]	Amberlyst-70	10:1	–	66	0	0	0	0
5	Amberlyst-36	16:1	–	39	0	13	3	2
6	H_2SO_4	10:1	–	16	0	48	0	0
7	Al-MFI-ns	80:1	–	18	16	4	0	2
8	Al-MFI-ns	32:1	–	40	0	4	0	2
9	Al-MFI-ns	20:1	–	58	0	3	0	3
10	Al-MFI-ns	16:1	–	62	0	2	0	2
11	Al-MFI-ns	16:1	5	68	0	2	0	8
12	Al-MFI-ns	16:1	10	65	0	2	1	8
13	Al-MFI-ns	16:1	15	58	0	4	4	7
14[e]	Al-MFI-ns	16:1	5	78	0	1	0	8
15[f]	Al-MFI-ns	16:1	ca. 6.5	70	0	2	0	5
16[e,g]	Al-MFI-ns	16:1	ca. 6.5	62	0	6	0	4

[a] Reaction conditions: Zr: 1 mol%, Fur (5 wt%) in 2-butanol (Fur/Zr 100:1), 393 K, 24 h. [b] The amount of tetrahedrally coordinated Al was determined by a combination of ICP spectroscopy and solid-state ^{27}Al NMR spectroscopy. [c] Yield: ([mmol product]/[mmol (feed initial)]) × 100; GVL, γ-valerolactone; FE, butyl furfuryl ether; BL, butyl levulinate; LA, levulinic acid; MF, 5-methyl-2(5*H*)-furanone. [d] See Table S2 in the Supporting Information for other Fur/H^+ ratios. [e] Reaction time: 48 h. [f] The reaction was carried out with a solution of Fur (5 wt%) in 2-butanol from a simulated biphasic system [2:1 (w/w) 2-butanol/water (30 wt% NaCl)]. [g] The reaction was carried out with the organic fraction of a biphasic system used for the dehydration of a 15 wt% xylose solution; see the Supporting Information for experimental details.

Further optimization studies were performed with Zr-Beta and Al-MFI-ns catalyst mixtures. The concentration of the Brønsted acid had a strong influence on product yields. Specifically, when Fur/Al(tetrahedral) ratios were decreased (i.e., the Brønsted acid concentration was increased with respect to tetrahedrally coordinated Al) while a fixed content of the Zr-based Lewis acid was maintained, progressively higher GVL yields and less by-product formation were observed. When the Fur/Al ratio was decreased from 80:1 to 16:1, the yield of GVL increased from 18 to 62% (Table 2, entries 7 and 10). The GVL yield approached a stable value for Fur/Al ratios lower than 20:1. A similar trend was observed when Amberlyst-70 was used and the Fur/H^+ ratio was varied; thus, this effect appeared to be a consequence of the varying Brønsted acid concentration (see Table S2). At optimal Fur/Al ratios, the catalytic activity decreased over multiple cycles; however, activity could be recovered by calcination (see Figure S11 in the Supporting Information). Induced coupled plasma (ICP) spectroscopy measurements of the postreaction solution and solids recovered by hot filtration confirmed the absence of metal leaching.

We investigated the effect of the water content on catalyst performance to determine the feasibility of performing the domino reaction with Fur solutions obtained directly from biomass. When hemicellulose is converted into Fur by the use of biphasic systems with homogenous acid catalysts, the organic phase may contain water in concentrations ranging from 1 to 20 wt%. In our system, an increase in the water content from 0 to 5 wt% resulted in an increase in the GVL yield from 62 to 68% (Table 2 entries 10 and 11). A further increase in the water content led to a decrease in TH activity. Pore hydrophobicity in Lewis acid zeolites has been shown to be critical for maintaining activity in the presence of water.[22] Figure 1 shows the product evolution for the system containing 5 wt% water over a period of 48 h. After 48 h, GVL, MF, and BL were obtained in 78, 8, and 1% yield, respectively (Table 2, entry 14). For the Zr-Beta/Al-MFI-ns combination, the carbon balance (calculated on the basis only of detectable species shown in Table 2) was approximately 66% after 24 h in the absence of water. When an initial 95:5 2-butanol/water mixture was used, this value increased to 77 and 87% after 24 and 48 h, respectively. After ruling out the adsorption of GVL in the zeolite pores and cautiously analyzing the GC–MS data for high-molecular-weight species, we hypothesize that the observed decrease in unaccounted carbon with the concomitant increase in the GVL yield at long reaction times is probably caused by the conversion of oligomeric by-products into monomeric GVL-producing reactive intermediates (Figure 1).

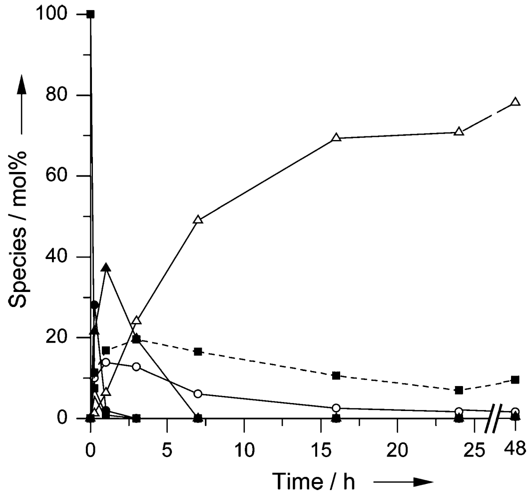

Figure 1. Evolution of species over 48 h for a solution of Fur (5 wt%) in 2-butanol/water (95:5 (w/w)) in the presence of a mixture of Zr-Beta (Fur/Zr 100:1) and Al-MFI-ns (Fur/Al 16:1) at 393 K. Legend: ■ Fur, □ FA, ● FE, ▲ LA, ○ BL, △ GVL, -----■----- MF.

Aqueous phases in biphasic systems may use homogenous acids (e.g., H_2SO_4) and be saturated with salts (e.g., NaCl) to maximize the yield of Fur from sugars. Therefore, we tested our catalytic system in two additional solutions: 1) a solution of Fur in 2-butanol as prepared by mixing Fur with a simulated biphasic system [2:1 (w/w) organic/aqueous (30 wt% NaCl)], and 2) a solution in 2-butanol separated from a biphasic system after the dehydration of 15 wt% xylose with H_2SO_4 (see Table S3). The simulated biphasic system generated GVL in 70% yield (intermediates were formed in 7% yield), which indicated strong compatibility with the sugar dehydration process (Table 2, entry 15). Notably, GVL was obtained in 62 % yield (with intermediates formed in 10 % yield) when the solution of Fur obtained from the xylose dehydration experiment was used (Table 2, entry 16).

In summary, we have demonstrated the one-pot conversion of Fur into GVL in yields approaching 80 %. A combination of solid Lewis and Brønsted acids catalyzed a domino reaction involving sequential TH and ring-opening steps to produce GVL in high yields without the need for high-pressure molecular H_2 or precious-metal catalysts. This zeolite combination is compatible with the process used to convert hemicellulose into Fur and thus offers a streamlined strategy for the conversion of pentoses into GVL. Our current objectives include performing detailed stability tests and investigations into the role of acidity in by-product formation.

Experimental Section

Detailed procedures for the synthesis of the catalyst as well as characterization and reactivity data are provided in the Supporting Information. Liquid-phase batch reactions were performed in a sealed vial placed in a temperature-controlled oil bath at 393 K with magnetic stirring. The optimal reaction conditions required a 100:1 Fur/Zr ratio (Zr-Beta, 25 mg), a 16:1 Fur/Al(tetrahdedral) ratio (Al-MFI-ns, 50 mg), and the use of a feed solution of Fur (5 wt %) in 2-butanol/water (95:5 (w/w), 0.75 mL). Reaction products were analyzed by GC.

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