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Direct transformation of carbohydrates to the biofuel 5-ethoxymethylfurfural by solid acid catalysts

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The direct conversion of glucose to 5-ethoxymethylfurfural (EMF) is a promising biomass transformation due to the products potential application as a biofuel. Here, the conversion of glucose to EMF was examined over several solid acid catalysts in ethanol between 96 and 125 °C. Among the catalysts employed, dealuminated beta zeolites [DeAl-H-beta-12.5 (700)] gave a moderate yield of EMF (37%) in a single step catalytic process. A combined catalytic system consisting of H-form zeolite and Amberlyst-15 was found to be more efficient for the transformation of glucose to EMF (46%) via an one-pot, two-step reaction protocol. Alternative biomass-based mono-, di- and polysaccharides formed also moderate to good yields of EMF with the catalytic systems, including fructose which yielded 67 % of EMF and 4% of ethyl levulinate (ELevu) along with 10 % 5-hydroxymethyl furfural (HMF) in the combined reaction protocol. A significant amount of ELevu (1-16 %), a rehydrated product of EMF and promising fuel additive, was observed in this study. Recyclability studies suggested that it was possible to reuse the DeAl-H-beta-12.5 (700) catalyst in consecutive reactions without significant changes in product yields due to its easy recovery and thermal stability during regeneration.

Today far most carboneous chemicals and fuels are derived from the fossil-based resources oil, coal and natural gas. However, increasing concern about, e.g. resource availability and diminution, pollution and global warming has sparked significant interest into utilization of biomass as a future renewable carbon source for fuels and value-added chemicals. In terrestrial biomass, carbohydrates account for up to 75% of the renewable carbon,¹ and several catalytic routes have been developed for transformation of carbohydrates to useful products via heterogeneous, homogeneous and enzymatic processes.² This includes in particular compounds like 5-hydroxymethylfurfural (HMF) which has been demonstrated to serve as a platform molecule for the production of various biofuels³ and chemicals such as, e.g. 2,5-furandicarboxylic acid (FDCA) - a promising substitute for

terphthalic acid in polyester - as well as 2,5-dimethylfuran (DMF), 2,5-diformylfuran (DFF), 2,5-bis(hydroxylmethyl)furan (BHMF), γ -valerolactone (GVL) and maleic anhydride (MA). However, commonly these products have rarely been reported to be efficiently produced from hexoses in a single one-pot reaction.⁴

In addition to the above mentioned furanic compounds, 5ethoxymethylfurfural (EMF) with a high energy density of 30.3 MJ L^{-1} , close to that of diesel (33.6 MJ L^{-1}), gasoline (31.1 MJ L^{-1}) and ethanol (23.5 MJ L^{-1}), is identified to be a promising liquid biofuel.⁵ The synthesis of EMF from HMF can be achieved in high yields (> 90%) by etherification with various acidic catalysts including chlorides (e.g., NH₄Cl, AlCl₃ and FeCl₃), dissolved acids (e.g., H₃PW₁₂O₄₀, H₂SO₄ and *p*-TSA), and solid acids (e.g., H₄SiW₁₂O₄₀/MCM-41, sulfonated graphene oxide, aluminumexchanged K-10 clay and Al-TUD-1).⁶ However, the cost of HMF is relatively high (price of 100 g HMF is 900 EUR at Sigma-Aldrich) and it is rather instable even at room temperature. Thus, from a processing viewpoint the development of a highly efficient catalytic system providing one-pot conversion of sugars into EMF would be desirable.

Sulfonated catalysts have generally been found to be efficient catalysts for the conversion of fructose into EMF. For instance, SO₃H-functionalized ionic liquids afforded 54 % yield of EMF and 6 % ELevu from fructose in hexane-ethanol (100 °C, 80 min).⁷ Also, a high EMF yield of 63 % could be obtained from fructose in ethanol (100 °C, 24 h) using sulfonic acid supported on silica as a heterogeneous catalyst.⁸ Similarily, sulfonic acid functionalised cellulose, graphene oxide, and silica-encapsulated Fe₃O₄ catalysts were all highly efficient for conversion of fructose to EMF in ethanol, consistently giving >70 % yield of EMF.⁹ Likewise, phosphotungstic acid (PA) based heterogeneous catalysts such as silica coated magnetic Fe₃O₄ nanoparticles and K-10 clay supported PA have also been reported to enable efficient synthesis of EMF

from fructose in ethanol yielding 55 and 62 % EMF, respectively.^{10a,b} Recently, we have further reported an EMF yield of 77 % from fructose in ethanol/DMSO solvent mixture with a bifunctional amino acid-heteropoly acid catalyst.^{10c}Notably, the highest EMF yield (91 %) achieved so far from fructose was obtained with an organic-inorganic hybrid solid catalyst methyl imidazolebutylsulfate phosphotungstate ([MImBS]₃PW₁₂O₄₀) in ethanol (90 °C, 24 h).¹¹

In comparison to the number of studies performed with fructose as substrate, significant less work has focused on the catalytic conversion of glucose to EMF via fructose as intermediate. This is surprising since glucose is by far the major carbohydrate source in terrestrial biomass as cellulose. Thus, only a few catalytic systems have been reported to be suitable for the conversion of glucose to EMF, ^{5b,6a,12} and a maximum EMF yield of 38 % was obtained in a homogeneous ethanolic systems with the Lewis acid AlCl₃ as catalyst.¹²

In the direct conversion of glucose to EMF, the isomerisation of glucose to fructose (Lobry-de Bruyn-van Ekenstein transformation) is an important - and often decisive - reaction step which is predominantly catalysed by base or Lewis acid.13 Tandem reaction systems combining glucose isomerisation promoted by Lewis acids/bases with subsequent dehydration of the formed fructose by Brønsted acids have been extensively investigated. A combination of such two types of catalysts, for example hydrotalcite and sulfonic acid-resin, promoting each reaction step were reported to yield >60 % of HMF from glucose.^{14b} On the other hand, zeolites containing both Lewis and Brønsted acid sites have shown to be efficient single standing catalysts for such conversions.¹⁵ Most recently, a commercial H-beta zeolite with a moderate Si/Al ratio of 25 was shown to form HMF from glucose in 50 % yield at 81 % glucose conversion (62 % selectivity) at 150 °C after 50 min in the ionic 1-butyl-3-methylimidazolium chloride ([BMIm]Cl).¹⁶ liauid Likewise, a modified beta zeolite prepared by calcinating at 750 °C gave 43 % yield of HMF at 78 % glucose conversion (55 % selectivity) in a mixture of solvents consisting of water, DMSO, and THF at 180 °C after 3 h.17

Recently, we have found that commercially available beta and USY zeolites are universally promising catalysts for efficient aldoseketose isomerisation in methanol and water in one-pot two-step or one-pot one-step reactions at 100-120 °C.¹⁸ This has been demonstrated for the isomerisation of glucose to fructose (>50 % yield), xylose to xylulose (47 % yield) and erythrose to erythrulose (42 % yield). Moreover, we have also shown that glucose can be directly converted to their corresponding alkyl levulinates in about 50 % yield with the same zeolite catalysts at higher temperatures.¹⁹ In contrast, sulfonic acid functionalised SBA-15 or ionic liquids afforded ethyl-D-glucopyranoside (EDGP) in high yields (70-80 %) in ethanol under identical reaction conditions rather than ethyl levulinate.²⁰ Hence, this clearly indicated that the product distribution could be well adjusted by proper selection of acid types contained in the used catalysts as well as by the reaction conditions. These findings have now prompted us to extrapolate a reaction protocol for the direct conversion of glucose to EMF.

In the present work, we have examined a series of solid acid catalysts - including commercial zeolites as well as modified zeolites - for the direct conversion of glucose into EMF in an one-pot one-step reaction protocol. Control of the formation of EMF is quite challenging as it gets rehydrated to form ELevu in the presence of strong acid catalysts. The study has thus also simultaneously focused on ELevu formation, as it is also an important fuel additive.²¹ One-pot two step reactions were also performed with a series of combined solid acids, for example zeolites and Amberlyst-15, in order to enhance the catalytic performance towards EMF formation. For comparison, the reactivity of both catalytic systems were further studied with different carbohydrate substrates under optimised reaction conditions. Lastly, catalyst recycling experiments were performed in order to demonstrate the versatility of the catalytic system.

Results and Discussion

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Catalytic conversion of glucose to EMF with zeolites in one-pot, one-step process

Intrigued by the previous studies described above, we have examined whether commercial zeolites - which are industrially common materials - could be used as efficient heterogeneous catalyst for the direct transformation of glucose into EMF. Initially, a series of preliminary experiments were carried out to evaluate the catalytic activity of commercial zeolites as well as sulfonated solid acids for the conversion of fructose to EMF in ethanol at 96 °C (Table S1, ESI). The obtained EMF yields were between 8 and 18 % with the zeolite catalysts. In contrast, sulfonated solid acids gave much higher yields of EMF, suggesting the presence of strong Brønsted acid sites promoted the dehydration of fructose to HMF and etherification of HMF to EMF but also rehydration of HMF/EMF to ELevu. Among the catalyst employed, Amberlyst-15 was found to be the most efficient catalyst for conversion of fructose to EMF yielding 61 % product along with 13 % ELevu under optimised reaction conditions. On the other hand, SO₃H-SBA-15, a mesoporous functionalised material, gave a global yield of 71 % (50 % EMF and 21 % Elevu). It should be noted that the formation of ELevu was also observed with all the catalysts, and the yield was between 3 and 21 %.

When glucose was used as substrate the commercial zeolites gave lower than 10 % combined yields of HMF and EMF in ethanol at 96 and 110 °C after 11 and 6 h, respectively (Table S2 and Fig. S1, ESI). Similary, Amberlyst-15 proved to form predominantly ethyl glucopyranosides and not EMF under these reaction conditions. However, significant increased EMF yields were obtained with the zeolites at reaction temperature of 125 °C as shown by the compiled results in Table 1. The H-beta (12.5) and H-beta (19) catalysts gave here yields of 18-20 % of EMF (Table 1, entries 5 and 6). Modification of the H-beta catalysts by calcination at high temperature (i.e., 700-850 °C) was further performed to induce Published on 04 August 2015. Downloaded by University of Pittsburgh on 05/08/2015 02:13:11.

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thermal dealumination by partial cleavage of Si-O-Al bonds in the framework.¹⁷ The resulting thermally dealuminated catalysts, DeAl-H-beta (12.5)-700, DeAl-H-beta (19)-700, DeAl-H-beta (12.5)-800 and DeAl-H-beta (12.5)-850 (Table 1, entries 7-10), all had improved catalytic performance yielding 33-37 % EMF along with 4 % ELevu. In order to get insight on the acid sites of the parent and modified H-beta (12.5), the catalysts were subjected to NH₃-TPD

measurements (Fig. S2, ESI). In the NH₃-TPD profiles, a peak with T_{max} at 190 °C corresponding to a weak acid site was found to be more intense in the DeAl-H-beta (12.5)-700 catalyst compared to the unmodified H-beta (12.5) material, indicating that weak acid sites could be responsible for the isomerisation of glucose to fructose, as also observed in our previous studies.¹⁸

Table 1 Zeonte-catalyzed conversion of glucose in one-pot, one-step reaction.	Table 1	l Zeolite-catalyz	ed conversion	of glucose in	one-pot, or	ne-step reaction. ^a
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Entry	Catalyst ^b	Conversion (%)		Product	Bio-HEs Yield (%) ^c		
			HMF	EMF	ELevu	EMFda	
1	H-Y (2.6)	96	5	13	7	<1	25
2	H-USY (30)	84	5	1	2	0	8
3	H-USY (6)	92	5	10	16	<1	31
4	H-mordenite (10)	37	14	1	1	0	16
5	H-beta (19)	85	7	18	9	< 0.5	34
6	H-beta (12.5)	90	8	20	10	< 0.5	38
7	DeAl-H-beta (12.5)-700	87	13	37	4	<1	54
8	DeAl-H-beta (19)-700	84	11	36	4	<1	52
9	DeAl-H-beta (12.5)-800	84	15	33	4	<1	52
10	DeAl-H-beta (12.5)-850	86	11	34	4	<1	49
11	Sn-beta	88	5	29	1	< 0.5	35
12	B-H-beta (12.5)	87	11	16	1	<1	28

^a Reaction conditions: 0.15 g glucose, 100 mg catalyst, 5 mL ethanol, T = 125 °C, t = 6 h. ^b Si/Al ratio of the zeolites are denoted in parenthesis. ^c Bio-HEs denote HMF, EMF, ELevu and EMFda (5-ethoxymethylfurfural diethyl acetal).

A time-course study was further conducted with DeAl-H-beta (12.5)-700 to examine the reaction pathway leading to EMF (Fig. S3, ESI). The results showed that glucose was relatively fast converted (> 70 %), but only about 20 % EMF was generated after 2 h of reaction. After a reaction time of 10 h, the formation of HMF and EMF reached 20 and 40 %, respectively. At prolonged reaction time EMF started to get rehydrated to ELevu and converted to undesired products (humins), clearly indicating that careful optimisation of reaction conditions are important in order to obtain a high yield of EMF. In a supplementary experiment with 2-13C-glucose in ethanold⁶ (step 1: 110 °C, 1 h; step 2: 125 °C, 3 h), ¹³C NMR analysis of reaction samples after each step (Fig. S4, ESI) confirmed that the sugar-based intermediates fructose ($\delta/ppm = 104.6$, α-Dfructofuranose; 102.1. β-D-fructofuranose; β-D-98.8. fructopyranose), ethyl-D-glucopyranoside (EDGP) (δ /ppm = 74.8, ethyl-β-D-glucopyranoside; 72.5, ethyl-α-D-glucopyranoside) and ethyl-D-fructofuranoside (EDFF) (δ /ppm = 107.6, ethyl- α -Dfructofuranoside; 103.9, ethyl-\beta-D-fructofuranoside; 100.4, ethyl-\beta-D-fructopyranoside) accounted for the high conversion of glucose (unconverted glucose: $\delta/\text{ppm} = 73.6$, β -D-glucopyranose; 72.1, α -Dglucopyranose). Likewise, the analysis corroborated that EMF $(\delta/\text{ppm} = 151.9)$ was preferentially formed from glucose via the two step cascade reactions.

The other examined zeolites, including H-USY (30) and Hmordenite (10), were found to be less active than the dealuminated samples for the catalytic transformation. On the other hand, Sncontaining beta zeolite yielded 29 % of EMF (Table 1, entry 11) which was higher than the yield obtained with the H-beta zeolites, thus indicating that the presence of strong Lewis acid sites promoted the glucose isomerisation. Recently, boric acid modified zeolites with extra-framework B–OH species and retained silanols were demonstrated to be highly efficient for dehydration reactions.²² Nevertheless, such a prepared catalyst, B-H-beta (12.5), showed poor catalytic activity for formation of EMF in the present reaction compared to the modified beta zeolites (Table 1, entry 12), possibly because dehydration of the glucose was difficult.

Based on the obtained results, the possible reaction pathways for the catalytic conversion of glucose to HMF, EMF, EMFda and ELevu are compiled in Scheme 1. Initially, glucose was rapidly converted into fructose as well as EDFF (confirmed by ¹³C NMR, see above), which were further partially transformed into EDGP by Lewis and Brønsted acid sites present in the zeolite. Subsequently, the obtained EDFF could form EMF via dehydration with strong acid sites of the catalysts. At the same time, fructose could also be dehydrated to produce HMF, which would be further etherified to give EMF. At this stage, strong acid sites at moderate reaction temperature or weaker acid sites at high reaction temperature could promote to increase the yield of EMF. It should be noted that EDGP could hardly be further converted as shown by the obtained results with EDGP as substrate (Table 4), while mannose could isomerise to fructose and successively convert to EMF. It is well known that HMF can be transformed into ELevu and formic acid/ethyl formate (FA) in ethanol,²⁰ and a similar reaction route is expected for conversion of EMF into ELevu.

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Scheme 1. Suggested reaction pathways for the catalytic conversion of sugars to HMF, EMF, EMFda and ELevu.

Catalytic conversion of glucose to EMF with combined solid acids in one-pot, two-step process

As mentioned above, commercial zeolites as well as Amberlyst-15 gave poor yields of HMF and EMF from glucose in ethanol at 96 °C. The latter catalyst was, however, a highly efficient catalyst for the conversion of fructose to EMF (Table S2, ESI). Accordingly, a reaction approach from glucose to EMF using the two different types of catalyst in cascade was examined. When performing the reaction with an optimised mass ratio of H-USY (6) and Amberlyst-15 of 3:1 (Fig. S5, ESI) the yield of EMF was significantly increased (as anticipated) compared to using H-USY (6) alone (Table 2, entries 1 and 4), implying that H-USY (6) was responsible for the isomerisation of glucose to fructose and Amberlyst for the dehydration of fructose and ethyl fructosides (as discussed earlier, based on ¹³C NMR results) to enhance the yield of EMF. Adversely, the formation of ethyl glucosides (confirmed by ¹³C NMR) in large amount in the presence of Amberlyst-15, indicated that conversion of glucose to ethyl glucoside was facile and that EMF was partly converted to a rehydrated product ELevu (14 %) thus lowering the vield of EMF. It has previously been reported that the addition of dimethylsulfoxide (DMSO) into ethanol could efficiently improve the yields of the furanic products.6f,9b Therefore, an appropriate amount of DMSO and ethanol was also used as the reaction solvent for the conversion of glucose to EMF (Figs. S6 and S7A, ESI). Under optimal reaction conditions (131 °C, 24 h) a combined yield of HMF and EMF of 46 % could be achieved with this approach (Table 2, entry 5), however the DMSO lowered considerably the selectivity to EMF. The combined yield was increased slightly to 54 % at 114 °C, but the selectivity remained low (results not shown). Based on these results, we speculate that the generation of EDPG in high yield as well as ELevu, 5-ethoxymethylfurfural diethyl acetal (EMFda) and humins account for the high glucose conversion and lowering of EMF yields.

Table 2. Catalytic conversion of glucose with solid acids via different processes.^a

Entry	Catalyst ^b	Conversion (%)	Product Yield (%)			Bio-HEs Yield (%) ^c	
			HMF	EMF	ELevu	EMFda	
1	H-USY (6)	92	2	6	1	<1	9
2	Amberlyst-15	98	<1	< 0.1	1	0	2
3	Sn-beta	76	2	2	<1	< 0.5	5
4	H-USY (6) + Amberlyst-15	91	3	17	14	<1	34
5 ^d	H-USY (6) + Amberlyst-15	98	20	26	1	< 0.5	47
6 ^e	H-USY (6) + Amberlyst-15	87	3	46	3	<1	53
$7^{\rm f}$	H-USY (6) + Amberlyst-15	83	5	40	2	< 0.5	48
8 ^e	Sn-beta + Amberlyst-15	86	1	43	1	<1	46
$9^{\rm f}$	Sn-beta + Amberlyst-15	84	4	36	<1	< 0.5	41
$10^{\rm e}$	DeAl-H-beta (12.5)-700 + Amberlyst-15	85	3	44	2	<1	50
11 ^e	DeAl-H-beta (19)-700 + Amberlyst-15	88	3	40	2	<1	46

^a Reaction conditions: 0.15 g glucose, 100 mg catalyst, 5 mL ethanol, T = 96 °C, t = 11 h. ^b Si/Al ratio of the zeolites are denoted in parenthesis. ^c Bio-HEs denote HMF, EMF, ELevu and EMFda. dT = 131 °C, t = 24 h, 5 mL DMSO/ethanol (3:7). One-pot, two-step process with successive addition of 75 mg zeolite for 5 h followed by 25 mg Amberlyst-15 for 6 h. f One-pot, two-step process where the zeolite was removed after 5 h followed by addition of Amberlyst-15 for 6 h.

In order to enhance the yield of EMF and to supress the protocol was developed with successive addition of H-USY (6) formation of EDGP, an optimised one-pot, two-step reaction and Amberlyst-15 catalysts for 5 and 6 h of reaction,

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respectively (Table S3, Figs. S8 and S9, ESI). Interstingly, a substantial improvement in the yield of EMF (46 %) with a relatively high selectivity of 53 % was achieved with glucose in ethanol with the two-step reaction protocol (Table 2, entry 6). For comparison, Sn-beta - a well-known catalyst for isomerisation and epimerization of glucose into fructose and mannose, respectively 23 - was also applied in the two-step reaction. Here a comparable yield of EMF (43 %) was observed (Table 2, entry 8), suggesting that similar intermediates might have formed as found with H-USY (6). To elucidate the role of H-USY (6) and Sn-beta in the second reaction step, the zeolites were separated from the reaction mixture before adding Amberlyst-15 for the subsequent reaction step (Table 2, entries 7 and 9). In these experiments, the yields of EMF decreased slightly whereas the yields of HMF increased slightly, thus demonstrating the ability of the zeolites to induce isomerisation as well as etherification also after the addition of Amberlyst-15.

Dealuminated H-beta (12.5) and H-beta (19) used in combination with Amberlyst-15 also exhibited good catalytic performance in the one-pot, two-step approach (Table 2, entries 10 and 11), clearly indicating the important role of the Lewis/weak acid sites generated by the dealumination for the glucose isomerisation in the first reaction step. To enhance the yield of EMF in the second reaction step, alternative Brønsted acid-containing catalysts were also explored instead of Amberlyst-15 in combination with H-USY (6) (Table 3). The four employed alternative sulfonic acid-based catalysts gave global yields of 31-42 % EMF and 2-4 % of ELevu (Table 3, entries 1-4), which were slightly lower than obtained with Amberlyst-15 (Table 2, entry 6). Moreover, sulphated zirconia only gave 10 % of EMF under the applied reaction conditions (Table 3, entry 4).

Table 3. Catalytic conversion of glucose with alternative Brønsted acid catalysts in one-pot, two step reaction.^a

Entry	Catalyst	Conversion (%)	Product Yield (%)			Bio-HEs Yield (%) ^b	
			HMF	EMF	ELevu	EMFda	
1	H-USY (6) + SBA-15-SO ₃ H	88	4	39	3	<1	47
2	H-USY (6) + Dowex 50WX8-100	92	4	42	4	<1	51
3	H-USY (6) + Nafion NR50	92	5	31	3	<1	40
4	H-USY(6) + Amberlyst 70	85	7	33	2	1	43
5	H-USY (6) + $SO_4(3.9 \text{ wt\%})$ -Zr O_2	54	2	10	1	<1	14

^a Reaction conditions: 0.15 g glucose, 100 mg catalyst, 5 mL ethanol, T = 96 °C, t = 11 h. One-pot, two-step process with successive addition of 75 mg zeolite for 5 h followed by 25 mg Brønsted acid catalyst for 6 h. ^b Bio-HEs denote HMF, EMF, ELevu and EMFda.

Catalytic conversion of carbohydrates to EMF with two different catalytic processes

The developed reaction approaches to form EMF were extended to include other carbohydrate substrates than glucose with selected catalysts. The results are compiled in Table 4. A relatively high total yield of EMF (67 %) and ELevu (4 %) was obtained with fructose using H-USY (6) in combination with Amberlyst-15 while lower total yield of EMF (55 %) and ELevu (7 %) was found using DeAl-H-beta (12.5)-700 (Table 4, entries 2 and 11), thus indicating the former catalyst combination to be advantageous for the dehydration of fructose/ethyl fructoside. In contrast, the two catalyst combinations yielded more comparable global yields (EMF and ELevu) from mannose (36 and 44 %) and glucose (45 and 49 %) (Table 4, entries 1, 3, 10 and 12), suggesting the reactivity towards formation of fructofuranose intermediates and HMF to be similar in line with ealier observations.²⁴ Noteworthy, relatively high yields between 43-58 % of EMF along with 4-13 % of ELevu could be obtained from sucrose and inulin over both catalytic systems (Table 4, entries 4-5 and 13-14), as a result of the higher reactivity of the fructose units of these sugars. On the other hand, only trace amounts of EMF was obtained from cellobiose systems (Table 4, entries 6 and 15) due to low substrate solubility in ethanol and less reactivity

towards hydrolysis to glucose under the applied reaction conditions.

In order to evaluate the stability of HMF, when formed as an intermediate, and the reactivity of EMF as a final product the two compounds were further used as substrates. Under the optimized reaction conditions, the stability of EMF in ethanol over DeAl-H-beta (12.5)-700 at 125 °C in the one-pot process was demonstrated to be higher than when using H-USY (6) + Amberlyst-15 at 96 °C in the two-step reaction process (Table 4, entries 7 and 16). This suggests that EMF was in part rehydrated to form ELevu (20 %) in the presence of the strong acid catalyst Amberlyst-15. When using HMF as substrate comparable yields of EMF were formed with the two catalytic systems (Table 4, entries 8 and 17), demonstrating that the etherification of HMF were facile with both zeolite catalysts.

Table 4.	Catalytic	conversion of	f carbohydrates	s via two	different	processes.
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Entry	Catalyst	Substrate		Prod	Bio-HEs Yield (%) ^c			
			Glucose	HMF	EMF	ELevu	EMFda	
1^{a}	H-USY (6) + Amberlyst-15	Glucose	13	3	46	3	<1	53
2 ^a	H-USY (6) + Amberlyst-15	Fructose	0	10	67	4	<0.5	81
3 ^a	H-USY (6) + Amberlyst-15	Mannose	0	1	40	4	0	45
4 ^a	H-USY (6) + Amberlyst-15	Sucrose	13	6	50	13	<0.5	69
5 ^a	H-USY (6) + Amberlyst-15	Inulin	2	6	58	7	<0.5	71
6 ^a	H-USY (6) + Amberlyst-15	Cellobiose	< 0.5	3	<0.1	2	0	5
7^{a}	H-USY (6) + Amberlyst-15	EMF	0	11	48	20	2	81
8^{a}	H-USY (6) + Amberlyst-15	HMF	0	14	70	5	<1	90
9 ^a	H-USY (6) + Amberlyst-15	EDGP	3	5	2	3	<1	11
10^{b}	DeAl-H-beta (12.5)-700	Glucose	6	11	41	4	1	57
11 ^b	DeAl-H-beta (12.5)-700	Fructose	1	6	55	7	<0.5	68
12 ^b	DeAl-H-beta (12.5)-700	Mannose	1	16	35	<0.5	<0.5	51
13 ^b	DeAl-H-beta (12.5)-700	Sucrose	4	5	43	4	1	53
14 ^b	DeAl-H-beta (12.5)-700	Inulin	2	3	52	5	1	61
15 ^b	DeAl-H-beta (12.5)-700	Cellobiose	< 0.1	5	1	<0.5	<0.5	6
16 ^b	DeAl-H-beta (12.5)-700	EMF	0	7	66	10	2	85
17 ^b	DeAl-H-beta (12.5)-700	HMF	0	13	63	8	3	87

^a Reaction conditions: 0.15 g glucose, 100 mg catalyst, 5 mL ethanol. ^a One-pot, two-step process with successive addition of 75 mg zeolite for 5 h followed by 25 mg Amberlyst-15 at 6 h at temperature of 96 °C. ^b One-pot, one-step process. T = 125 °C, t = 10 h. ^c Bio-HEs denote HMF, EMF, ELevu and EFMda.

Influence of glucose concentration and catalyst amount on the catalytic conversion of glucose to EMF

DeAl-H-beta (12.5)-700 exhibited a slightly lower catalytic performance for the production of EMF from glucose compared to the combined catalyst approach, but the catalyst was easily operated and separated from the reaction mixture at the end of the reaction. Accodingly, the influence of glucose concentration and catalyst amount on reactivity was studied using this catalyst (Table 4). When increasing the glucose amount from 0.15 g (3.7 wt%) to 0.30 g (7.1 wt%) an unchanged EMF yield was observed (40 %), showing that the catalyst remained active also at higher concentration of glucose (Table 5, entries 1 and 2). Also when the amount of glucose was increased further to 0.50 g (11.3 wt%; Table 5, entry 3) a significant amount of EMF (31 %) was formed, despite the solubility limit of glucose in ethanol was surpassed (making it impossible to report a conversion). As to catalyst dosage, it was found that the yield of EMF decreased only slightly from 40 to 38 % when the catalyst loading was reduced from 100 to 75 mg (Table 5, entries 2 and 4), but more drastically to 30 and 24 % EMF at catalyst loadings of 50 and 25 mg, respectively, as expected (Table 5, entries 5 and 6). Consequently, 0.30 g glucose in 5 mL of ethanol (7.1 wt%) and 75 mg DeAl-H-beta (12.5)-700 was used as the optimized reaction conditions to evaluate catalyst recyclability.

Catalyst recycling in the catalytic conversion of glucose to EMF

The DeAl-H-beta (12.5)-700 catalyst was evaluated for the transformation of glucose to EMF (and HMF) in ethanol in five consecutive reaction cycles under optimized reaction conditions (Fig.

1). After each reaction run, the catalyst was regenerated by calcination at 550 °C for 6 h to ensure that deposited carbonaceous products was removed. Through all five consecutive catalytic runs, the EMF yield remained between 28-38 % along with a HMF yield of 10-12 %. This demonstrated that the catalytic performance of the DeAl-H-beta (12.5)-700 catalyst was preserved in the consecutive cycles, suggesting that the catalyst system is highly suitable for reuse.



Fig. 1 Recycling of DeAl-H-beta (12.5)-700 in the catalytic conversion of glucose to EMF. Reaction conditions: 1.20 g glucose, 300 mg DeAl-H-beta (12.5)-700, 20 mL ethanol, T = 125 °C, t = 10 h. Glucose and solvent were adjusted to the amount of recovered DeAl-H-beta (12.5)-700 in reaction runs number two-five.

Journal Name

Entry	Catalyst amount	Glucose amount	Conversion	Product Yield (%)			Bio-HEs Yield (%) ^b	
	(mg)	(g)	(%)	HMF	EMF	ELevu	EMFda	
1	100	0.15	94	11	41	4	1	57
2	100	0.30	95	11	40	5	2	58
3	100	0.50 ^c	-	3	31	9	2	45
4	75	0.30	92	13	38	2	1	54
5	50	0.30	89	11	30	1	< 0.5	43
6	25	0.30	69	8	24	0.3	< 0.5	32

^a Reaction conditions: 5 mL ethanol, T = 125 °C, t = 10 h. ^b Bio-HEs denote HMF, EMF, ELevu and EFMda. ^c Glucose amount above the solubility limit.

Conclusions

In summary, we have demonstrated that a combination of the solid catalysts H-USY (6) and Amberlyst-15 can directly and efficiently transform biomass-derived carbohydrates such as, e.g. glucose, sucrose and inulin, to the biofuel EMF in high yields (40-60%) along with 3-13% of ELevu in ethanol via an one-pot, two-step reaction process. On the other hand, dealuminated beta zeolites, including DeAl-H-beta (12.5)-700 and DeAl-H-beta (19)-700, can give comparable yields of EMF (~40%) through a single step process. Moreover, a high yield of EMF (67 %) and ELevu (4 %), a global yield of 71 %, was obtained from fructose with a combined catalytic system. The proposed reaction pathway showed that fructose and EDFF formed from glucose, and both compounds were important intermediates for obtaining enhanced yields of EMF with zeolite-based catalytic systems. Importantly, the dealuminated beta zeolites seemed to maintain their structural integrity in ethanol, allowing the catalysts to be reused for at least five consecutive reaction cycles.

Experimental Section

Chemicals and materials

5-hydroxymethylfurfural (99 %), 5-ethoxymethylfurfural (97 %), ethyl levulinate (99 %), glucose (99.5 %), fructose (99 %), mannose (99 %), sucrose (99.5 %), inulin (from dahlia tubers), cellobiose (98 %), ethanol (99.9 %) and dimethyl sulfoxide (99.9 %, DMSO) were purchased from Sigma-Aldrich and used as received.

All commercially available zeolites used in the study were provided by Zeolyst International as pure compounds in NH_4 -form without content of binder materials. The received zeolites were calcined at 550 °C in static air for 6 h with a heating ramp of 1.2 °C/min prior to use in order to produce the acidic forms (H-forms). The thermally dealuminated zeolites were prepared by further calcining at 700-850 °C in air for another 6 h. Boron modified zeolites with boron oxide content of 4 wt%²³ and Snbeta were synthesized according to literature procedures.²⁶

NH₃-TPD measurement

The number of acid sites present in the zeolites was measured by NH_3 -TPD using an AutoChem II 2920 pore analyzer. 100

mg of the sample was placed in a quartz reactor and degassed at 600 °C for 1 h in a flow of helium of 50 mL/min. The reactor was then cooled to 100 °C and ammonia (50 mL/min) was allowed to get adsorbed at the same temperature for 2 h. The sample was then flushed with helium at a flow of 50 mL/min to remove physisorbed ammonia, before ammonia desorption was measured every one second from 100 to 600 °C with a heating ramp of 10 °C/min.

Reaction procedure

Catalytic batch experiments were all performed in Ace pressure tubes. In the one-pot, two-step reaction process zeolite catalyst (75 mg), sugar (150 mg) and ethanol or DMSO/ethanol (3:7 v/v) (5 mL) were first added and mixed in the pressure tube using a magnetic stirrer bar. The tube was then heated in a thermally controlled oil bath to a desired reaction temperature. The internal reaction temperature was measured and found to be 96, 110 and 125 °C (±1 °C) in ethanol and 96, 114 and 131 °C (±1 °C) in DMSO/ethanol mixture with external oil bath temperatures of 100, 120 and 140 °C, respectively. After a specific reaction time, the tube was removed from the oil bath and rapidly cooled down to room-temperature and the catalyst filtered off. In the second reaction step, Amberlyst-15 (25 mg) was added to the reaction mixture from the first step, where after the tube was re-immersed into the oil bath under the designed reaction conditions. Finally the tube was cooled down to room-temperature and the reaction mixture analysed after removal of the catalyst. In the one-pot, one-step conversion of glucose to EMF the tube was charged with catalyst (100 mg), sugar (150 mg) and ethanol (5 mL) and stirred under heating in a thermally controlled oil bath set at a desired reaction temperature (80-140 °C). After a specific reaction time the reaction mixture was quenched with cold water and analysed after removal of the catalyst.

Reactant and product analysis

5-Hydroxymethylfurfural (HMF), 5-ethoxymethylfurfural (EMF), ethyl levulinate (ELevu), 5-ethoxymethylfurfural diethyl acetal (EMFda), formaldehyde diethyl acetal (FAda), formic acid (FA), diethyl ether and the ethylated form of intermediates, e.g. ethyl-D-glucopyranoside (EDGP) and ethyl-D-fructofuranoside (EDFF), were identified by authentic samples, ¹³C NMR and GC-MS (Agilent 6850 GC system

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coupled with an Agilent 5975C mass detector). Sugar conversions and the yields of HMF, EMF and acetals were determined by HPLC (Agilent 1200 series, Aminex© HPX-87H 30 cm column, column temperature of 65 °C, 0.005 M aqueous sulfuric acid solution as eluent at a flow rate of 0.6 ml/min). HPLC standards were made from commercial samples. The conversions of sucrose and inulin were calculated from fructose, glucose and mannose on a carbon-basis since they invert to the monosaccharides on the acidic HPLCcolumn. Likewise, the yields of HMF, EMF and acetals were calculated assuming each monosaccharide to give equimolar of product. The yields of ELevu were quantified by GC-FID analysis (Agilent 6890N instrument, HP-5 capillary column $30.0 \text{ m} \times 320 \text{ }\mu\text{m} \times 0.25 \text{ }\mu\text{m}$) using a series of ELevu standards by assuming one mole of monosaccharide to give equimolar amount of ELevu. Notably, the yields of unidentified intermediates observed by HPLC were calculated using glucose as standard.

Recycling study

An Ace pressure tube was charged with glucose (1200 mg), methanol or ethanol (20 mL) and DeAl-H-beta (12.5)-700 catalyst (300 mg). The tube was heated to 140 °C and the stirring started once the temperature reached 130 °C (600 rpm). After 10 h of stirring, the tube was quenched with cold water and aliquots of the reaction mixture was subjected to GC and HPLC analysis. The catalyst was regenerated after each cycle by calcination at 550 °C for 6 h to remove any deposited humins. After the first to fifth run, the mass of the glucose and solvent were scaled down with respect to the amount of recovered DeAl-H-beta (12.5)-700.

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Biomass-based mono-, di- and polysaccharides are in ethanol directly converted to the biofuel 5ethoxymethylfurfural (EMF) in 37-67 % yield at 100-140 °C by solid acid zeolite catalysts or by combined zeolite-Amberlyst catalyst system using an one-pot, two-step reaction protocol.