



One-pot tandem conversion of fructose into biofuel components with in-situ generated catalyst system

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ABSTRACT

In this contribution, one-pot tandem conversion of fructose into biofuel components, including 5-ethoxymethylfurfural (EMF), 2,5-bis(ethoxymethyl)furan (BEMF) and ethyl levulinate (EL), was performed in an in-situ generated catalyst system through consecutive dehydration, etherification, and transfer hydrogenation. Specifically, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was in-situ decomposed into HCl and $\text{ZrO}(\text{OH})_2$ in ethanol, which effectively catalyzed the dehydration/etherification of fructose to 5-ethoxymethylfurfural (EMF) and subsequent reductive etherification of EMF using ethanol as H-donor, respectively. EMF, BEMF and EL were detected as the main products, and total yield of detectable products of up to 65.4% was obtained at 200 °C in only 2 h.

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1. Introduction

Recently, the production of fuel additives from biomass-derived carbohydrates is of increasing interest, which include 5-ethoxymethylfurfural (EMF) [1–5], alkyl levulinates [6–10], alkyl valerates [11,12], and ethanol [13]. Ethanol is widely used as gasoline additive in Brazil and in the United States, which is produced by the fermentation of sugars [13]. Theoretically, two molecules of ethanol can be produced from one glucose molecule with the release of two molecules of CO_2 [13]. Thus, it is undesirable to ferment sugars into ethanol from the perspective of atom economy. In this sense, the formation of furan-like additives from carbohydrates would be a better alternative, because all carbon atoms in carbohydrates can be retained in the furan products, such as EMF.

EMF is generally formed by the etherification of 5-hydroxymethylfurfural (HMF) with ethanol and is currently regarded as a promising biofuel component [14]. EMF has an energy density of 30.3 MJ L^{-1} , which is similar to that of gasoline

(31.1 MJ L^{-1}) and diesel (33.6 MJ L^{-1}), and substantially higher than ethanol (23.5 MJ L^{-1}) [15]. Moreover, commercial diesel blended with EMF could result in significant reduction of soot in exhaust [16]. Many solid acid catalysts, such as sulfonated graphene oxide and $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{MCM-41}$ [17,18], were active for the etherification of HMF to EMF in ethanol. Recently, Zhang and co-workers prepared numerous solid acid catalysts, including MCM-41 supported tungstophosphoric acid [19], silica supported sulfonic acid [20], and AlCl_3 [21], for the direct conversion of fructose to EMF in ethanol, offering EMF yields ranging from 40%–70% at 100–140 °C. Furthermore, mixed solvent systems containing ethanol and dimethylsulfoxide (DMSO) or tetrahydrofuran (THF) were also reported to give comparable EMF yields [22,23].

Notably, EMF showed relatively inferior miscibility with commercial diesel, and phase separation was observed when diesel blended with EMF at a blend rate of 25 or 40 vol% [24]. In contrast, 2,5-bis(alkoxymethyl)furans (BAMFs), which are formed by sequential reduction and etherification of HMF with alcohols and had much higher cetane number than that of commercial diesel, were completely miscible with commercial diesel at blend rates below 40 vol% [25–27]. Several studies so far focused on the reductive etherification of HMF into BAMFs. For example, Mu and co-workers reported that 2,5-bis-methoxymethylfuran (BMMF) yield of up to 68% could be obtained from HMF by sequential

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hydrogenation and etherification in the presence of Cu/SiO₂ and HZSM-5 under 2.5 MPa H₂ at 120 °C for 12 h [26]. Later, Sn-Beta and Zr-Beta were prepared and acted as efficient dual-functional catalysts for the transfer hydrogenation and subsequent etherification of HMF to BAMFs in alcohols, with BAMF yields of up to 80% being archived at 120–180 °C [28,29]. In these cases, alcohols are employed as both H-donor and reaction medium in transfer hydrogenation process by Meerwein–Ponndorf–Verley (MPV) reduction [30], and no molecular H₂ is needed.

However, it is a big challenge to produce BAMFs directly from carbohydrates, due to the instability of active intermediate HMF especially in the presence of acid catalysts. Recently, Bell and co-workers proposed a one-pot two-step process for the conversion of fructose to BEMF (yield 51%) in ethanol, in which fructose was firstly dehydrated to HMF catalyzed by Amberlyst-15 at 110 °C for 30 h and the reductive etherification of HMF then proceeded at 60 °C for 18 h over Pt₁Sn₁/Al₂O₃ [31]. Apparently, the above catalytic systems for BAMFs production from carbohydrates or HMF suffer from low efficiency or the use of noble metals and molecular H₂.

In this contribution, we presented an in-situ generated catalyst system for the production of biofuel components by one-pot tandem conversion of fructose in ethanol. To be specific, ZrOCl₂·8H₂O was in-situ decomposed into HCl and Zr(OH)₂ in ethanol, which catalyzed the dehydration/etherification of fructose to EMF and subsequent reductive etherification of EMF using ethanol as H-donor, respectively. Biofuel components including EMF, BEMF and ethyl levulinate (EL) were detected as the main products, and total yield of detectable products of up to 65.4% was obtained at 200 °C in 2 h. This in-situ generated catalyst system is simple and efficient for the production of biofuel components from fructose, without the usage of precious metal catalysts and molecular H₂.

2. Experimental

2.1. Materials

HMF (98%) was purchased from Shanghai Energy Chemical Indus-trial Co. Ltd (Shanghai, China). Fructose (99%), glucose (99%), EL (98%), ZrOCl₂·8H₂O (99%), *n*-dodecane (98%) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). EMF (98%) and 5-methyl furfural (MF, 98%) were purchased from Sigma–Aldrich. BEMF was synthesized and purified according to the methods described by Balakrishnan et al. [31]. Other reagents and chemicals were all of analytical grade from Sino-pharm Chemical Reagent Company Co. Ltd (Shanghai, China) and used without further purification.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained on a Panalytical X'pert Pro diffractometer using a Cu K_α radiation source with the following parameters: 40 kV, 30 mA, 2θ from 20° to 90° at a scanning speed of 7 °/min. Fourier transform infrared spectroscopy (FT-IR) spectrums were recorded on a Nicolet 380 spectrometer. The morphology of the recovered catalyst powder was observed by scanning electron microscopy (SEM) (Hitachi S-4800), equipped with an energy dispersive X-ray spectroscopy (EDS) that was served to analyze the element content (Zr/O/Cl) of the recovered catalyst solid. The content of each element was calculated by the average value of at least five times scanning on the different areas of the catalyst. Thermal gravimetric analysis (TGA) was carried out on a Netzsch STA 449 thermal analyzer under a dynamic N₂ atmosphere (100 mL min^{−1}) at the temperature range of 20–900 °C with a heating rate of 20 °C min^{−1}. The surface area of the recovered catalysts was calculated by N₂

adsorption–desorption isotherms using a Micromeritics ASAP 2020 HD88 with the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. Specifically, the samples were degassed at 90 °C for 4 h in vacuum before N₂ adsorption. Elemental analysis (C deposit) was performed by an Elementar Vario EL III (Elementar Analysensysteme GmbH, Germany); each sample was measured twice to determine the content of C.

2.3. Typical procedure for the conversion of fructose in in-situ generated catalyst system

All experiments were carried out in a 400 mL Hastelloy-C high pressure reactor (Dalian-controlled Plant, Dalian, China). The reactor was heated in an adjustable electric stove. The temperature of the reactor contents was monitored by a thermocouple connected to the reactor. In a typical run, substrate (fructose, 2 g), solvent (ethanol, 98 g) and catalyst salt precursor (ZrOCl₂·8H₂O, 5 mol%, relative to substrate) were charged into the reactor, which was sealed, purged three times with N₂ and then heated to the prescribed temperature for a desired reaction time with stirring at 500 rpm. After reaction, the reactor was cooled to room temperature. Upon opening the reactor, the solid catalysts (white powder) were recovered by filtration in vacuum and dried in a vacuum oven at 60 °C for 4 h.

2.4. Analytical methods

The liquid products were centrifuged at 8000 rpm for 5 min and then quantitatively analyzed using an Agilent 7890 series GC equipped with a DB-WAXETR column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector (FID) operating at 270 °C. The carrier gas was N₂ with a flow rate of 1.0 mL min^{−1}. The following temperature program was employed in the analysis: 40 °C (4 min)–5 °C min^{−1}–100 °C–10 °C min^{−1}–260 °C (2 min). HMF conversion and other product yields were determined based on an internal standard method using *n*-dodecane as internal standard, and the standard curves for different products were given in the Supplementary Material (Fig. S2). Because 5-(ethoxymethyl)-furfural diethyl acetal (EMFDEA), 5-(ethoxymethyl)furfuryl alcohol (EMFA), and 2-(ethoxymethyl)-5-methyl furan (EMMF) are not commercially available, the FID sensitivities of these compounds are assumed to be equal to that for BEMF due to their similar chemical structure. The MS spectra of these compounds were also provided in the Supplementary Material (Fig. S3). The yields (%) of products (X = EMF, BEMF, EL ...) were calculated by the following equations:

$$Y_X(\%) = \frac{\text{Mole of X in the products}}{\text{Initial mole of substrate}} \times 100\%$$

The qualitative analysis of the products was determined on a GC–MS (Thermo Trace 1300 and ISQ LT). The following programmed-temperature was employed in the analysis: 40 °C (2 min)–10 °C min^{−1}–280 °C (2 min). The carrier gas was He with a flow rate of 1.2 mL min^{−1} and the split ratio was 1:50. The mass spectra were obtained by electron impact ionization (EI), at electron energy of 70 eV and with a 25 μA emission current.

Quantitative analysis of fructose was performed by HPLC method on an Waters 2695 Separation Module equipped with a refractive index detector and a Bio-Rad Aminex HPX-87H ion exclusion column (300 mm × 7.8 mm). The column oven temperature was 60 °C and the mobile phase was 0.005 M H₂SO₄ aqueous solution at a flow rate of 0.6 mL min^{−1}. External standard method was used for quantitative analysis. The liquid products were centrifuged at 8000 rpm for 5 min and then 0.2 g of the reaction mixture was diluted with 3.8 g of deionized water. Before the HPLC test, liquid samples were syringe-filtered (0.22 μm PES membrane). The conversion of fructose or glucose was calculated based on an external

Table 1. The effects of various reaction conditions on the conversion of fructose in situ-generated system.

Entry	ZrOCl ₂ (mol%)	T (°C)	t (h)	Yield (%)							
				EMF	EMFDEA	EMFA	BEMF	MF	EMMF	EL	Total
1	5	160	4	19.3	17.2	3.7	13.6	ND	ND	8.0	61.2
2	5	200	2	7.9	4.0	7.4	27.9	5.9	4.7	7.6	65.4
3	5	240	2	ND	ND	ND	27.1	2.3	15.7	7.8	52.9
4	5	200	6	ND	ND	ND	21.0	4.1	14.4	8.9	48.4
5	10	200	2	1.1	ND	ND	29.1	3.6	15.1	10.6	59.5
6 ^a	5	200	2	15.6	2.9	2.5	15.0	4.0	3.8	10.4	54.4
7 ^b	5	200	2	–	8.4	10.0	38.7	4.8	8.4	2.5	72.8
8 ^c	20	200	2	1.0	3.2	8.8	–	ND	5.0	ND	18.0

Reaction conditions: fructose 2 g, ethanol 98 g, ZrOCl₂·8H₂O (relative to the mole of substrate).

ND: not detected.

^a HMF is the substrate.

^b Reaction conditions: EMF 0.2 g, ethanol 9.8 g, 5 mol% ZrOCl₂·8H₂O (relative to the mole of substrate). The conversion of EMF is 87.4%.

^c Reaction conditions: BEMF 0.05 g, ethanol 9.95 g, 20 mol% ZrOCl₂·8H₂O (relative to the mole of substrate). The conversion of BEMF is 20.4%.

standard method and the standard curves were given in the Supplementary Material (Fig. S4). In all experiments, fructose and glucose were found to be completely converted after reaction.

2.5. Products separation

Preliminary separation/purification of the products was performed in this study. After reaction, the solid catalyst was separated from the reaction mixture by centrifugation. The resulting HCl in the liquid product was first neutralized by the addition of CaO and then a crude product mixture containing EMF, BEMF and EL was obtained after removal of ethanol by evaporation under vacuum. The individual component in the crude product was purified by column chromatography on silica gel using ethyl acetate and petroleum (1:6) as eluent. BEMF (a yellow liquid) could be isolated from the crude product by column chromatography; however, it is difficult to separate EMF from EL, resulting in a mixture of EMF and EL. Identification of the products was performed by GC–MS and the qualitative analysis of BEMF was also conducted by ¹H/¹³C NMR (Figs. S3–S5).

3. Results and discussion

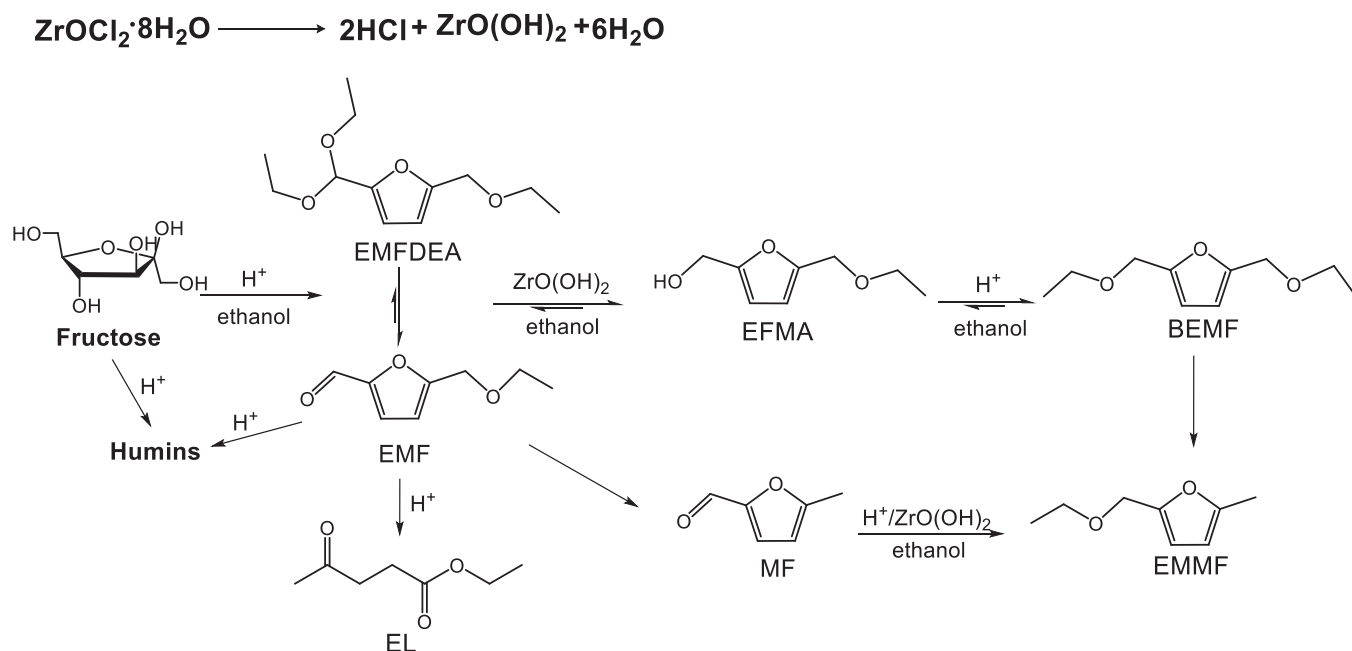
ZrOCl₂ can be used as Lewis acid catalysts for the conversion of fructose into HMF or EMF in ethanol at reaction temperatures around 100 °C. For example, Saha and co-workers reported that ZrOCl₂ could effectively catalyze the dehydration of carbohydrates to HMF and subsequent etherification of HMF to EMF in ethanol at 120 °C [32]. However, no products coming from transfer hydrogenation of HMF or EMF were detected in these cases, suggesting that ZrOCl₂ did not possess the catalytic activity for the transfer hydrogenation of HMF or EMF at relatively moderate temperatures. Metal chlorides such as ZrOCl₂·8H₂O could be stable at relatively low temperatures. However, we found that ZrOCl₂·8H₂O could decompose into HCl and ZrO(OH)₂ in ethanol at relatively high temperatures, which could be active for acid-catalyzed dehydration and transfer hydrogenation, respectively [33]. Therefore, we proposed a promising one-pot process in this study for the conversion of fructose into biofuel components (such as EMF, BEMF, and EL) by in-situ generated catalyst system.

As shown in Table 1, BEMF yield of 27.9% as well as EMF (7.9%) and EL (7.6%) was obtained from fructose in the presence of ZrOCl₂·8H₂O at 200 °C in 2 h (Table 1, entry 2). Prior to our study, only a one-pot two-step process was reported for the direct conversion of fructose to BEMF, in which a quite prolonged reaction time (48 h) as well as acidic resin and noble metal catalysts was required to offer a BEMF yield of 51% [31]. In comparison, in-situ

generated catalyst system from metal chlorides is more effective for the BEMF production from fructose, although a relatively low BEMF selectivity was achieved in this work. It is should be pointed out that other products (such as EMF and EL) in this study are also appealing biofuel additives, which could make up for the relatively low BEMF selectivity.

As shown in Scheme 1, a plausible reaction pathway of the conversion of fructose into EMF, EL, and BEMF was depicted based on the detected compounds in the product. Specifically, fructose is first subjected to dehydration followed by etherification to give EMF catalyzed by in-situ generated HCl in ethanol. The resulting EMF then converts to 5-(ethoxymethyl)furfuryl alcohol (EMFA) by MPV reduction over ZrO(OH)₂ in-situ generated using ethanol as the in-situ H-donor. Finally, BEMF forms by the etherification of EMFA with ethanol in the presence of HCl. EMF can also be converted to EL by acid-catalyzed ethanolysis in ethanol. Notably, ethanol is applied as the solvent, reactant and H-donor at the same time in this study. Dehydrogenation of ethanol gives acetaldehyde during the MPV reduction. However, neither HMF nor 2,5-bishydroxymethyl furan (BHMF), which could be formed by the transfer hydrogenation of HMF over metal hydroxides [30], were detected in the liquid product in this study. When HMF instead of fructose was used as the substrate, EMF yield of 15.6% and BEMF yield of 15.0% were offered with a completed conversion of HMF under the same reaction conditions (Table 1, entry 6). The above observation indicates that HMF was rapidly consumed by transfer hydrogenation, etherification, and other side-reactions at the given reaction conditions. Consequently, EMF rather than HMF was the intermediate for the conversion of fructose to BEMF in this study.

Several by-products, including 5-(ethoxymethyl)-furfural diethyl acetal (EMFDEA), 5-(ethoxymethyl)furfuryl alcohol (EMFA), MF and 2-(ethoxymethyl)-5-methyl furan (EMMF) were also detected in the liquid product. As shown in Scheme 1, EMFDEA is formed by the acetalization of EMF with ethanol. The resulting EMF also can be easily converted to EL by ethanolysis in the presence of acid catalyst [6]. Intermediate EMFA comes from the transfer hydrogenation of EMF over ZrO(OH)₂ and can further convert to BEMF by acid-catalyzed etherification with ethanol. MF or EMMF likely was formed by the degradation of EMF or BEMF at severe reaction conditions. When EMF was employed as the substrate in the presence of ZrOCl₂·8H₂O at 200 °C in 2 h, BEMF yield of 38.7% was obtained (entry 7, Table 1). MF (4.8%), EMMF (8.4%), and EL (2.5%) were also detected in this case. In contrast, EMMF (5.0%) was detected without MF and EL in the case of BEMF as the substrate at the identical reaction conditions (entry 8, Table 1). These observations reveal that EMMF could form starting from both EMF and BEMF, whereas MF could only derive from EMF under the reaction conditions ap-



Scheme 1. A plausible reaction pathway of the conversion of fructose into EMF, EL, and BEMF in in-situ generated catalyst system.

Table 2. Blank experiments and reusability of the catalyst.

Entry	Catalyst loading (mol%)	Yield (%)					
		EMF	EMFDEA	EMFA	BEMF	EL	Total
1	HCl (10)	29.8	12.9	ND	ND	5.3	80.5 ^a
2	ZrO(OH) ₂ (5)	ND	ND	ND	ND	ND	5.0 ^b
3	HCl (10) + ZrO(OH) ₂ (5)	28.1	6.2	2.0	4.1	4.6	79.3 ^c
4	HCl (10) + Recovered ZrO(OH) ₂ (5)	13.7	0.8	16.4	18.9	8.7	72.4 ^d
5	Recovered ZrO(OH) ₂ (5)	ND	ND	39.3	24.3	1.1	67.1 ^e
6	Recovered ZrO(OH) ₂ (5)	ND	ND	ND	ND	ND	4.9 ^f

Reaction conditions: fructose 2 g, ethanol 98 g, catalyst loading (relative to the mole of substrate), 200 °C, 2 h.

ND: not detected.

^a HMF yield of 32.5% was obtained.

^b HMF yield of 5.0% was obtained.

^c HMF yield of 32.0% and MF yield of 2.3% were obtained.

^d HMF yield of 5.3%, EMMF yield of 2.2% and MF yield of 6.4% were obtained and the catalyst was recovered from the experiment of entry 2 in Table 1.

^e HMF was used as the substrate, the catalyst was recovered from the experiment of entry 2 in Table 1, and EMMF yield of 2.4% was obtained.

^f The catalyst was recovered from the experiment of entry 2 in Table 1, and HMF yield of 4.9% was obtained.

plied in this study (as shown in Scheme 1). However, the detailed mechanism for the formation of MF and EMMF is not yet clear. Notably, small amounts of EMF, EMFDEA, and EMFA were also obtained in the case of BEMF as the substrate (entry 8, Table 1), which suggests that the MPV reduction of EMF and subsequent etherification are partially reversible, but the equilibrium is beneficial to the formation of BEMF. Besides these detectable compounds in the liquid products, humins are the main by-products that have relatively high molecular weight and thus cannot be detected by GC or GC–MS. Humins are the inevitable by-products during the acid-catalyzed degradation of carbohydrates, which could be easily generated by the polymerization of carbohydrates and/or active intermediates, such as HMF or EMF (Scheme 1) [34].

The effects of reaction temperature, time, and catalyst loading on the distribution of products were also investigated. No MF and EMMF were detected at a relatively low reaction temperature (160 °C), whereas the yields of EMF, EMFDEA, EMFA, and BEMF were measured as 19.3%, 17.2%, 3.7%, and 13.6%, respectively (Table 1, entry 1). With the increase of temperature to 200 °C, the yields of EMFA and BEMF increased to 7.4% and 27.9% at the cost of the yields of EMF and EMFDEA (Table 1, entry 2). Meanwhile, small amounts of MF and EMMF were also detected in

this case. Further increasing reaction temperature, time, or catalyst loading resulted in an almost completed consumption of intermediates EMF, EMFDEA, and EMFA, although pronounced increase of BEMF yield was not observed (Table 1, entries 3–5). On the other hand, the yields of MF and EMMF significantly increased in these cases; however, the total yield of products decreased from 65.4% to 48.4% (Table 1, entries 2–5). One can thus infer that an appreciable amount of fructose or intermediates (such as EMF) eventually converted to undetectable by-products (primarily humins) under relatively harsh reaction conditions.

To shed more light in the proposed reaction mechanism, several blank experiments were carried out starting from fructose or HMF at 200 °C in 2 h, and the substrate completely converted in all cases (Table 2). When 10 mol% HCl was used as the catalyst alone, HMF (32.5%) and EMF (29.8%) were determined as the main product (entry 1, Table 2). Small amount of EMFDEA (12.9%) and EL (5.3%) were also detected in this case, whereas no products were formed by the transfer hydrogenation of HMF (such as EMFA, BEMF, EMMF). On the other hand, when ZrO(OH)₂ prepared by either precipitation method or in-situ decomposition of ZrOCl₂·8H₂O was used as the catalyst alone, only about 5.0% of fructose converted to HMF (entries 2 and 6, Table 2), and most of fructose

Table 3. The composition and specific surface area of in situ generated $\text{ZrO}(\text{OH})_2$ catalysts.

Sample	Carbon deposit (wt%) ^a	Atomic ratio Zr/O/Cl ^b	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)
S1	0.0	24.1/75.9/0.0	345.7
S2	22.9	23.4/73.9/1.7	376.7
S3	4.2	27.1/70.0/2.9	188.3

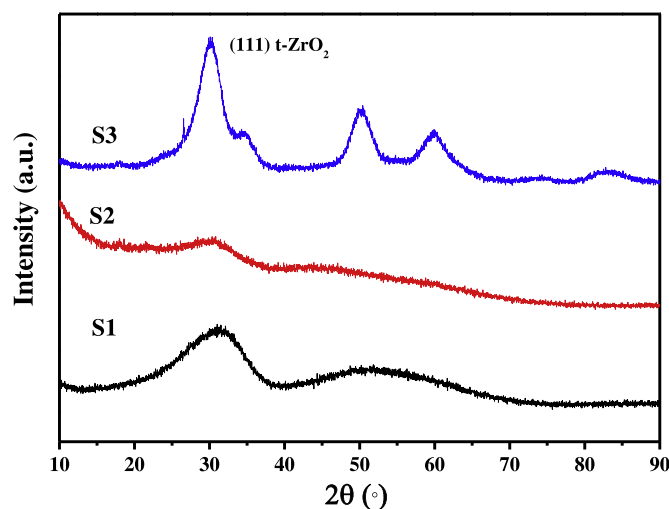
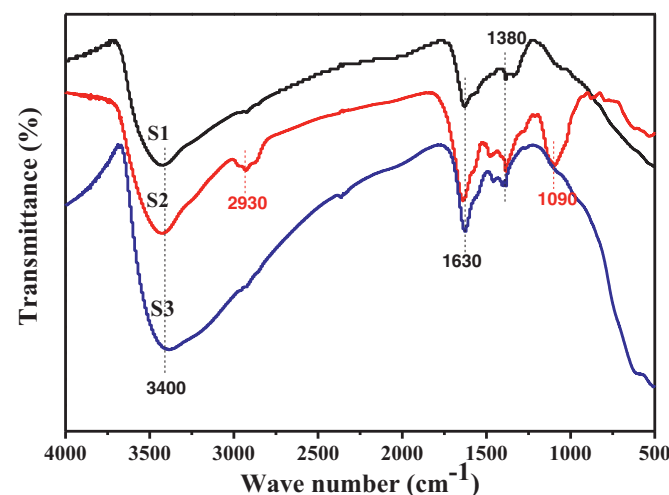
^a Determined by an Elementar Vario EL III (Germany).^b Measured by energy dispersive X-ray spectroscopy (EDS).

probably converted to undetectable products (mainly humins). In contrast, when HCl and $\text{ZrO}(\text{OH})_2$ were used as the catalysts at the same time, products derived from reductive etherification of HMF were detected (entry 3, Table 2). The above results obviously indicate that HCl catalyzes dehydration, etherification and ethanolsis of fructose or HMF, and $\text{ZrO}(\text{OH})_2$ is responsible for the transfer hydrogenation of HMF or EMF.

However, $\text{ZrO}(\text{OH})_2$ formed in-situ by the decomposition of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ displayed a higher catalytic activity in the MPV reduction of HMF than $\text{ZrO}(\text{OH})_2$ prepared by precipitation method. When HCl and $\text{ZrO}(\text{OH})_2$ prepared by precipitation method were used as the catalysts, BEMF yield of only 4.1% was obtained, and HMF (32.0%) and EMF (28.1%) were detected as main products in this case (entry 3, Table 2). In contrast, BEMF (18.9%), EMFA (16.4%) and EMF (13.7%) were obtained as the main products when HCl and recovered $\text{ZrO}(\text{OH})_2$ were used as the catalysts under the same reaction conditions (entry 4, Table 2). Furthermore, $\text{ZrO}(\text{OH})_2$ recovered from the experiment of entry 2 in Table 1 could give an EMFA yield of 39.3% and a BEMF yield of 24.3% starting from HMF (entry 4, Table 2), which further corroborates that $\text{ZrO}(\text{OH})_2$ formed in-situ decomposition of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ is highly active for the MPV reduction of HMF.

To verify if there is soluble active Zr species in the liquid product, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (0.18 g) and ethanol (98 g) were loaded into a 400 mL Hastelloy-C high pressure reactor and then heated to 200 °C for 2 h. Afterward, the reactor was cooled to room temperature and the resulting ethanol solution was separated from solid catalyst by filtration (0.22 μm filter) in vacuum. HMF (2 g) and the obtained filtrate were charged into the reactor again, and heated to 200 °C for another 2 h of reaction. HMF conversion of only 17.9% and negligible yield of EMF (0.9%), EMFA (2.0%) or BEMF (1.6%) were obtained in this case. In contrast, a complete conversion of HMF, BEMF yield of 24.3% and EMFA yield of 39.3% were given in the presence of recovered $\text{ZrO}(\text{OH})_2$ at the same conditions (entry 4, Table 2). This observation indicates that there are no soluble active Zr species in the liquid product.

To gain more insights into this in-situ generated catalyst system, the liquid product was concentrated by rotary evaporation and white floc was then observed by adding AgNO_3 solution into the resulting concentrated solution. This observation clearly indicated that dissociative Cl^- existed in the initial liquid product. Furthermore, we have performed comprehensive characterization for the recovered solid derived from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ after reaction, which clearly supported the fact that $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ decomposed into $\text{ZrO}(\text{OH})_2$ and HCl during the reaction. To verify the chemical nature of the recovered solids, three solid samples were prepared from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$: (1) $\text{ZrO}(\text{OH})_2$ was obtained starting from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ by conventional precipitation method (denoted as S1); (2) $\text{ZrO}(\text{OH})_2$ was recovered from the experiment of entry 2 in Table 1 (denoted as S2); (3) $\text{ZrO}(\text{OH})_2$ was prepared by reacting $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ with neat ethanol (without any substrate) at 200 °C for 2 h (denoted as S3). As shown in Table 3, only negligible Cl content was measured in the samples S2 and S3, suggesting that the decomposition of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ occurred during the reaction at 200 °C. In addition, both samples S1 and S2 have a Zr/O atomic ratio of about 1/3 (Table 3) with similar XRD patterns (Fig. 1). As shown in Fig. 2, these samples also give similar FT-IR spectra. The

**Fig. 1.** XRD patterns of $\text{ZrO}(\text{OH})_2$ catalysts generated under different conditions (S1: precipitation method; S2: in-situ generated in ethanol with fructose; S3: in-situ generated in neat ethanol).**Fig. 2.** FT-IR spectra of $\text{ZrO}(\text{OH})_2$ catalysts generated under different conditions (S1: precipitation method; S2: in-situ generated in ethanol with fructose; S3: in-situ generated in neat ethanol).

broad band at around 3400 cm^{-1} is due to the stretching vibration of the hydroxyl. The O–H bending bands at 1380 and 1630 cm^{-1} characterize the $\text{ZrO}(\text{OH})_2$ polymer structure [35]. Compared with samples S1 and S3, new absorption peaks appear at about 2930 and 1091 cm^{-1} in the sample S2, which are probably attributed to the adsorbed carbon deposits (Table 3). For example, the new peak at 2920 cm^{-1} is representative of the stretching vibration of –C–H. It is known that the catalytic reaction takes place on the surface of solid catalyst in a heterogeneous system. Therefore, substrate or intermediates (such as fructose, HMF, or EMF) could easily attach on the in-situ generated $\text{ZrO}(\text{OH})_2$ particles during the reaction.

However, several diffraction peaks ascribed to ZrO_2 are observed in sample S3 (Fig. 1), revealing that a fraction of in-situ generated $\text{ZrO}(\text{OH})_2$ could further dehydrate to ZrO_2 at the absence of substrates (fructose or HMF) [36]. As shown in the TGA curves (Fig. 3), the weight loss before 100 °C is attributed to the physically adsorbed water. The sample S2 shows a total weight loss of 35.5% during heat treatment, which is well in line with a sum of the theoretical weight loss of $\text{ZrO}(\text{OH})_2$ (12.8%) and carbon deposits (22.9%, Table 3). In comparison, there is only 4.2 wt% carbon deposits in sample S3 (Table 3), disclosing that carbon deposits in sample S2 were presumably resulted from the adsorption of sub-

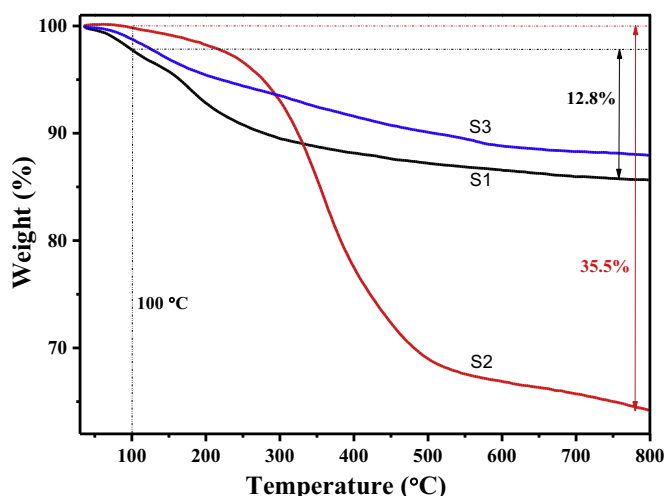


Fig. 3. TGA curves of $\text{ZrO}(\text{OH})_2$ catalysts generated under different conditions (S1: precipitation method; S2: in-situ generated in ethanol with fructose; S3: in-situ generated in neat ethanol).

strate, products, or by-products, such as EMF, humins. These carbon deposits were assumed to prevent the further dehydration of in-situ generated $\text{ZrO}(\text{OH})_2$ at the given reaction temperature. In short, these characterizations of recovered solid catalysts indicated that $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ decomposed into HCl and $\text{ZrO}(\text{OH})_2$ in ethanol during the reaction under the prescribed conditions in this study.

Notably, sample S2 had a surface area of $376.7 \text{ m}^2 \cdot \text{g}^{-1}$ comparable to sample S1, but much higher than that of sample S3 (Table 3). It is known that the transfer hydrogenation of HMF or EMF should be proceeded on the surface of $\text{ZrO}(\text{OH})_2$ catalyst. Therefore, these attached substrate or intermediates (such as fructose, HMF, or EMF) could prevent the agglomeration of in-situ generated $\text{ZrO}(\text{OH})_2$ particles, resulting in a relatively high surface area of sample S2. The above inference also can be reinforced by the fact of high carbon deposit of sample S2 (22.9 wt%, Table 3). The SEM images also show that samples S1 and S2 have similar morphology, whereas relatively big particles are observed in sample S3 (Fig. S1).

4. Conclusions

In this contribution, we proposed an in-situ generated catalyst system for the one-pot tandem conversion of fructose into bio-fuel components, such as EMF, EL, and BEMF, by consecutive acid-catalyzed dehydration, etherification and transfer hydrogenation. BEMF yield of near 30% with total products yield of 65.4% was offered using $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ at the catalyst precursor at 200 °C in only 2 h.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jechem.2018.01.002.

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