Simultaneous Catalytic Conversion of C6 and C5 Sugars to Methyl Lactate in Near-critical Methanol with Metal Chlorides

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Cellulose and hemicellulose make up roughly two-thirds of lignocellulose. Currently, research is mainly focused on converting them to different chemicals, which causes low utilization rates and high separation costs. In this work, the simultaneous conversion of C6 and C5 sugars from cellulose and hemicellulose to methyl lactate in near-critical methanol with 15 different types of metal chlorides was studied. The trends of the catalytic conversions of C6 and C5 sugars with different metal chlorides were similar. Methyl lactate yield initially increased and then decreased steadily with an increase in the pKa value of the metal ions, which suggested that medium Lewis acidity was favorable for the production of methyl lactate. A possible reaction mechanism was proposed. The results will provide direction for the preparation of heterogeneous catalysts for simultaneously converting cellulose and hemicellulose to methyl lactate.

Keywords: Glucose; Xylose; Simultaneous conversion; Lewis acidity; Methyl lactate

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INTRODUCTION

Lignocellulose, mainly consisting of cellulose, hemicellulose, and lignin, is an abundant and renewable resource (Singh *et al.* 2016) that can be converted to fuels and value-added chemicals (Van de Vyver *et al.* 2011). Cellulose and hemicellulose make up approximately two-thirds of lignocellulose (Yang *et al.* 2007). Cellulose and hemicellulose mainly consist of C6 and C5 sugar, respectively (Huber *et al.* 2006). Glucose and xylose are the most common C6 and C5 sugars, and they share many similarities because they both have multiple hydroxyl groups, and they are both aldose types of monosaccharide, which can isomerize to the ketose types of monosaccharide. Hence it is possible to convert cellulose and hemicellulose to the same product in a one-pot reaction (Hu *et al.* 2013) with lignin, which is more stable (Yoshikawa *et al.* 2013), remaining in the solid residue (Pan *et al.* 2015), as shown in Fig. 1. Hu *et al.* (2017) successfully carried out the one-pot conversion of xylose and glucose to methyl levulinate with Amberlyst 70 in dimethoxymethane/methanol without added hydrogen, meaning that the one-pot production of methyl lactate from C6 and C5 sugars is feasible and promising.

Methyl lactate (MLA) is a nontoxic and highly biodegradable platform chemical (Datta and Henry 2006; Aparicio 2007) that can be used as a green solvent with a high boiling point. Furthermore, MLA has important applications in the food and medical industries (Maki-Arvela *et al.* 2013) as well as the skin care industry (de Clippel *et al.* 2012). The chemical MLA is usually produced by the esterification of lactic acid with methanol (de Clippel *et al.* 2012), and the production of lactic acid is based on fermentation. The slow reaction rate, the high separation cost (Pereira *et al.* 2011), and a large amount of salt waste (Holm *et al.* 2010) significantly hinder its development in industry. Therefore, the synthesis of MLA from lignocellulose *via* chemical catalysis is a potential industrial process and has attracted much attention.

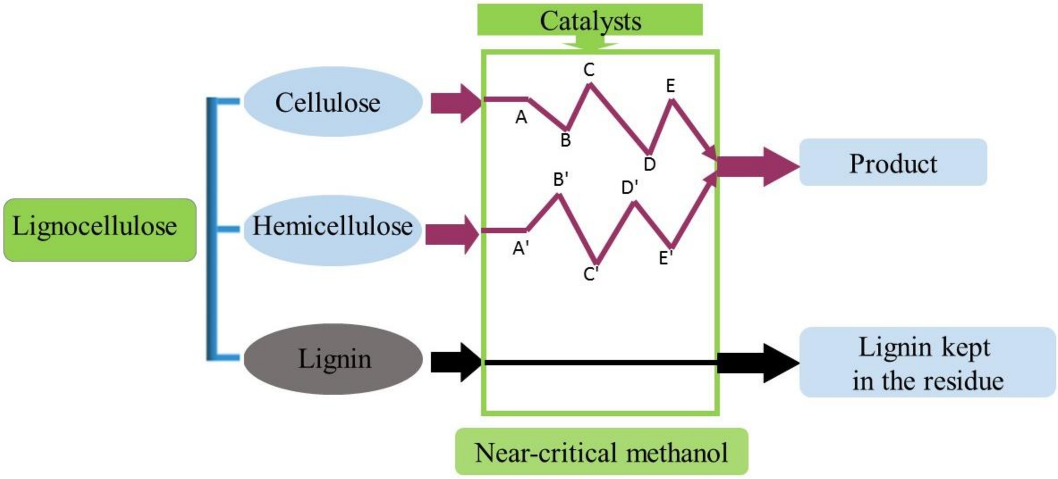


Fig. 1. Schematic diagram for the simultaneous conversion of cellulose and hemicellulose to the same product in near-critical methanol

In the chemical catalytic conversion of biomass to MLA, zeolites of Sn-β (Holm *et al.* 2010; Holm *et al.* 2012), Sn-MWW (Guo *et al.* 2013), Sn-Si-CSM (de Clippel *et al.* 2012), Sn-MCM-41 (Murillo *et al.* 2014), Sn-SBA-15 (Pang *et al.* 2017), and Zr-SBA-15 (Yang *et al.* 2016) have been reported to efficiently convert sugars to MLA. Furthermore, ZIF-8 (Murillo *et al.* 2016) and solid base (Liu *et al.* 2011) catalysts have also been reported to be efficient for the reaction. For homogeneous catalysts, alkali and metal salts have been used as catalysts for the reaction (Lv *et al.* 2014; Zhou *et al.* 2014; Nemoto *et al.* 2016). Nemoto *et al.* (2016) proposed a catalysis mechanism of an In^{3+} and Sn^{2+} system to convert fructose to MLA, in which In^{3+} is efficient for the retro-aldol reaction of fructose to 1,3-dihydroxyacetone, and Sn^{2+} facilitates isomerization of 1,3-dihydroxyacetone to MLA.

Although a high yield of MLA has been achieved by catalytic reactions using homogeneous or heterogeneous catalysts, there is no clear explanation to demonstrate the role of acidity of metal salts in the conversion of C6 and C5 sugars to MLA. The rational design of a metal catalyst for this reaction thus lacks fundamental evidence. Furthermore, although an initial attempt for the one-pot conversion of xylose and glucose was conducted by Hu *et al.* (2017), an electrophile, namely dimethoxymethane, was required in this catalysis system, increasing the separation cost for the products.

In this work, near-critical methanol (critical temperature of 239.5 °C, critical pressure of 8.09 MPa) with good solubility, transport ability, and reactivity (Wu *et al.* 2012) was employed. As shown in Table 1, 15 types of non-noble and common metal ions were selected as catalysts. The conversions of glucose, fructose, xylose, and a mixture of glucose and xylose to MLA in near-critical methanol were studied. The catalytic results relative to the Lewis acidity of the metal ions have been demonstrated based on the experimental and calculated results.

Table 1. The pKa Values for Aqueous Solutions of Different Metal Ions at 25 °C (Dean 1985)

Metal Ion	pKa
Sb^{3+}	0.87
Bi^{3+}	1.58
Sn^{2+}	1.70
Fe^{3+}	2.83
In^{3+}	4.40
Pd^{2+}	7.80
Zn^{2+}	8.96
Cd^{2+}	9.00
Co^{2+}	9.85
Ni^{2+}	9.86
Mn^{2+}	10.59
Mg^{2+}	11.41
Ca^{2+}	12.80
Sr^{2+}	13.18
Ba^{2+}	13.36

EXPERIMENTAL

Materials

D-(+)-glucose (≥ 99.5%), D-xylose (98%), D-fructose (99%), methyl β-D-xylopyranoside (98%), $CoCl_2{\bullet}6H_2O$ (99.99%), $BiCl_3$, $SnCl_2$ (99%), $CdCl_2{\bullet}2.5H_2O$ (99.95%), $SbCl_3$ (99.9%), $MgCl_2{\bullet}6H_2O$ (99.0% to 102.0%), $FeCl_3{\bullet}6H_2O$ (99%), $MnCl_2{\bullet}4H_2O$ (99%), and methyl glycolate (98%) were purchased from the Aladdin Industrial Corporation, Shanghai, China. Methyl lactate (98% +), $ZnCl_2$ (≥ 98%), $BaCl_2{\bullet}2H_2O$ (99.5%), methanol (AR), and sulfuric acid (98%) were purchased from the Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. The $SrCl_2{\bullet}6H_2O$ (99.99%), $InCl_3$ (99.9%), and $PdCl_2$ (99.99%) were purchased from the Shanghai Macklin Biochemical Technology Co., Ltd., Shanghai, China. Nickel (II) chloride ($NiCl_2$; 98%) was purchased from Alfa Aesar, a Johnson Matthey Company, Beijing, China. Calcium chloride ($CaCl_2$; ≥ 96%) was purchased from the Shanghai Lingfeng Chemical Reagent Co., Ltd., Shanghai, China. Methyl α-D-glucopyranoside (99%), methyl β-D-glucopyranoside (99%), and D-xylulose (98%, 0.5 M solution in H_2O) were purchased from J&K Chemical, Ltd., Beijing, China. Glycolaldehydedimethylacetal (98%) was purchased from Beijing InnoChem Science & Technology Co., Ltd., Beijing, China. The deionized water was made in the laboratory.

Experimental procedure

In a typical experimental run, 0.4 mmol of reactant (glucose, fructose, or xylose), 0.02 mmol of metal chloride, and 7 mL of methanol were added into a 14-mL stainless steel reactor. The sealed reactor was placed into a furnace that was previously heated to a desired temperature. After 6 h, the reactor was quickly removed and placed into cold water. The sample was rinsed in a 25-mL volumetric flask by methanol and filtered through a 0.22-μm filter membrane. The calculated conversion of the reactant and product yields were based on the equivalent amount of carbon, and the experimental result was the average value of two replicate experiments.

Methods

The sample was quantitatively analyzed by high performance liquid chromatography with a refractive index detector (HPLC/RID) and gas chromatography with a flame ionization detector (GC/FID).

The HPLC analysis was carried out on an Agilent 1100 instrument (Agilent Technologies, Santa Clara, CA, USA). The HPLC column was Aminex HPX-87H (300 mm × 7.8 mm I.D., Bio-Rad Laboratories, Inc., Hercules, CA, USA). The flow rate of the mobile phase (5 mmol/L H_2SO_4) was 0.4 mL/min. The temperature of the column and the RID were 60 °C and 35 °C, respectively.

The GC/FID analysis was performed on an Agilent 7890A instrument (Agilent Technologies, Santa Clara, CA, USA). The column was Agilent HP-5 (30 m × 0.32 mm × 0.25 μm). The flow rate of carrier gas (nitrogen), air, and hydrogen were 25 mL/min, 400 mL/min, and 30 mL/min, respectively. The injector and detector temperatures were 250 °C and 320 °C, respectively. The temperature program of the oven consisted of a 2 min soak at 40 °C, followed by a 5 °C/min ramp up to 100 °C and then by a 20 °C/min ramp up to 280 °C, which was maintained for 2 min. The identifications of glucose, fructose, xylose, methyl β-D-glucopyranoside, methyl α-D-glucopyranoside, and methyl β-D-xylopyranoside were performed by comparison of the retention times with those for standard solutions of the pure compounds by HPLC. Methyl lactate, glycolaldehydedimethylacetal, and methyl glycolate were confirmed by a GC/MS instrument (Agilent 7890B-5977A, Agilent Technologies, Santa Clara, CA, USA).

RESULTS AND DISCUSSION

Effects of Different Metal Chlorides on the Catalytic Conversion of Monosaccharide

Figure 2 shows the reaction behaviors of glucose with different metal chlorides.

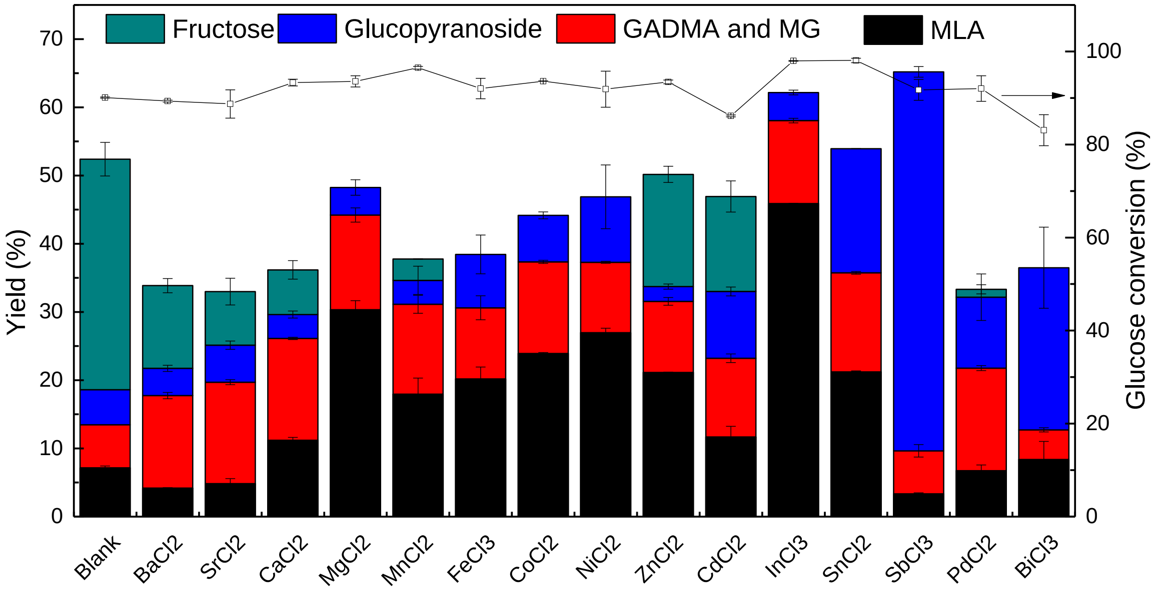


Fig. 2. The effects of different metal chlorides on the glucose conversion and the product yields; reaction conditions: 170 °C, 6 h, 0.4 mmol glucose, 0.02 mmol metal ion, and 7 mL methanol

The conversions of glucose were all greater than 80% for the catalysis of all 15 types of metal chlorides. The magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), strontium chloride ($SrCl_2$), and barium chloride ($BaCl_2$) group IIA metal chlorides catalyzed relatively small amounts of glucose to MLA, with the exception of $MgCl_2$ (30%). Most of the transition metal chlorides, except $BiCl_3$ (8.4%), $SbCl_3$ (3.4%), and $PdCl_2$ (6.7%), exhibited good activity for the conversion of glucose to MLA. The maximum yield of MLA reached 46%, with $InCl_3$. The by-products were mainly detected as glycolaldehyde-dimethylacetal (GADMA), methyl glycolate (MG), methyl α-D-glucopyranoside, and methyl β-D-glucopyranoside (the latter two together referred to as glucopyranoside). The yields of GADMA and MG did not vary remarkably with different metal chlorides. However, the yields of glucopyranoside varied remarkably with different metal chlorides, and $BiCl_3$ and $SbCl_3$ exhibited remarkable activity for the yield of glucopyranoside.

Figure 3 shows the reaction behaviors for fructose with different metal chlorides. The yields of MLA show similar trends as those for glucose. The chloride $InCl_3$ gave the highest MLA yield of 57%. Without a catalyst or with $BaCl_2$ alone, MLA was the only product. Under these conditions, GADMA, MG, and glucopyranoside were not detected. Apart from $BaCl_2$ (7.5%) and $SrCl_2$ (9.2%), the other metal chlorides had positive effects on the yields of MLA, compared with the yield without a catalyst (11%).

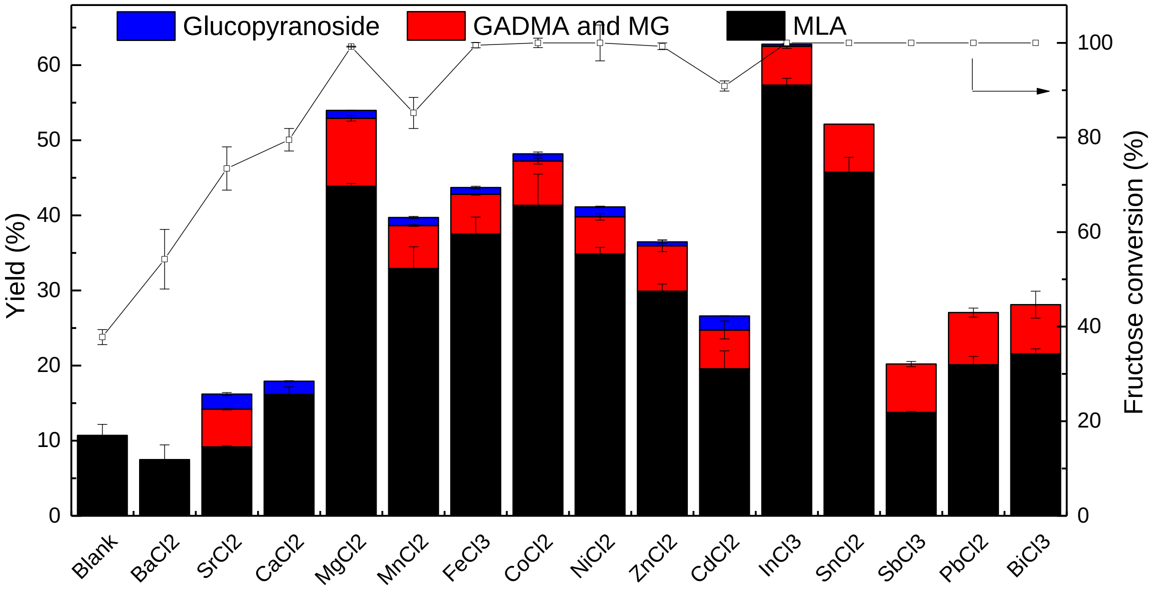


Fig. 3. The effects of different metal chlorides on the fructose conversion and the product yields; reaction conditions: 170 °C, 6 h, 0.4 mmol fructose, 0.02 mmol metal ion, and 7 mL methanol

Figure 4 shows the conversion of xylose with different metal chloride catalysts. Compared with the results shown in Fig. 2, the catalytic conversions of glucose and xylose with different metal chlorides showed similar trends. In the presence of $InCl_3$, the maximum yield of MLA reached 32% from xylose. Both $SbCl_3$ and $BiCl_3$ produced methyl β-D-xylopyranoside (referred to xylopyranoside) as the major product. The yields of GADMA and MG were very close to those of MLA with most metal chlorides. For some metal chlorides, the yields of GADMA and MG were much higher than those of MLA, such as $SrCl_2$, $CaCl_2$, $CdCl_2$, and $PdCl_2$.

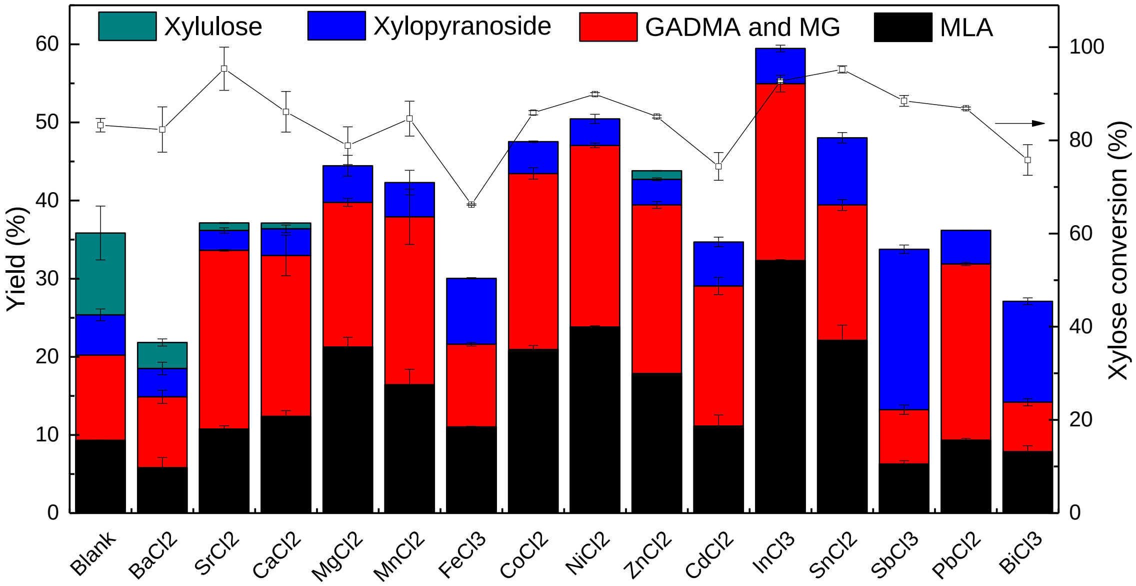
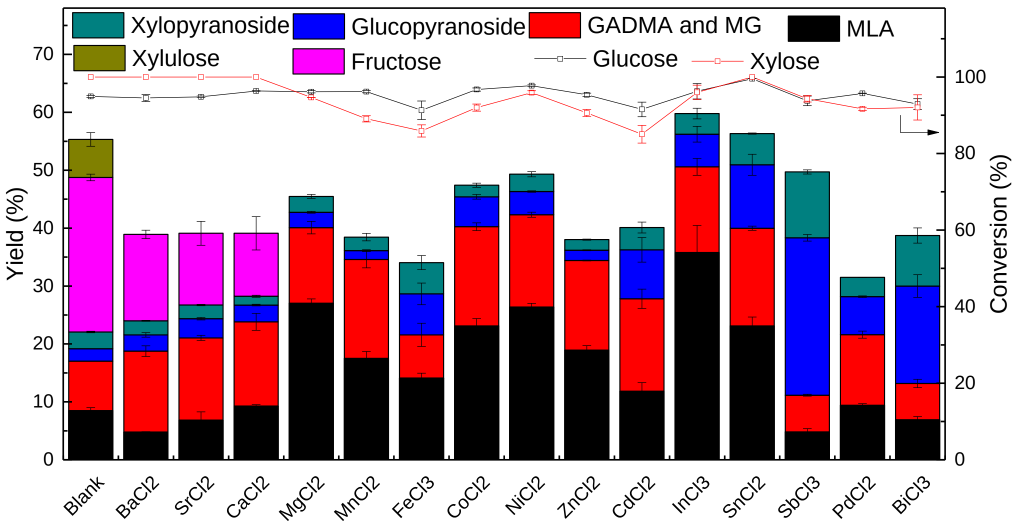
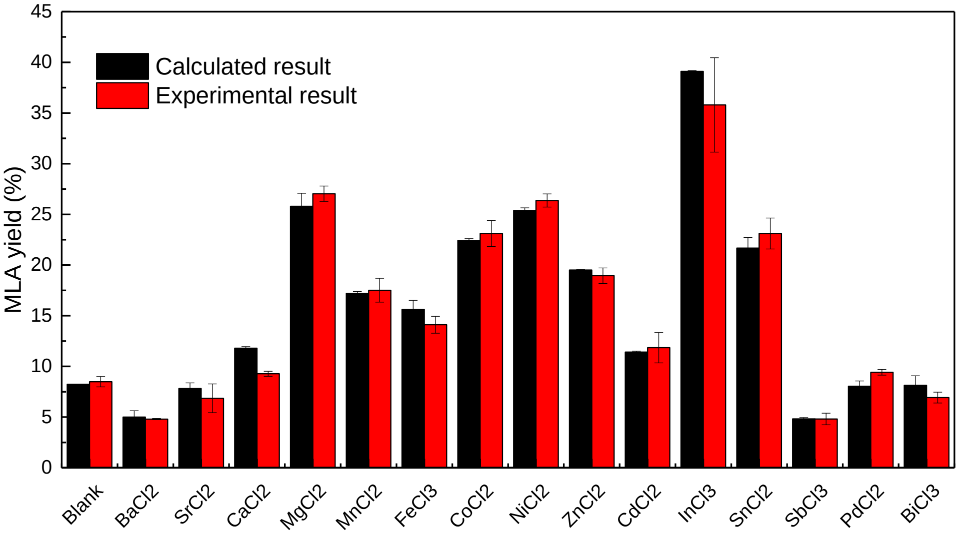


Fig. 4. The effects of different metal chlorides on the xylose conversion and the product yields; reaction conditions: 170 °C, 6 h, 0.4 mmol xylose, 0.02 mmol metal ion, and 7 mL methanol

Figure 5(a) shows the conversion of the glucose and xylose mixture with different metal chlorides. A total of 0.2 mmol of xylose, 0.2 mmol of glucose, and 0.02 mmol of metal chloride were dissolved in 7 mL of methanol. The trends produced were similar to the results for glucose and xylose as separate reactants. $InCl_3$ gave the highest MLA yield of 36%, compared with the predicted yield of 39%, which was calculated from the average yield of the individual components, namely glucose (46%) and xylose (32%). As shown in Fig. 5(b), the calculated (predicted) result was close to the experimental result of the MLA yield from the mixture of glucose and xylose, which indicated that glucose and xylose reacted independently and did not influence each other under these conditions.



(a) Glucose and xylose mixture



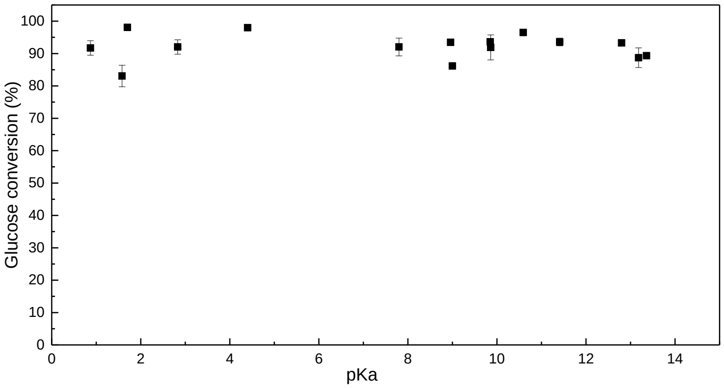
(b) Calculated and experiment yields of MLA from the mixture of glucose and xylose

Fig. 5. Effects of different metal chlorides on the (a) mixture of glucose and xylose (mole ratio of 1:1) conversion and (b) the product yields; reaction conditions: 170 °C, 6 h, 0.4 mmol monosaccharide, 0.02 mmol metal ion, and 7 mL methanol

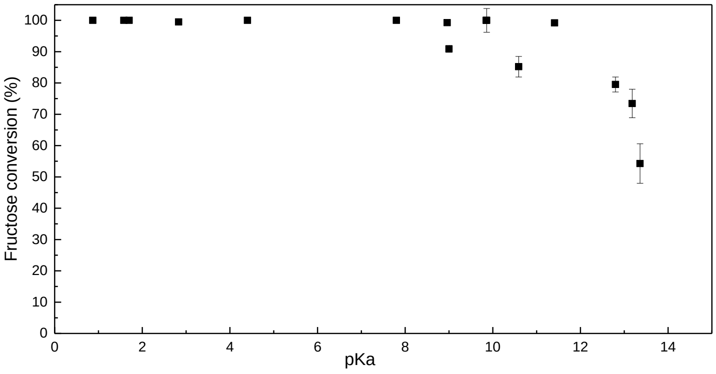
Relationship between the pKa Value of the Metal Ions and the Conversion of Monosaccharides

With different metal chlorides, the conversion of different monosaccharides and the yields of the products varied remarkably. In addition to the intrinsic characteristic of the metal elements, Lewis acidity is another important characteristic of metal chlorides in methanol as a solvent. Acid-base equilibrium is affected by a small amount of water in the solution (Zhou *et al.* 2014), which comes from: 1) the hydration water of the metal chloride; 2) the water absorbed by the metal chloride and the raw material; and 3) the water generated from the reaction. Table 1 shows the pKa values for aqueous solutions of different metal ions at 25 °C (Dean 1985), and lower pKa values correspond to higher acidities of the solutions.

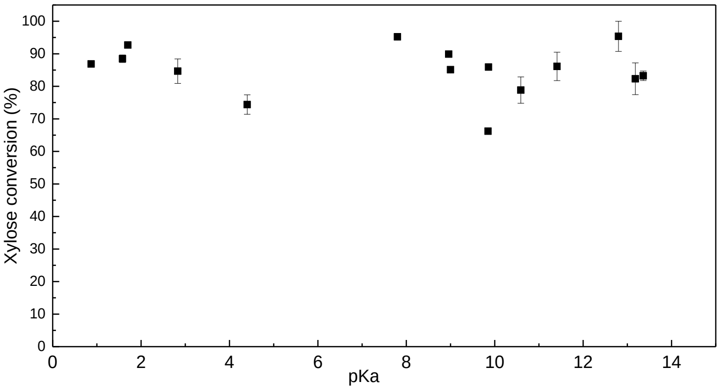
Figure 6 shows the relationship between the conversion of the monosaccharide and the pKa values for the aqueous solutions of different metal ions.



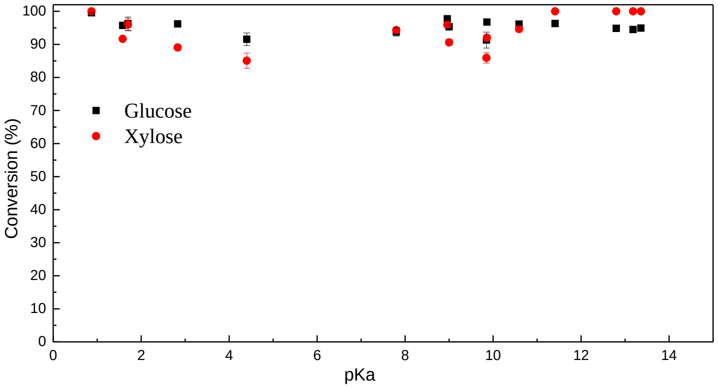
(a) Glucose



(b) Fructose



(c) Xylose



(d) Glucose and xylose mixture

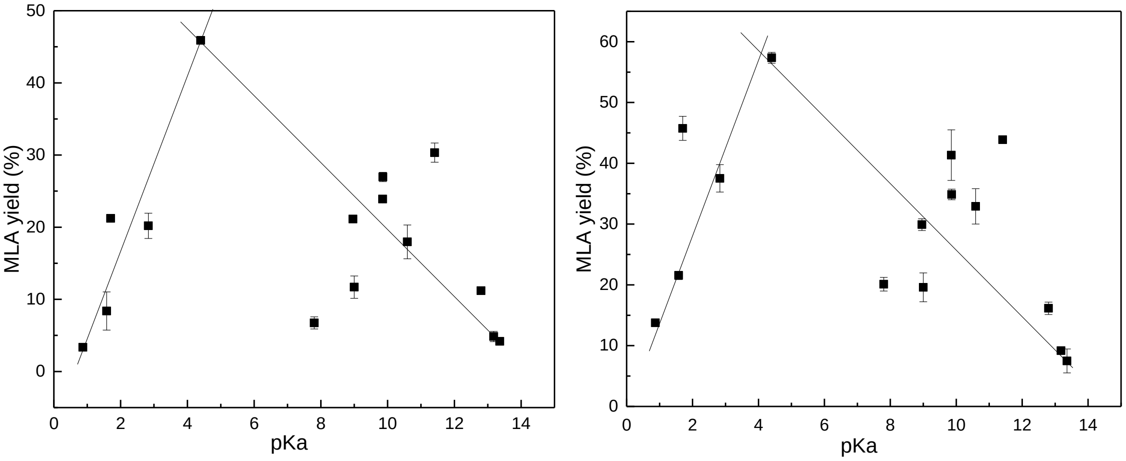
Fig. 6. The relationship between the conversion of the monosaccharides and the pKa values for the aqueous solutions of different metal ions

The conversions of glucose with different metal ions were similar, and the pKa value did not appear to influence the conversion of glucose. By contrast, the conversion of fructose was initially steady and then gradually decreased with an increase in the pKa value. With Ba^{2+} (pKa value of 13.36), which has the greatest pKa value of all the compounds in this study, the conversion of fructose was 54%, while that of glucose was 89%. Similar to the trends for glucose, the conversions of xylose did not vary remarkably with different metal chlorides.

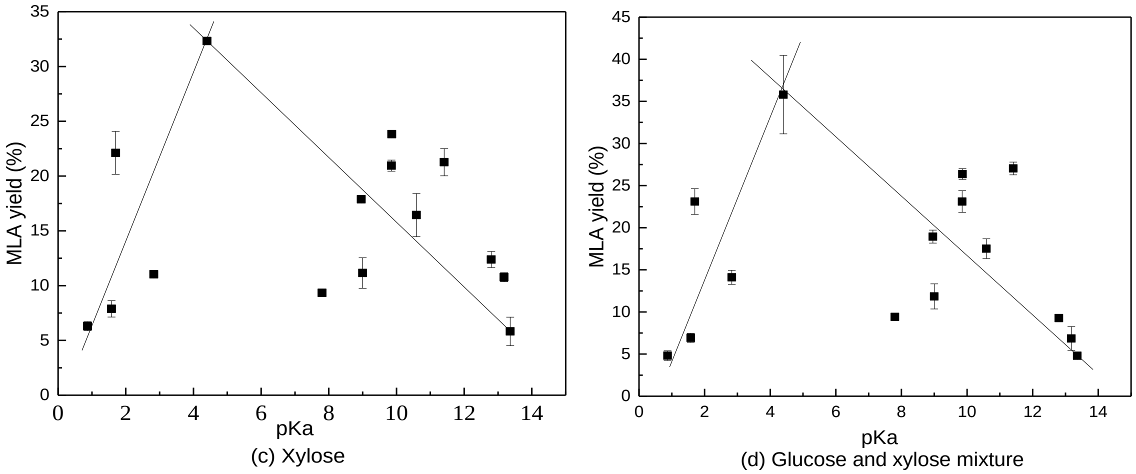
With different metal chlorides, the conversion of the glucose and xylose mixture was high and did not vary remarkably with different metal ions. These results indicate that near-critical methanol is a good solvent for the one-pot conversion of C6 and C5 sugars mixture to MLA.

Relationship between the pKa Value of the Metal Ions and the Product Yields from the Monosaccharides

Figure 7 shows the relationship between the pKa value of the metal ions and the yields of MLA from the monosaccharides. For different monosaccharides, the yields of MLA initially increased and then steadily decreased with the increase in the pKa value of the metal ions. These results suggested that a medium Lewis acidity was favorable for producing MLA. By comparing Fig. 7(a) and Fig. 7(b), the yield of MLA from fructose was much higher than that from glucose. With $InCl_3$, the maximum yield of MLA reached 57% from fructose, while it was 46% from glucose. With Sn^{2+}, Sb^{3+}, and Bi^{3+}, which all have low pKa values, the yields of MLA were 46%, 14%, and 22% from fructose, respectively, but the corresponding yields of MLA from glucose were 21%, 3.4%, and 8.4%, respectively. Compared with glucose, stronger Lewis acidity was more efficient for the conversion of fructose. By comparing Fig. 7(a) and Fig. 7(c), the yields of MLA from glucose were much higher than those from xylose.



(a) Glucsoe (b) Fructose



(c) Xylose

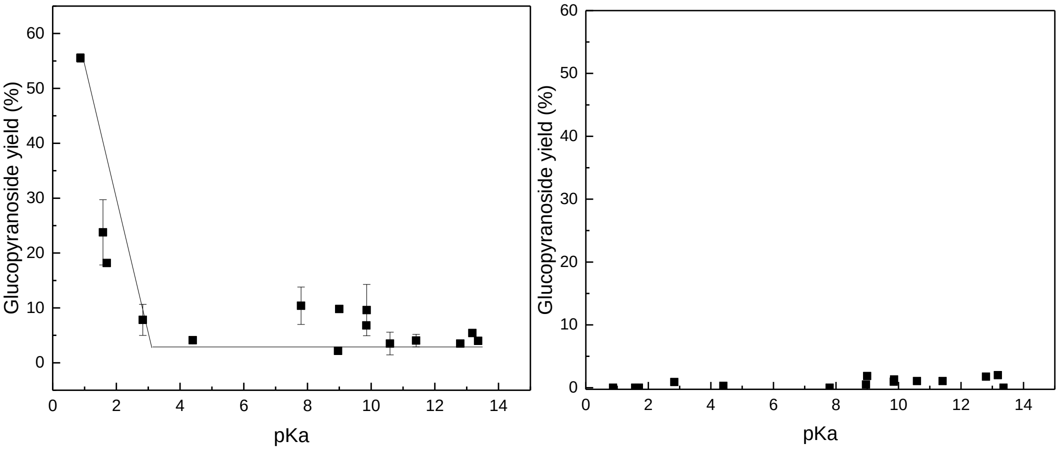
(d) Glucose and xylose mixture

Fig. 7. The relationship between the yield of methyl lactate and the pKa values of the aqueous solutions for different metal ions

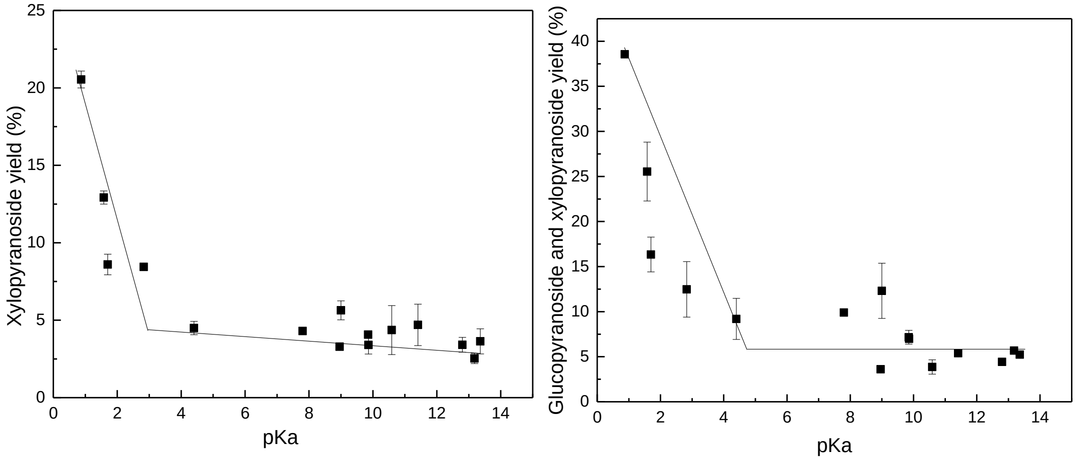
Regarding the mixture of glucose and xylose, MLA yield showed a similar trend to that of glucose and xylose as separate reactants. $InCl_3$, with a medium Lewis acidity, resulted in the highest MLA yield, which reached 36%. The conversion of C6 and C5 sugars in a one-pot reaction can be achieved under mild reaction conditions. With the exception of $InCl_3$, other metal salts, such as $MgCl_2$, $NiCl_2$, $CoCl_2$, and $SnCl_2$, were also active for the conversion of glucose and xylose mixture to MLA. Lewis acidity plays an important role for the yield of MLA, while other properties of metal ions may also affect the reaction, as zeolites containing Sn (Holm *et al.* 2010, 2012; de Clippel *et al.* 2012; Guo *et al.* 2013; Murillo *et al.* 2014; Pang *et al.* 2017) and MgO (Liu *et al.* 2011), have been employed as efficient catalysts for the reaction. More heterogeneous catalysts related to the elements mentioned above may possibly be employed in the future to improve the simultaneous conversion of cellulose and hemicellulose.

As mentioned above, Lewis acidity is necessary for the reaction, but strong Lewis acidity may lead to side reactions. Figures 8(a) and 8(c) show that the yields of the by-products glucopyranoside and xylopyranoside decreased as the pKa values of the metal ions increased. In contrast, the yields of glucopyranoside from fructose were all very low (Fig. 8(b)), which indicated that it was difficult for fructose to isomerize to glucose. Sb^{3+} has the lowest pKa value among the metal ions used in this study and gave the maximum glucopyranoside yield of 56% from glucose and the maximum xylopyranoside yield of 21% from xylose, which indicated that a strong Lewis acidity led to a high yield of glucopyranosides or xylopyranoside.

The relationship between the pKa value of the metal ions and the yield of glucopyranoside mixed with xylopyranoside from the mixture of glucose and xylose is shown in Fig. 8(d), and the trend was similar to those for glucose and xylose as separate reactants. The yield of mixed glucopyranoside and xylopyranoside decreased as the pKa value of the metal ions increased. For the one-pot conversion of C6 and C5 sugars, strong Lewis acidity may lead to high yields of glucopyranoside and xylopyranoside and may also hinder the production of MLA.



(a) Glucose (b) Fructose



(c) Xylose (d) Glucose and xylose mixture

Fig. 8. The relationship between the yields of glucopyranoside or xylopyranoside and the pKa values of aqueous solutions for different metal ions

Proposed Mechanism of Conversion of Glucose and Xylose into MLA

According to previous literature (Holm *et al.* 2010, 2012; Yang *et al.* 2016; Wang *et al.* 2017) and the authors' experimental results, a reaction mechanism for the conversion of glucose and xylose, as shown in Fig. 9, is proposed. Glucose and xylose are both aldose types of monosaccharides, which can isomerize to the ketose types of monosaccharide, fructose, and xylulose, respectively. From Figs. 2 and 4, without a catalyst, fructose was detected as the major product of the glucose conversion. Its yield reached 34%, and the highest yield of xylulose obtained was 10% from the conversion of xylose. This result indicated that the conversions of glucose to fructose and xylose to xylulose can be achieved without catalysts in near-critical methanol, and fructose and xylulose were the intermediate products from the reaction. Higher yields of MG and GADMA were obtained over metal ions with higher pKa values on the conversion of glucose as shown in Fig. 2. On the contrary, the yields of fructose and xylulose decreased dramatically when catalysts were added, especially over metal ions with lower pKa values as shown in Figs. 2 and 4. These results indicated that a retro-aldol reaction of fructose or xylulose followed the isomerization, and a certain degree of Lewis acidity was favorable for the retro-aldol reaction of fructose or xylulose to break the carbon chain. A retro-aldol reaction of fructose or xylulose resulted in glyceraldehyde, which can be isomerized to 1, 3 dihydroxyacetone.

With dehydration, methanol addition, and tautomerization (Holm *et al.* 2010; Wang *et al.* 2017), MLA is formed, and this is the main reaction pathway as shown by the green line.

Both GADMA and MG, the two main side-products formed by the reaction of methanol and glycolaldehyde, are derived from the retro-aldol reaction of glucose, xylose, or xylulose. As shown in Fig. 3, during the conversion of fructose, small amounts of GADMA and MG were detected, which indicated that GADMA and MG were derived from glucose, and that the isomerization of fructose to glucose was difficult. Comparing Figs. 2 and 4, the conversion of xylose and the yield of MLA were lower than those for glucose, whereas the yields of GADMA and MG were correspondingly much higher. As xylose is a C5 sugar, the retro-aldol reaction of xylose or xylulose results in a two-carbon product and a three-carbon product, which may result in a higher yield of GADMA and MG and a lower yield of MLA.

Glucopyranoside is derived from the etherification of the -OH group between glucose and methanol, and xylopyranoside from xylose. Comparing Figs. 8(a) and 8(c), strong Lewis acidity led to the etherification between methanol and glucose or xylose to glucopyranosides or xylopyranoside. Additionally, the yield of xylopyranoside from xylose was lower than the yield of glucopyranoside from glucose, which suggested that the etherification of glucose was easier than that of xylose.

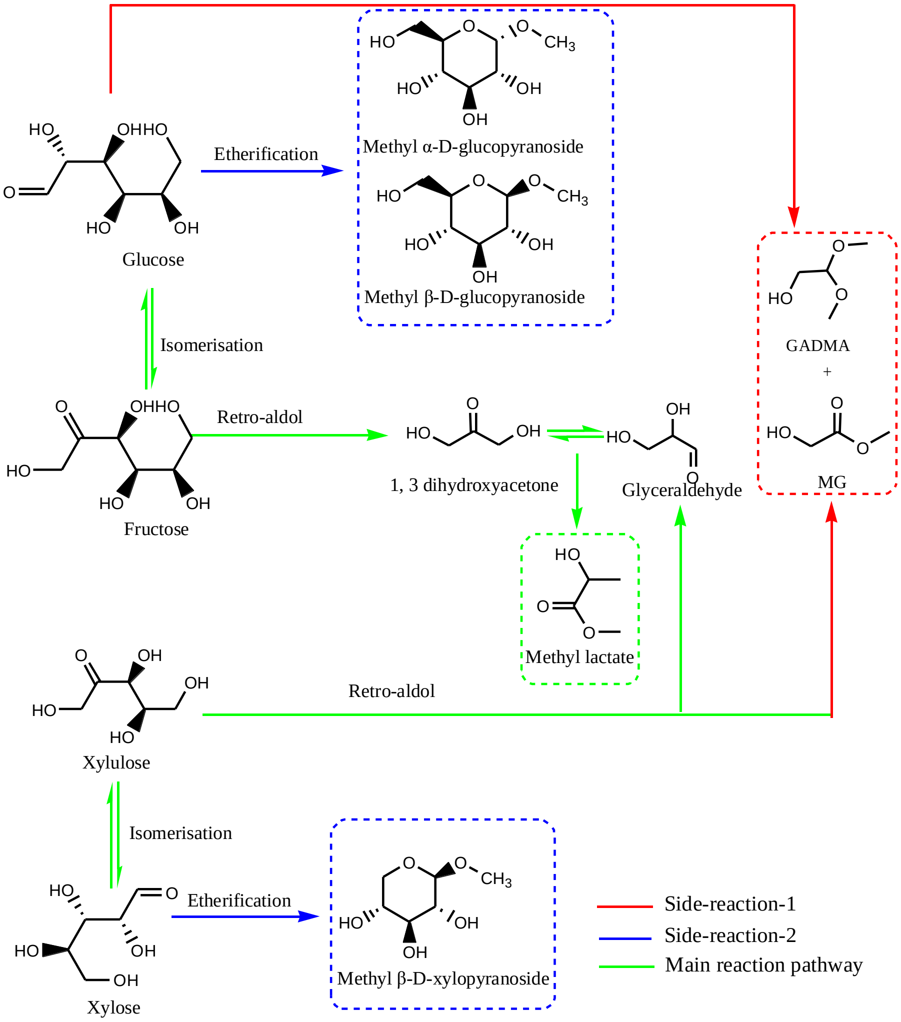


Fig. 9. Possible reaction pathways for the conversion of glucose and xylose in near-critical methanol

CONCLUSIONS

1. The feasibility of simultaneous catalytic conversion of C6 and C5 sugars to MLA in near-critical methanol was confirmed.
2. Lewis acidity, related to the pKa value of the metal ions, affected the yield of MLA. A medium Lewis acidity was favorable for the MLA production.
3. $InCl_3$ exhibited the best catalytic activity for the conversion of sugars. With $InCl_3$, MLA yield reached 36% on the simultaneous conversion of C6 and C5 sugars.
4. Trends of catalytic conversion of C6 and C5 sugars were similar.
5. Possible reaction pathways for simultaneous conversion of C6 and C5 sugars to MLA in near-critical methanol were proposed.

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