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Cascade of Liquid-Phase Catalytic Transfer Hydrogenation and Etherification of 5-Hydroxymethylfurfural to Potential Biodiesel Components over Lewis Acid Zeolites

Jungho Jae, Eyas Mahmoud, Raul F. Lobo,* and Dionisios G. Vlachos*[a]

We report a one-step process for the production of diesel fuel from biomass-derived 5-hydroxymethylfurfural (HMF). The reaction proceeds through the sequential transfer hydrogenation and etherification of HMF to 2,5-bis(alkoxymethyl)furan, a potential biodiesel additive, catalyzed by a Lewis acid zeolite, such as Sn-Beta or Zr-Beta. An alcohol is used as a hydrogen donor and as a reactant in etherification. This cascade reaction can selectively produce high yields of the biodiesel additive (>80 % yield) from HMF with the Sn-Beta catalyst and secondary alcohols, such as 2-propanol and 2-butanol.

Introduction

Lignocellulosic biomass is being studied worldwide for the renewable production of liquid fuels.[1] The major building blocks of the hemicellulosic and the cellulosic part of lignocelluloses are C5–C6 carbohydrates, such as xylose and glucose. These carbohydrates are dehydrated to furfural or 5-hydroxymethylfurfural (HMF) under aqueous acidic conditions, which are species that can be used as intermediates in the production of biofuels, such as transportation fuels and chemicals.[2] It is thus critical to develop catalytic strategies for the production of fuel-compatible species from these furan compounds.

Several groups have reported catalytic processes that convert furan compounds to diesel range fuels.[3] Huber et al. introduced a catalytic process in which HMF first undergoes aldol condensation with acetone and then hydroprocessing of the products to produce C9–C15 alkanes.[3a] Sutton et al. modified the Huber process by additional conversion of aldol intermediates to polyketones, which allows for mild hydroprocessing to produce alkanes.[3c] Corma et al. reported the Sylvan diesel process, in which 2-methylfuran, obtained from the hydrogenation of furfural, is trimerized or condensed with aldehydes or ketones followed by hydrodeoxygenation of these compounds to an alkane mixture.[3e] The key step in all these processes is the increase in the number of carbon atoms of the furan compounds through aldol condensation or alkylation to make them suitable for diesel range molecules.

Another promising approach for the production of biodiesel components is the etherification of HMF with alcohols. The resulting product HMF ether, such as 5-(ethoxymethyl)furfural, could serve as a potential biodiesel additive owing to its high miscibility in diesel fuel and a high energy density of 30.3 MJ/L, which is similar to that of diesel (33.6 MJ/L).[4] Several groups have reported the production of 5-(ethoxymethyl)furfural from either HMF or glucose/fructose in excess ethanol with homogeneous acid catalysts[5] or solid acid catalysts: the H^+ form of zeolites,[4d] Al-containing mesoporous silica,[4c] ion-exchange resins,[4a] and heteropolyacids[4e] with moderate yields and selectivity (31–92 %). The remaining aldehyde functional group in 5-(ethoxymethyl)furfural, however, reduces the stability of the molecule, and it is desirable to hydrogenate aldehydes to alcohols[6] or subsequent ether linkages.[5]

To this end, Balakrishnan et al. studied the one-pot reductive etherification of HMF to 2,5-bis(alkoxymethyl)furan with PtSn/Al_2O_3 and Amberlyst 15 catalysts under hydrogen pressure.[5] They obtained the corresponding 2,5-bis(alkoxymethyl)furan in yields of 64 and 47 % for ethanol and *n*-butanol, respectively. Gruter studied the production of 2,5-bis(ethoxymethyl)furan through the sequential hydrogenation and etherification of HMF, in which HMF is first hydrogenated to 2,5-bis(hydroxymethyl)furan (BHMF) over a Pt/C catalyst at room temperature and 5 bar (1 bar = 0.1 MPa) of hydrogen pressure and is then etherified to 2,5-bis(ethoxymethyl)furan at 348 K without hydrogen.[7] He obtained a 2,5-bis(ethoxymethyl)furan yield of 75 %. Importantly, the two ether linkages lead to a higher miscibility in commercial diesel and to a lower crystallization temperature than does 5-(ethoxymethyl)furfural.[8]

Because 2,5-bis(alkoxymethyl)furan is a higher-grade fuel than 5-(alkoxymethyl)furfural, it is of considerable interest to produce 2,5-bis(alkoxymethyl)furan from HMF by using a less energy intensive process. The hydrogenation of HMF to BHMF requires the use of noble metals (e.g., Ru[9] or Pt[5]) and high hydrogen pressures (>5 bar). In addition, complete hydrogenation and etherification requires the use of two catalysts

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[a] Dr. J. Jae,[+] E. Mahmoud, Prof. R. F. Lobo, Prof. D. G. Vlachos
Catalysis Center for Energy Innovation
Department of Chemical and Biomolecular Engineering
University of Delaware, Newark, DE 19716 (USA)
Fax: (+1) 302-831-1048
E-mail: lobo@udel.edu
vlachos@udel.edu
Homepage: http://www.efrc.udel.edu/

[+] Current Address:
Korea Institute of Science and Technology
Seoul 136-791 (Republic of Korea)

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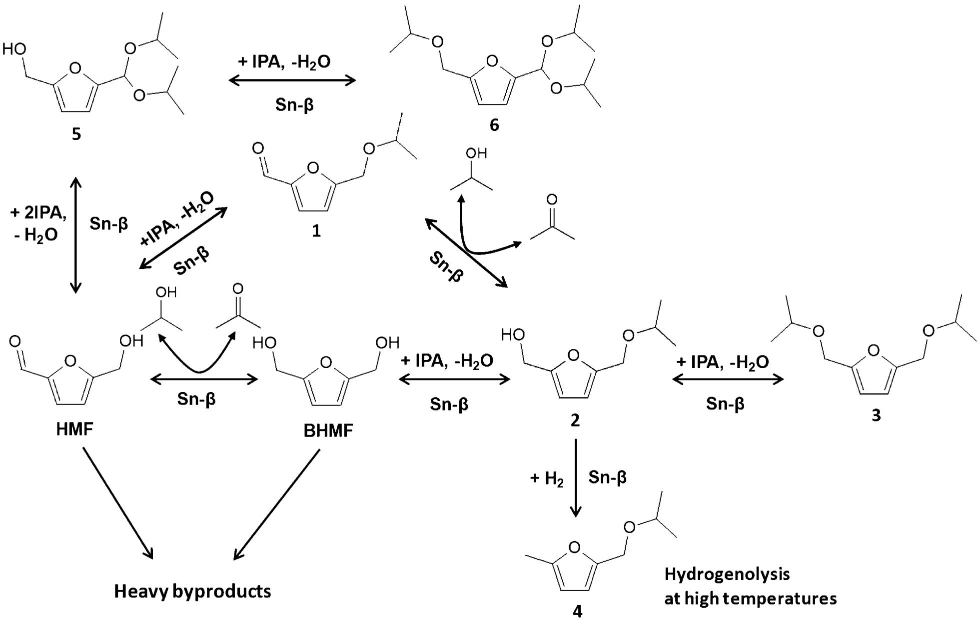
(metal and acid catalysts) increasing the process cost. Transfer hydrogenation (TH) via the Meerwein–Ponndorf–Verley (MPV) reaction using sacrificial alcohols as hydrogen donors is an alternative to this hydrogenation step. Importantly, dehydrogenated products of alcohols can easily be recycled through hydrogenation over base metals[10] or used as chemicals.[11] Because the formation of ether requires alcohols, we envision a one-step process in which the alcohol is used as a hydrogenation and as an etherification agent. Many catalysts, such as aluminum alkoxides,[12] transition metals,[11,13] and metal oxides,[10] are used as TH catalysts. Zeolites with framework Sn or Zr are solid Lewis acids and are active for the TH reaction, as originally reported by Corma et al.[14] Moreover, these isolated Lewis acid sites in the beta framework can catalyze etherification.[14b,15]



Scheme 1. Reaction network of sequential catalytic TH and etherification of HMF to 2,5-bis(alkoxymethyl)furan with 2-propanol and Sn-Beta catalyst. Compounds obtained are as follows: HMF, BHMF, 5-[(1-methylethoxy) methyl]furfural (compound **1**), 5-[(1-methylethoxy)methyl]-2-furanmethanol (compound **2**), 2,5-bis[(1-methylethoxy)methyl]furan (compound **3**), 2-methyl-5-[(1-methylethoxy)methyl]furan (compound **4**), 5-[bis(1-methylethoxy)methyl]-2-furanmethanol (compound **5**), and 2-[bis(1-methyl ethoxy)methyl]-5-[(1-methylethoxy)methyl]furan (compound **6**). IPA = 2-propanol.

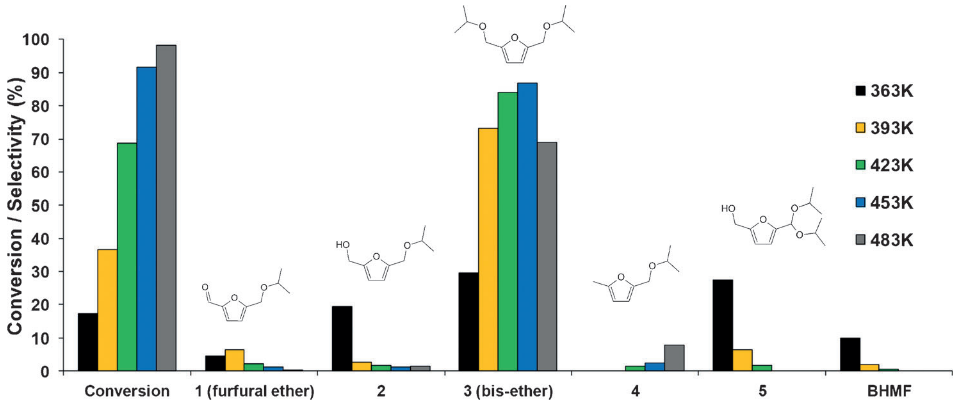


Figure 1. HMF conversion and product selectivity as a function of temperature. Reaction conditions: batch reactor, 1.2 wt% HMF in 2-propanol solution with Sn-Beta (molar ratio of HMF to Sn = 100:1), 20.4 bar N_2, and 6 h of the reaction time at defined temperatures.

Herein, we report a one-step catalytic process for the efficient production of 2,5-bis(alkoxymethyl)furan through sequential TH and etherification reactions of HMF catalyzed by a Sn-containing zeolite (Scheme 1). We show specifically that a solid Lewis acid catalyst, zeolite beta with framework Sn (Sn-Beta), can selectively hydrogenate HMF to BHMF followed by etherification of BHMF to 2,5-bis(alkoxymethyl)furan with an excellent yield (>80%). Sn-Beta appears to be better than zeolite beta with framework Zr (Zr-Beta) and superior to nonframework Sn-Beta (EF-Sn-Beta) zeolites and Sn-MFI.

Results and Discussion

Effect of temperature

Initial tests were performed with 1.2 wt% HMF in 2-propanol with a Sn-Beta catalyst (Si/Sn = 120), which gave an HMF/Sn ratio of 100:1. XRD, UV/Vis spectroscopy, and ^{119}Sn MAS NMR analyses of the calcined catalysts confirmed their crystallinity and the presence of isomorphically substituted Sn sites (see the Supporting Information). HMF conversion and product selectivity as a function of temperature at 6 h of the reaction time is plotted in Figure 1. The conversion of HMF increases from 17.3 to 98.3% with the increase in temperature from 363 to 483 K. The selectivity toward the products at 363 K is 29.4% for **3**, 27.4% for **5**, 19.4% for **2**, 10.0% for BHMF, and 4.6% for **1**. The formation of acetal **5** indicates that the acetalization of the aldehyde group of HMF with 2-propanol occurs in parallel with the MPV reaction. The selectivity toward the targeted product **3** increases with the increase in temperatures up to a point. The selectivity quickly reaches 73.1% at 393 K and increases up to 87% at 453 K at the expense of other intermediates. Increasing the temperature to 483 K decreases the selectivity toward bis-ether **3** to 68% and increases the selectivity toward **4** to 8%, which indicates that some hydrogenolysis occurs at temperatures above 483 K, presumably by using the hydrogen produced from the dehydrogenation of 2-propanol.

Reaction evolution

Conversions and product yields in a reaction starting from HMF and BHMF as a function of time at 403 K are plotted in Figures 2 and 3, respectively. Bis-ether **3** is the major product, whereas furfural ether **1** (2.4%) and compound **2** (1.2%) are present in low concentrations during the entire reaction time.

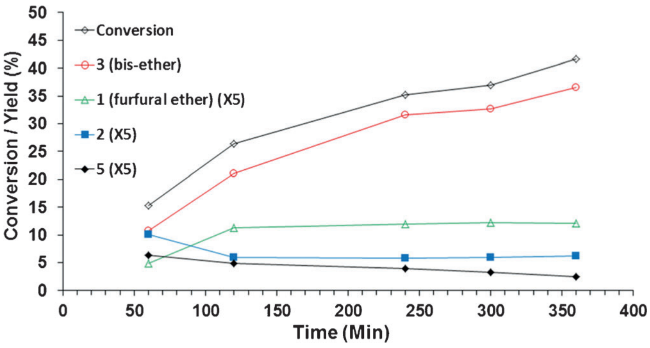


Figure 2. Conversion and product yields as a function of time at 403 K starting from HMF. Reaction conditions: batch reactor, 1.2 wt% HMF in 2-propanol solution with Sn-Beta (molar ratio of HMF to Sn = 100:1), and 20.4 bar N_2.

It is clear that HMF is first hydrogenated to BHMF via the MPV reaction and quickly undergoes subsequent etherification. However, the presence of compound **1** over time suggests that HMF could first be etherified to **1** with 2-propanol and then undergo the MPV reaction (Scheme 1). The yield of acetal **5** steadily decreases over the entire reaction time, and it could be converted to other products such as bis-ether **3**. The conversion of BHMF is much faster than that of HMF (Figure 3). The conversion of BHMF reaches 100% at 403 K after 6.5 h, whereas the conversion of HMF is only 41% under the same conditions. BHMF is progressively etherified to compound **2** and then to bis-ether **3** during the reaction. The fast etherification of BHMF suggests that the MPV reaction of HMF to BHMF and of **1** to **2** is the rate-determining step to produce bis-ether **3**. As a control experiment, the classical MPV reduction of cyclohexanone to cyclohexanol was studied with use of 2-propanol and the Sn-Beta catalyst at 373 K for 4 h. The conversion of cyclohexanone was 92% and the selectivity toward cyclohexanol was 98%, which indicated that the MPV reaction of cyclohexanone is fast, as reported previously.[14c]

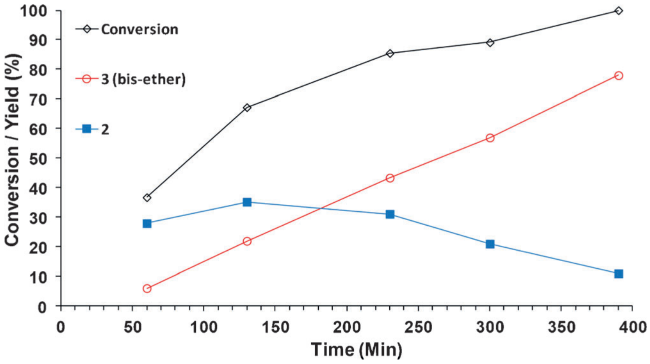


Figure 3. Conversion and product yields as a function of time at 403 K starting from BHMF. Reaction conditions: batch reactor, 1.2 wt% BHMF in 2-propanol solution with Sn-Beta (molar ratio of BHMF to Sn = 100:1), and 20.4 bar N_2.

Active sites and pore size

To better understand the active sites of the catalyst, we prepared four catalyst samples (Figure 4): the siliceous form of zeolite beta (Si-Beta), EF-Sn-Beta, zeolite beta with framework Al (Al-Beta), and Sn-Beta. Textural properties of these catalysts as well as concentration and strength of the acid sites are given in our previous report.[16] The same amounts of the catalysts based on metal (Al or Sn) sites were used for each reaction to see the intrinsic activity of different sites (molar ratio of HMF to metal Sn or Al = 100:1). Si-Beta, having a zeolite beta structure without any active sites, is completely inactive for the reaction. EF-Sn-Beta shows some reactivity toward the production of BHMF and some ether intermediates; however, the conversion of HMF is less than 20%, which indicates that the activity of nonframework Sn is small for both MPV reaction and etherification. Al-Beta, having both Brønsted and Lewis acid sites, shows 98% conversion of HMF and comparable activity to Sn-Beta. However, Al-Beta produces **1** as a major product (70% selectivity). As expected, etherification occurs over Brønsted acid sites of Al-Beta whereas the MPV reaction is not catalyzed by the Lewis acid sites of Al-Beta. Al-Beta also shows

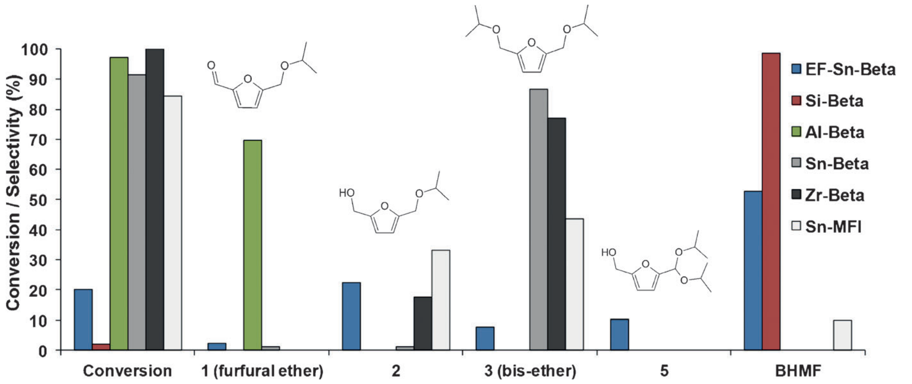


Figure 4. HMF conversion and product selectivity over different catalysts such as EF-Sn-Beta, Si-Beta, Al-Beta, Sn-Beta, Zr-Beta, and Sn-MFI at 453 K for 6 h. Reaction conditions: batch reactor, 1.2 wt% HMF in 2-propanol solution with various catalysts (molar ratio of HMF to metals Al, Sn, or Zr = 100:1), and 20.4 bar N_2.

significant formation of diisopropyl ether (18% yield) through the self-etherification of 2-propanol. Overall, these control experiments suggest that isolated Lewis acid sites in Sn-Beta are the active sites for both MPV reaction and etherification to selectively produce bis-ether **3**.

Zr-Beta, also an active catalyst for the classical MPV reaction, is highly active for this cascade reaction. The conversion of HMF is 100% and the selectivity to bis-ether **3** and compound **2** are 77 and 17%, respectively. The etherification activity of Zr-Beta is, however, lower than that of Sn-Beta under the reaction conditions investigated. In addition to the active sites, structural effects may play a role. Sn-MFI has a lower activity for HMF conversion and etherification to bis-ether than Sn-Beta. The bis-ether **3** selectivity is low (44%) and the selectivity to compound **2** and BHMF is high (33 and 10%, respectively) with Sn-MFI. This result is attributed to the slower diffusion of the reactants and products, such as bis-ether **3** with the kinetic diameter of 7.4 Å, within the channels of the MFI structure (pore size of 6.2–6.3 Å adjusted by Norman radii) than within Sn-Beta (6.3–7.4 Å by Norman radii).[17]

Effect of initial HMF concentration and catalyst stability

The effect of HMF concentration on catalytic TH and etherification of HMF was studied at 453 K (Figure 5). The selectivity toward bis-ether **3** decreased from 87.3 to 57.7% with the increase in HMF concentration from 1.2 to 8.0 wt%. The selectivity toward unidentified species (undetectable by using GC) increased significantly from 8.0 to 35.7% with the increase in HMF concentration. These results indicate that heavy byproducts (presumably humins) are formed at high HMF concentrations. It is possible that these heavy byproducts are produced through the self-etherification of HMF as their selectivity increases with the increase in HMF concentration. The temperature programmed oxidation of solid residues obtained through the reactions of 1.2 and 4.0 wt% HMF confirmed the presence of 5.0 and 12.0 wt% solid products, respectively. In addition, Figure 6 shows the IR spectra (500–2000 cm^{-1}) of the fresh and spent Sn-Beta catalysts for the reactions of 1.2 and 4.0 wt% HMF, respectively. The band associated with the carbonyl group at 1670–1750 cm^{-1} is clearly visible on the spent catalyst for the reaction of 4.0 wt% HMF, which reveals the accumulation of more organic compounds on this sample during the reaction. This result also suggests that heavy byproducts are likely produced through the reactions of HMF.

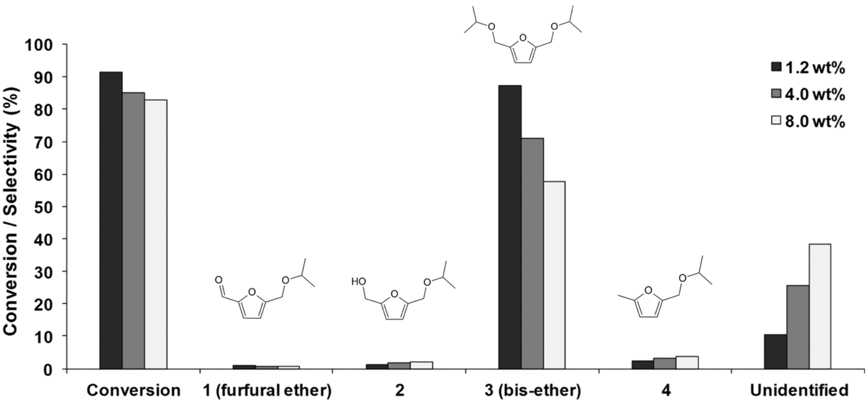


Figure 5. Effect of the initial HMF concentration on HMF conversion and product selectivity at 453 K for 6 h. Reaction conditions: batch reactor, HMF in 2-propanol solution with Sn-Beta (molar ratio of HMF to Sn = 100:1), and 20.4 bar N_2.

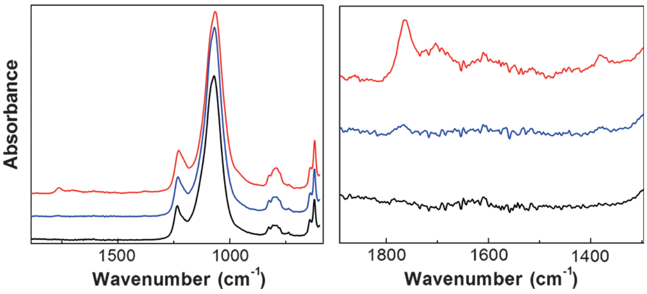


Figure 6. IR spectra of fresh Sn-Beta (black), spent Sn-Beta from the reaction of 1.2 wt% HMF (blue), and spent Sn-Beta from the reaction of 4.0 wt% HMF (red).

To investigate the deactivation of the catalyst from the formation of heavy byproducts, the spent catalyst for the reaction of 1.2 wt% HMF was reused under the same reaction conditions. As shown in Table 1, the recycled catalyst showed a lower activity than the fresh Sn-Beta (68% vs 92% HMF conversion) and a lower selectivity toward bis-ether **3** (87.0% vs 81.1%). However, after simple calcination of the spent catalysts in air at 773 K, the catalytic activity was recovered completely. This result indicates that the decrease in catalytic activity is attributed to the loss of some active sites by deposition of heavy byproducts. We further investigated the reuse of catalyst samples for the etherification of BHMF to determine whether the catalyst is stable. The conversion of BHMF over the fresh catalyst reached 97.7% and the selectivity toward bis-ether **3** and compound **2** was 72.1 and 14.5%, respectively, after 0.83 h at 453 K. The reuse of the spent catalyst also shows loss of catalytic activity. The conversion of BHMF decreased to 29.8% and the selectivity toward **2** (64.6%) was higher than that toward bis-ether **3** (19.7%) after 0.83 h. The deactivation of the catalyst appears to be more significant with BHMF than with HMF, which could be due to the fact that BHMF has two hydroxyl groups. BHMF could be more susceptible to the formation of heavy byproducts via self-etherification than HMF, which has only one hydroxyl group. Overall, these results suggest that heavy byproducts are formed from both HMF and BHMF; in both cases, the catalyst is reusable after regeneration in air.

Table 1. Stability of the Sn-Beta catalyst in the MPV reaction and etherification of HMF and BHMF at 453 K.[a]

Feed	Catalyst	*t* [h]	Conv. [%]	Selectivity [%] 1	2	3	4	5
HMF	fresh	6	91.5	1.1	1.2	87.0	2.4	0.0
HMF	spent	6	68.0	1.9	2.4	81.1	2.0	0.9
HMF	regen.[b]	6	90.5	0.7	2.7	86.8	2.7	0.4
BHMF	fresh	3	100.0	–	0.7	85.6	–	–
BHMF	fresh	0.83	97.7	–	14.5	72.1	–	–
BHMF	spent	5.5	100.0	–	0.0	67.3	–	–
BHMF	spent	0.83	29.8	–	64.6	19.7	–	–

[a] Reaction conditions: batch reactor, 1.2 wt% of HMF or BHMF in 2-propanol solution with Sn-Beta (molar ratio of HMF or BHMF to Sn: 100), and 20.4 bar N_2; [b] Regenerated catalyst.

Alcohol structure

In addition to the use of 2-propanol as a hydrogen donor, a number of alcohols such as 1-propanol, 1-butanol, 2-butanol, and ethanol were tested for the catalytic TH and etherification of HMF. Of the alcohols examined, secondary alcohols (2-propanol and 2-butanol) were more selective than primary alcohols (1-propanol, 1-butanol, and ethanol) toward the production of bis-ether **3**. The selectivity toward bis-ether **3** using secondary alcohols was greater than 85% in all cases. All the tested primary alcohols produced approximately 10% of **1** along with 70% of bis-ether **3**, which indicated that TH using primary alcohols was slower than that using secondary alcohols, as expected from previous reports.[18] This result is attributed to the fact that secondary alcohols are more susceptible to dehydrogenation than primary alcohols.[19]

Overall, the high selectivity for the production of bis-ether **3** with various alcohols demonstrates the versatility of this process, in which the molecular mass of the biodiesel compounds can easily be tuned with use of different alcohols. In comparison to previous studies, our highest yields are higher than those obtained through the one-pot reductive etherification of HMF to 2,5-bis(alkoxymethyl)furan with two catalysts (PtSn/Al_2O_3 and Amberlyst 15) under hydrogen pressure[5] (64 and 47% in ethanol and *n*-butanol, respectively) or those obtained through the two step process, hydrogenation with a Pt/C catalyst followed by etherification (75% yield of 2,5-bis(ethoxymethyl)furan) (Figure 7).[7]

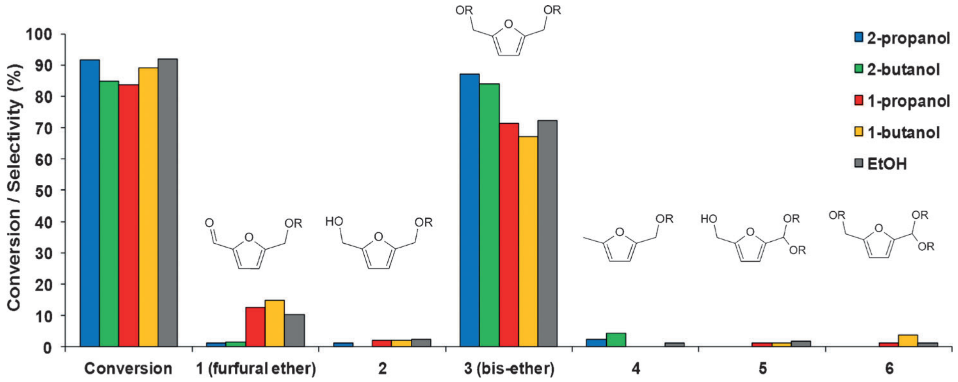


Figure 7. HMF conversion and product selectivity over Sn-Beta with different alcohols at 453 K for 6 h. Reaction conditions: batch reactor, 1.2 wt% HMF in different alcohol solutions with Sn-Beta (molar ratio of HMF to Sn = 100:1), and 20.4 bar N_2.

Conclusions

We developed a one-step process to selectively convert 5-hydroxymethylfurfural (HMF) to 2,5-bis(alkoxymethyl)furan (**3**), a potential biodiesel component. The reaction proceeds through the Meerwein–Ponndorf–Verley reaction via hydride transfer from a secondary or primary alcohol to HMF to produce 2,5-bis(hydroxymethyl)furan (BHMF), followed by etherification of BHMF to **3** in greater than 80% yield over solid Lewis acid catalysts, such as Sn-Beta and Zr-Beta. The etherification of BHMF or HMF with alcohols is a fast reaction over Sn-Beta, whereas the Meerwein–Ponndorf–Verley conversion of HMF to BHMF is the rate-determining step. Importantly, the molecular mass of the biodiesel components can be tuned from C10 to C14 with use of different alcohols (EtOH, PrOH, or BuOH). The results of these investigations demonstrate the upgrading of biomass-derived oxygenates to fuels through transfer hydrogenation and condensation reactions using a solid Lewis acid catalyst.

Experimental Section

Catalyst preparation

Sn-Beta with a Si/Sn ratio of 118 was prepared by the method described by Corma et al.[14a] Si-Beta and EF-Sn-Beta with a Si/Sn ratio of 106 were prepared by the method reported by Roy et al.[16a] In brief, EF-Sn-Beta was prepared through the simple impregnation of Sn into Si-Beta with use of $SnCl_4{\cdot}5H_2O$ dissolved in methanol. Al-Beta used herein was obtained by thermal treatment in air (1 h at 368 K and 8 h at 723 K, with heating rates of 2 $K\,min^{-1}$) of the commercial ammonium form (CP 814N, powder, Zeolyst International) of zeolite beta. The SiO_2/Al_2O_3 ratio of the zeolite is 18 according to the provider's specifications. Sn-MFI with a Si/Sn ratio of 120 and Zr-Beta with a Si/Zr ratio of 100 were prepared by the method reported by Mal et al.[20] and Corma et al.,[21] respectively.

Characterization

The XRD patterns were recorded by using a Philips X'Pert X-ray diffractometer with CuK_α radiation. The samples were analyzed by using a UV/Vis spectrometer (Jasco V-550) equipped with a diffuse reflectance cell.[22] The micropore volumes of the samples were determined from nitrogen adsorption isotherms at 77 K measured by using a Micromeritics ASAP 220 instrument. All samples were degassed for 8 h under vacuum at 573 K before adsorption. The micropore volumes and surface areas of zeolite beta were determined by using the t-plot method. The ^{119}Sn MAS NMR spectra were recorded by using a Bruker AVIII 500 MHz solid-state NMR spectrometer operating at a Larmor frequency of 186.5 MHz for ^{119}Sn. A 4 mm HX MAS probe was used. The magic angle spinning rate was set to $12\,000 \pm 2$ Hz for all measurements. The 90° ^{119}Sn

pulse was calibrated to 6.0 μs with use of the saturated $SnCl_4$ solution. The single-pulse experiment with a recycle delay of 50 s was used with the number of scans ranging from 1024 to 4320, and it depended on the signal-to-noise ratio of the spectrum. The spectra were referenced externally to a peak of the ^{119}Sn spectrum of SnO_2 at -604.3 ppm.[23] The results for catalyst characterization are given in the Supporting Information.

Catalytic experiments

The catalytic TH and etherification of HMF were performed in a 100 mL stainless steel Parr reactor. For a typical reaction, the reactor was charged with HMF (160 mg, 99%, Sigma–Aldrich), Sn-Beta catalyst (80 mg), and 2-propanol (16 mL). The reactor was sealed, purged with air along with N_2, and charged with N_2 to a pressure of 20.4 bar. The reactor was heated to the reaction temperature with a silicon oil bath and mixing was accomplished with a magnetic stirrer. After the reaction, the reactor was quenched in ice water and the liquid products were collected, filtered, and analyzed. The liquid products were identified with a combination of GC–MS (Shimadzu GCMS-QP2010 Plus) and ^{1}H and ^{13}C NMR spectroscopy, whereas they were quantified with a gas chromatograph (Agilent 7890A) equipped with a flame ionization detector by creating a calibration curve with use of standard solutions. The detailed method is described elsewhere.[11] Herein, conversion is defined as the moles in the feed that reacted (determined from GC analysis) divided by the initial moles in the feed loaded in the reactor. Product selectivity is defined as the moles in the product divided by the moles in the feed that reacted. Yield is defined as the moles in the product divided by the initial moles in the feed loaded in the reactor.

HMF (99%) and BHMF (98%) were purchased from Sigma–Aldrich and Penn A Kem LLC, respectively. Compound **1** was obtained from the isolation of the reaction mixture with a Waters Fraction Collector III attached to the HPLC with a Bio-Rad HPX-87H (300× 7.8) column. Compound **3** was obtained from the product mixture by removal of the solvent with a rotary evaporator. For quantification, the GC sensitivity for compounds **2** and **4** was assumed to be equal to that for compound **1**. The GC sensitivity for compounds **5** and **6** was assumed to be equal to that for compound **3**.

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Keywords: alcohols · biomass · etherification · transfer hydrogenation · zeolites

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