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### **Biomass Conversion**

## Simultaneous Conversion of C5 and C6 Sugars into Methyl Levulinate with the Addition of 1, 3, 5-Trioxane

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Abstract: The simultaneous conversion of C5 and C6 mixed sugars into methyl levulinate (MLE) has emerged as a versatile strategy to eliminate the costly separation steps. However, the traditional upgrading of C5 sugars into MLE is very complex as it requires both acid-catalyzed and hydrogenation processes. Herein, we report for the first time, a one-pot, hydrogenation-free conversion of C5 sugars into MLE over different acid catalysts at near-critical methanol conditions with the help of 1, 3, 5-trioxane. For the conversion of C5 sugars over zeolites without the addition of 1, 3, 5trioxane, the MLE yield is quite low due to low hydrogenation activity. Interestingly, the addition of 1, 3, 5-trioxane significantly boosts the MLE yield by providing an alternative conversion pathway that does not include the hydrogenation step. A direct comparison of the catalytic performance of the five different zeolites reveals that  $H\beta$  zeolite, which has both high Lewis and Brønsted acid sites density contributes to the highest MLE yield. With the addition of 1, 3, 5-trioxane, the hydroxymethylation of furfural derivative and formaldehyde is a key step. Notably, the simultaneous conversion of C5 and C6 sugars using  $H\beta$  zeolite as the catalyst can attain an MLE yield as high as 50.4% when the reaction conditions are fully optimized. More importantly, the  $H\beta$  zeolite catalyst can be reused for at least five times without significant change in performance.

 $\boldsymbol{L}$ ignocellulosic biomass as the most abundant carbon-containing organic resources can be depolymerized and hydrolyzed into C5 and C6 sugars.<sup>[1]</sup> These mixed sugars are difficult to be separated due to their many similarities and having no fixed boiling points.<sup>[2]</sup> An efficient approach is to convert them to volatile chemicals such as C5-derived furfural (FAL) C6-derived and 5-(hydroxymethyl)furfural (HMF).<sup>[3]</sup> However, the resultant products of these conversion processes are usually different, leading to the occurrence of some costly separation processes.<sup>[1a]</sup> To avoid this situation, the simultaneous conversion of C5 and C6 sugars into the same platform chemical by further converting FAL and HMF has become a promising solution.<sup>[3e,4]</sup> Brønsted acid (B acid) has been identified as the main active site for the production of FAL and

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HMF from the hydrolysis of sugars; HMF can be easily converted to methyl levulinate (MLE).  $\ensuremath{^{[5]}}$ 

The traditional upgrading of hemicellulose-derived C5 sugars to MLE is very complex.<sup>[3e]</sup> This multi-step conversion process include the hydrogenation of FAL into furfuryl alcohol (FOL) in addition to acid-catalyzed alcoholysis as seen in Scheme 1 (blue arrows).<sup>[6]</sup> The hydrogenation process, in particular, requires high-pressure H<sub>2</sub>, hydrogenation active site, and other harsh reaction conditions that hinders the effectiveness of the conversion process.<sup>[7]</sup> The available one-pot production strategies for the conversion of C5 sugars into MLE has shown only limited success. Hu et al., for example, attempted a one-pot conversion of MLE from xylose at 7 MPa H<sub>2</sub> pressure over Amberlyst 70 (acid) and Pd/Al<sub>2</sub>O<sub>3</sub> (hydrogenation) catalysts, with less than 30% MLE yield.<sup>[8]</sup> Nevertheless, the simultaneous conversion of C5 and C6 sugars into MLE still possess a difficult challenge due to the existence of hydrogenation step. The provision of an alternative pathway that does not include this hydrogenation step seems highly promising and very therefore desirable.

Based on Scheme 1, the reaction routes that include the conversion of glucose to HMF, xylose to FAL and HMF to MLE (black arrows) can all be carried out over acid catalysts.<sup>[9]</sup> In 1999, Lecomte et al. reported the use of formaldehyde over Mordenite catalyst for hydroxymethylation of FAL derivatives to produce HMF derivatives.<sup>[10]</sup> Following this, the upgrading of C5 sugars through HMF derivatives route seem more promising. For the preparation of MLE, however, the aqueous system of formaldehyde renders this conversion strategy unsuitable since MLE would be further converted to the hydrolyzed counterpart - levulinic acid.<sup>[11]</sup> Hence, the development of non-aqueous-based, acid-catalyzed hydroxymethylation of FAL derivatives route holds great promises for simultaneous conversion of C5 and C6 sugars into MLE.



**Scheme 1.** The traditional process and new 1,3,5-trioxane-added strategy for the preparation of MLE from the conversion of C5 and C6 sugars.

In the present study, therefore, a simultaneous conversion of C5 and C6 sugars into MLE over a series of zeolite catalysts with the addition of 1, 3, 5-trioxane was attempted. Without the addition of 1, 3, 5-trioxane, almost no MLE was obtained from the conversion of xylose; surprisingly, a "volcano" type increase in MLE yield after the addition 1, 3, 5-trioxane was observed under the same reaction

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conditions. Following this, the roles of 1, 3, 5-trioxane and the possible reaction pathway was studied. Additionally, important reaction parameters such as the 1, 3, 5-trioxane loading, the catalyst types, catalyst loading, different reactants, reaction temperature and time were all optimized. The acidity of the zeolite catalysts was characterized by FTIR spectra of pyridine adsorption (Py-FTIR).

The effect of 1, 3, 5-trioxane loadings on the conversion of xylose in near-critical methanol was first studied and the results presented in Figure 1a. In the absence of 1, 3, 5-trioxane, the MLE yield was only 4.9% over screened HB catalyst in methanol. The generation of a small amount of MLE (4.9% yield) could be ascribed to weak transfer hydrogenation activity of FAL in methanol over HB catalyst. The major intermediates were FAL and β-Methoxy-2-furanethanol (MFE). FAL is the hydrolysis product of xylose, and MFE on the other hand, is obtained from the acetalization and etherification of FAL and methanol.<sup>[6a]</sup> The total carbon balance was guite low, which could be attributed to the formation of humins from the polymerization of FAL and xylose.<sup>[12]</sup> Surprisingly, the addition of 1, 3, 5-trioxane significantly boosted the MLE yield up to 47.4% (Figure 1a). Additionally, the carbon balance increased dramatically due to fast transformation of FAL. Considering the fact that FOL was never obtained, we believe that a new conversion pathway may be developed after the addition of 1, 3, 5-trioxane.



**Figure 1.** a) Effect of 1, 3, 5-trioxane loadings on the catalytic conversion of xylose over H $\beta$  catalyst; b) Catalytic conversion of xylose to MLE over different zeolites with 0.42 g 1, 3, 5-trioxane. Reaction condition: 0.06 g xylose, 0.12 g catalyst, 6 mL methanol, 160 °C for 18 h.

Having adopted the new conversion pathway engineered by the addition of 1, 3, 5-trioxane, the effect on the conversion of xylose over different zeolites was studied and the results presented in Figure 1b. More than 80% conversion of xylose was achieved for all catalysts including the blank experiment. This is because the near-

critical methanol solutions are favorable for the conversion of sugars.<sup>[4]</sup> In the absence of any catalyst, methyl β-D-xylopyranoside (MDX, Scheme 2) was found as the major product, which indicates that hydrolysis of xylose and MDX is difficult to proceed without the acid catalysts.<sup>[13]</sup> For SAPO-11 and MCM-41, FAL can be produced with almost no traces of MLE formation, which indicates that hydrolysis reaction occurred but further conversion of FAL is difficult over these two catalysts. The Mordenite catalyst, on the other hand, gave an MLE yield of approximately 5%. The Py-FTIR spectroscopic measurement was used to investigate the acidity of the different zeolite samples in order to rationalize the MLE formation efficiency trend observed in Figure 1b.<sup>[14]</sup> The FTIR spectra are shown in Figure S1. When compared to SAPO-11 and MCM-41, the Mordenite catalyst exhibited higher B acid sites density from the quantitative results in Table 1. We believe that the higher B acid sites density exhibited by Mordenite over SAPO-11 and MCM-41 is directly responsible for the higher production of MLE. In a similar trend, the MCM-22 catalyst, which has even higher L and B acid sites densities, contributed even more MLE yield.

Table 1. The surface area and acidity of different samples determined by BET and Py-FTIR spectra.

	Surface area	B acid sites	L acid sites	B/L
	$(m^2/g)$	(µmol/g)	(µmol/g)	
SAPO-11	77.8	70.0	38.2	1.8
MCM-41	740.8	21.4	38.5	0.6
Mordenite	496.2	182.1	34.1	5.4
MCM-22	549.6	248.7	56.7	4.4
Нβ	634.5	218.9	112.8	1.9

As seen in Figure 1b, the highest MLE yield was found over H $\beta$  catalyst, presumably due to the presence of both high L and B acid sites densities (Table 1). It can be deduced from the above results that strong B acid sites are favorable for hydroxymethylation reaction, which could be further accelerated in conjunction with strong L acid sites. Based on the N<sub>2</sub> adsorption-desorption isotherms (Figure S2a) and the corresponding pore size distributions (Figure S2b), the Mordenite, MCM-22, and H $\beta$  are mainly dominated by micropores.<sup>[15]</sup> SAPO-11 has much lower surface area (77.8 m<sup>2</sup>/g) in comparison to the other four zeolites (Table 1). From the combined analysis of the observations of the results from Mordenite, MCM-22, and H $\beta$  catalysts, the MLE yield appears more sensitive to acidity than pore structure. To further improve the MLE yield, the H $\beta$  loading, reaction temperature and time were optimized for the conversion of xylose with the addition of 1, 3, 5-trioxane.







*Figure 2.* a) Effect of reaction temperature and time on MLE yield from the conversion of xylose; b) Reusability of H $\beta$  on conversion of xylose at 160 °C for 18 h (recycled H $\beta$  was calcined at 550 °C for 6<sup>th</sup> reuse experiment). Reaction conditions: 0.06 g xylose, 0.42 g 1, 3, 5-trioxane, 0.12 g H $\beta$ , 6 mL methanol.

As seen in Figure S3, the HB loading considerably affected the product distributions. With 0.03 g H $\beta$ , the yields of FAL, MLE and MFE significantly increased which underscores the role of acidity in promoting the hydrolysis of xylose and hydroxymethylation of FAL derivatives. As the H $\beta$  loading increases from 0.03 to 0.12 g, the MLE yield increased gradually at the expense of yields of FAL and MFE, but remained constant with further increase in H $\beta$  loading. This suggested that the acidity of 0.12 g H $\beta$  is sufficient for optimum production of MLE from the conversion of xylose and intermediates. The effect of reaction temperature and time on the conversion of xylose are shown in Figure 2a and S4. Based on Figure S4a, temperatures above 150 °C are sufficient for this conversion process. In general, the MLE yield has a direct relationship with reaction temperature as increased temperature enhances the production rate of MLE in Figure 2a. The slight decrease in MLE yield at prolonged reaction time at 170 °C can be ascribed to the occurrence of some side reactions.<sup>[16]</sup>

Thereafter, the reusability of the HB catalyst was analyzed after multiple cycles of usage. The results are presented in Figure 2b. As the number of cycles increase, (1st to 5th), the MLE yield gradually decreases continuously as increasing yields of FAL and MFE. Fortunately, the catalytic activity of a used H $\beta$  can be mostly recovered by mere calcination at 550 °C for 6 h. The N2 adsorptiondesorption isotherms of fresh and used H $\beta$  in Figure S5 suggests that pore blockages, especially micropores by coke or humins may have been the major cause of the decrease in catalytic activity; although the pore structure can almost be restored after regeneration at 550 °C. Li and co-workers reported a similar system in which 41.6% MLE yield was obtained from the conversion of xylose over Amberlyst 70 with dimethoxymethane.<sup>[3e]</sup> However, the acid density of Amberlyst 70 significantly reduced after the initial use, thereby affecting the reusability performance of the catalyst. These results indicate that our 1, 3, 5-trioxane-added strategy with the use of H $\beta$ catalyst is better suited for the conversion of xylose into MLE.



**Scheme 2.** The proposed reaction pathway for one-pot conversion of xylose to MLE with 1, 3, 5-trioxane.

A series of intermediate products such as FAL, MDX, MFE and 2-dimethoxymethyl-5-methoxymethylfuran (DMMF) were observed during the conversion process. Their variations with respect to reaction times and temperatures are crucial for the study of possible reaction pathway. Based on the results in Figure S4, the possible reaction routes for the one-pot conversion of xylose to MLE with the help of 1, 3, 5-trioxane is proposed in Scheme 2. Xylose could be converted to MDX in near-critical methanol even without catalysts. They could be further hydrolyzed to FAL with B acid.<sup>[8,17]</sup> Also, MFE as main intermediate was detected which possibly originated from the acetalization and etherification of furfural and methanol, as shown by previous studies.<sup>[6a,18]</sup> According to previous study, a new selective route to HMF from FAL and FAL derivatives (-CH2OH was grafted onto furan ring) can be achieved over microporous solid acidic catalysts.<sup>[5e]</sup> Therefore, we believed that DMMF as an intermediate may have resulted from the etherification of hydroxymethylated HDMF at near-critical methanol conditions despite having not detected HDMF. The undetectable HDMF might be due to fast HDMF etherification to DMMF in methanol solution.

The production of HDMF from hydroxymethylation reaction is perhaps the most important step of the overall reaction. As previously reported, the aldehyde group in FAL would deactivate the position 5 in the furan ring owing to its electron-withdrawing character.<sup>[3e,9]</sup> This can be bypassed by protecting the aldehyde group with functionalities with electro-donating capacity which automatically renders the hydroxymethylation of MFE and DOF more likely to occur as compared to FAL. For the conversion of MFE to HDMF, it was quite difficult to determine the sequence of rearrangement and hydroxymethylation reaction, owing to the fact that DOF and the hydroxymethylated products of MFE (HMFE in Scheme 2) were not detected. The formaldehyde detected after the reaction was obtained as a decomposition product of 1, 3, 5trioxane,<sup>[19]</sup> and was used as an electrophile for the production of HMF derivative from FAL derivative. The catalytic conversion of the intermediate products - MDX, FAL, and HMF over HB were evaluated as well. The effect of the addition of 1, 3, 5-trioxane on the conversion of FAL exhibited a similar trend as MLE obtained from the conversion of xylose in Figure S6. For the conversion of HMF without the addition 1, 3, 5-trioxane (Figure S7), DMMF was detected as the main intermediate product from the acetalization and etherification of HMF; this observation is consistent with previous study.<sup>[5e]</sup> Furthermore, MDX could be also converted to MLE with the help of 1, 3, 5-trioxane (Table 2, entry 9).



Besides xylose, other C5 monosaccharides such as arabinose can also be efficiently converted to MLE using our proposed 1, 3, 5trioxane-added strategy (Table 2, entry 10). Also, a C5 polysaccharide - xylan (Table 2, entry 11) equally displays high conversion efficiency to MLE (46.0%), which can be attributed to fast acid-catalyzed hydrolysis of xylan to xylose.<sup>[3f]</sup> For C6 monosaccharides and disaccharides (Table 2, entry 3-8), the high conversion efficiency to MLE exhibited without the addition of 1, 3, 5-trioxane, additionally collaborates our claim that this new addition strategy is only favorable for hydroxymethylation reaction. The mixture of glucose and xylose afforded high MLE yield of 50.4% (Table 2, entry 12) which is similar to the calculated average yield of 49.6% based on their respective entries in Table 2.

#### Table 2. Catalytic conversion of different sugars to MLE.

Entry	Reactant	MLE yield/%	
1	Xylose	47.4	
2	Xylose <sup>a</sup>	4.9	
3	Glucose	48.3	
4	Glucose <sup>a</sup>	51.8	
5	Fructose	53.5	
6	Fructose <sup>a</sup>	60.8	
7	Mannose <sup>a</sup>	63.9	
8	Sucrose <sup>a</sup>	66.0	
9	MDX	43.8	
10	Arabinose	48.3	
11	Xylan	46.0	
12	Glucose + xylose <sup>b</sup>	50.4	

Reaction condition: 0.06 g reactant, 0.42 g 1, 3, 5-trioxane, 0.12 g H $\beta$ , 6 mL methanol, 160 °C for 18 h. <sup>a</sup>In the absence of the 1, 3, 5-trioxane; <sup>b</sup>0.03 g glucose, 0.03 g xylose and 0.21 g 1, 3, 5-trioxane.

Summarily, the present study involved the development of an alternative pathway in which one-pot conversion of C5 sugars into MLE can be accomplised over an optimized HB catalyst with the addition of 1, 3, 5-trioxane at near-critical methanol conditions. Unlike the traditional upgrading of hemicellulose-derived C5 sugars into MLE, our new conversion strategy is very less complex and does not require H<sub>2</sub> and hydrogenation reaction; instead, it involves hydroxymethylation reaction of FAL derivative and formaldehyde to produce HMF derivative, in which formaldehyde is derived from the consumption of 1, 3, 5-trioxane. The entire reactions can be catalyzed by acid catalysts with both high Lewis and Brønsted acid sites densities, such as H<sub>β</sub>. The effect of catalyst types, 1, 3, 5trioxane and  $H\beta$  loadings, reaction temperature and time on the conversion of xylose were investigated for optimum MLE yield. The highest MLE yield realized was 47.4%. The HB catalyst can be regenerated by mere calcination to remove carbon deposition, and then reused for at least five cycles without significant drop in activity. In addition to xylose, other C5 monosaccharides and polysaccharide are also efficiently converted to MLE with the help of 1, 3, 5-trioxane. More importantly, a high MLE yield of 50.4% is observed from the simultaneous conversion of C5 and C6 sugars via this 1, 3, 5-trioxane-added conversion strategy. We believe that this new conversion strategy holds great promises for simultaneous conversion of cellulose and hemicellulose into MLE.

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### Entry for the Table of Contents

### **Biomass Conversion**

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Simultaneous Conversion of C5 and C6 Sugars into Methyl Levulinate with the Addition of 1, 3, 5-Trioxane



Herein, we for the first time report simultaneous conversion of C5 and C6 sugars into methyl levulinate via 1, 3, 5-trioxane-added strategy. This new strategy can be accomplished by hydroxymethylation of furfural (or its derivatives) and formaldehyde derived from the 1, 3, 5-trioxane. H $\beta$  zeolite with both strong L and B acid sites was found to be the most efficient candidate.

