

One-Pot Conversion of Cellulose into 2,5-Hexanedione in H₂O-Tetrahydrofuran Co-Solvents

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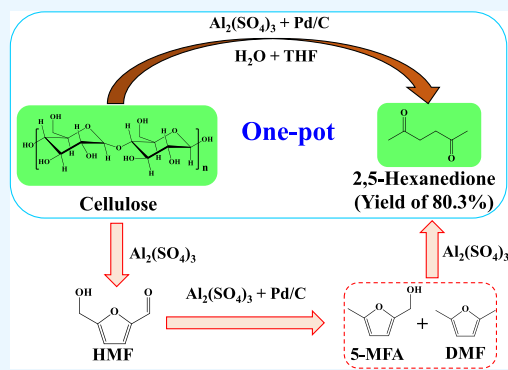
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ABSTRACT: Catalytic conversion of cellulose into the novel platform molecule 2,5-hexanedione (HXD) is regarded as one feasible approach for high-value utilization of biomass resources. Here, we reported one efficient way of one-pot conversion of cellulose into HXD with high yield of 80.3% in H₂O and tetrahydrofuran (THF) mixture within Al₂(SO₄)₃ combined with Pd/C as a catalyst. In the catalytic reaction system, Al₂(SO₄)₃ could catalyze the conversion of cellulose into 5-hydroxymethylfurfural (HMF), and Pd/C combined with Al₂(SO₄)₃ could catalyze the hydrogenolysis of HMF into furanic intermediates such as 5-methylfurfuryl alcohol and 2,5-dimethylfuran (DMF) without causing over-hydrogenation of these furanic intermediates. These furanic intermediates were finally transformed into HXD catalyzed by Al₂(SO₄)₃. Besides, the H₂O/THF ratio could significantly influence the reactivity of the hydrolytic furanic ring-opening of the furanic intermediates. The catalytic system also showed excellent performance on the conversion of other carbohydrates (glucose and sucrose) into HXD.



1. INTRODUCTION

The social concerns on energy shortage and environment pollution drive our human society to develop efficient methods to produce fuel, energy, and materials from the renewable and sustainable resources. In such a context, the catalytic conversion of the abundant lignocellulose to high-quality transportation fuels and value-added chemicals has drawn tremendous attention.^{1–3} During the past decades, great efforts have been devoted to the conversion of the biomass into simpler and more easily processed platform chemicals such as 5-hydroxymethylfurfural (HMF),⁴ 2,5-dimethylfuran (DMF),^{5,6} levulinic acid,⁷ lactic acid,⁸ and 2,5-hexanedione (HXD),^{9–11} because these platform chemicals could bridge biomass feedstocks and downstream high-end chemicals. Among these platform chemicals, the linear diketone HXD could be used as an intermediate for producing liquid fuels, fine chemicals, and polyesters from lignocellulosic biomass.^{9,12–16} For example, HXD could be used as a key intermediate for producing polycycloalkanes, which are the primary components of some advanced aviation fuels (such as JP-10, RJ-4, JP-900, etc.).^{9,17} The conversion of HXD into *p*-xylene, one basic chemical for polyester and pharmaceutical industries, has also been reported.¹⁸ Besides, HXD could also be used to synthesis pyrrole derivatives by Paal-Knorr condensation with primary amines.^{19,20} Thus, the production of HXD from lignocellulosic biomass has received extensive attention.

As shown in Figure 1, producing HXD from cellulose involves the steps of hydrolysis of cellulose into glucose,

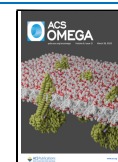
isomerization–dehydration of glucose into HMF, hydrogenolysis of HMF into 5-methylfurfuryl alcohol (5-MFA) and DMF, and hydrolytic ring-opening of these furanic intermediates into HXD.^{21–23} Multiple side reactions could occur during the conversion of cellulose into HXD. For example, the formed glucose could undergo hydrogenation to form sorbitol,^{24–26} while the furanic intermediates all could undergo hydrolytic furan ring-opening to form non-furanic compounds such as levulinic acid and 1-hydroxy-2,5-hexanedione (HHD),^{21,27–29} or be over-hydrogenated into tetrahydrofuran (THF) derivatives such as 2,5-dihydroxymethyltetrahydrofuran (DHMTHF) and 2,5-methyltetrahydrofuran (DMTHF).³⁰ Besides, the formed intermediates containing 1,2-dicarbonyl structure (such as 3-deoxyglucosone and 2,5-dioxo-6-hydroxy-hexanal) could undergo condensation/polymerization to form humin type polymers.^{31,32}

As mentioned above, conversion of cellulose into HMF is one crucial step for synthesis of HXD from cellulose. Multiple catalytic reaction systems have been developed for conversion of biomass into HMF, and the biphasic systems consisting of H₂O and organic solvents such as THF, methyl

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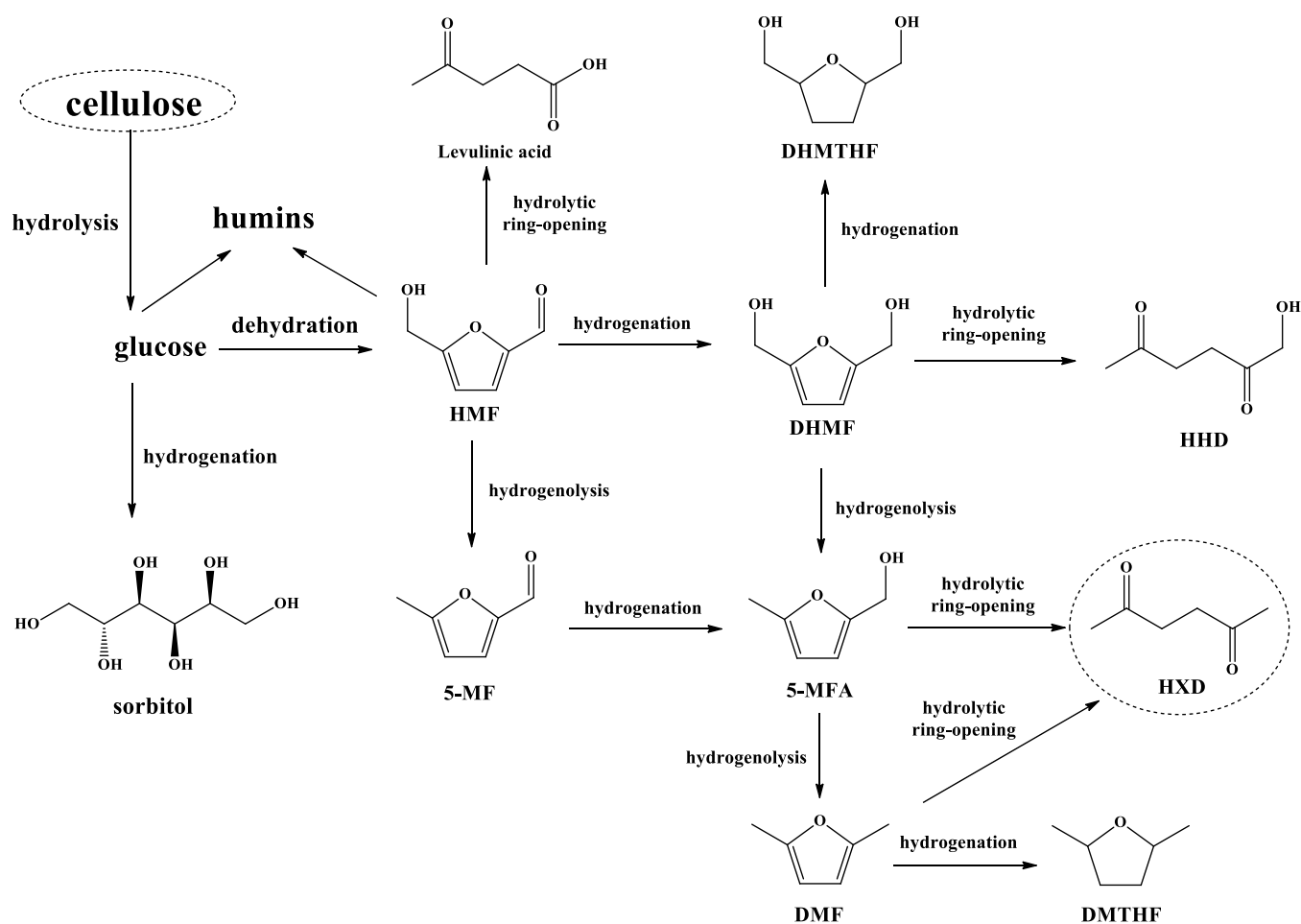


Figure 1. Route of conversion of cellulose into HXD and byproducts.

isobutyl ketone (MIBK), butanol, and γ -valerolactone (GVL) are reported to be efficient for the process.^{33–36} For example, Cao et al. reported that the excellent HMF yield of 69.8% from cellulose could be achieved in the NaCl–H₂O/THF biphasic system over solid catalyst HfO(PO₄)₂,³⁶ and Shen et al. reported that Al₂(SO₄)₃ could catalyze the conversion of the ball-milled cellulose in the H₂O–NaCl–GVL co-solvents to obtain modest HMF yield of 43.5%.³³ Previously, we reported that the Al₂(SO₄)₃-catalyzed conversion of cellulose in the H₂O–THF co-solvents could produce HMF with yield of 45.7%.³⁷

On the other hand, the conversion of the biomass-derived furanics into HXD is also widely studied. The conversion of DMF into HXD could be easily achieved with yield over 90% catalyzed by acids.^{28,38} Multiple literature also reported the high HXD yield of over 70% with 5-MF as feedstock. For example, Fujita et al. reported the high HXD yield of 86% could be achieved from 5-MF in water with Ni₂P/mordenite as a catalyst,³⁹ and Nie et al. reported the high HXD yield of 79% from 5-MF in the water-dichloromethane co-solvents, with Ni₂P and HZSM-5 as a catalyst.¹⁴ However, selective conversion of HMF into HXD is more difficult. Tong et al. reported that the high HXD yield of 94% could be achieved from 5-MF with PdI/Al₂O₃ as a catalyst, but the yield of HXD from HMF was only 50% with the same catalyst.⁴⁰

Although selective conversion of cellulose into HMF and conversion of HMF into HXD have been achieved, the robust structure of cellulose and the longish route of conversion of

cellulose into HXD lead to the one-pot conversion of cellulose into HXD, which is a challenge. In the pioneering work, Chambon et al. reported that ZrW could catalyze the direct conversion of cellulose in aqueous solution to produce HXD with a yield of 24%.⁴¹ Liang et al. reported that H₃PO₄ combined with Ni@NC could catalyze the conversion of cellulose into HXD with a yield of 34.1% in aqueous solution, accompanied by yielding 24.5% of 1-hydroxy-2-hexanone.⁴² One breakthrough research advance was reported by Liu et al., in which the one-pot conversion of cellulose into HXD with a high yield of 64.2% was achieved in H₂O–CH₂Cl₂ co-solvents, with HCl and Pd/C as the catalyst.⁹ In this work, HCl with a high concentration of 36 wt % was employed to catalyze the conversion of cellulose into 5-chloromethyl furfural (CMF), while Pd/C was employed for hydrodechlorination of CMF into DMF, whereas the formed DMF was converted to HXD with the aid of HCl. They proposed that the higher stability of CMF than HMF in the H₂O–CH₂Cl₂ co-solvents was the main reason for the high efficiency of the catalytic reaction system. This research progress greatly inspired the research enthusiasm on one-pot conversion of cellulose into HXD. Recently, the same research team reported that 66% of HXD could be produced from cellulose by direct hydrogenolysis over a commercial Pd/C catalyst in a toluene/NaCl aqueous solution biphasic system.¹⁰ They also proposed that NaCl could catalyze the conversion of cellulose into CMF, and the NaCl-treated Pd/C could selectively catalyze the hydrogenolysis of CMF into DMF.

Table 1. Influence of H₂O/THF Ratio on the Conversion of HMF into HXD^a

entry	solvent (mL)		conversion (%)	yield (%)				
	H ₂ O	THF		5-MF	5-MFA	DMF	HXD	others ^b
1	1	10	100	11.9	5.8	43.6	26.1	12.6
2	2	9	100	14.3	4.6	32.5	35.2	13.4
3	3	8	100	9.1	4.1	13.8	66.1	6.9
4	4	7	100	2.1	5.6	4.6	82.8	4.9
5	5	6	100	4.4	3.6	1.8	72.7	17.5
6	6	5	100	3.8	0	2.0	56.6	37.6
7	7	4	100	2.6	0	0	43.7	53.7
8	11	0	86.9	0	0	0	8.2	78.7

^aReaction condition: 0.5 g of HMF, 0.15 g of Al₂(SO₄)₃·18H₂O, 0.05 g of Pd/C, 2.0 MPa H₂, 190 °C, 60 min. ^bThe yield was calculated by carbon balance.

Given that the satisfactory yield of HMF could be obtained from cellulose in H₂O–THF co-solvents,³⁷ we proposed that direct conversion of cellulose in the H₂O–THF co-solvents in the presence of homogeneous acidic catalysts and noble metal may provide satisfactory yield of HXD. Herein, we designed one H₂O–THF reaction system for one-pot conversion of cellulose into HXD, within Al₂(SO₄)₃ and metal Pd/C as catalysts, and high HXD yield of 80.3% was obtained. This work could provide new insights into the catalytic reaction system for the conversion of biomass into valuable chemicals.

2. MATERIALS AND METHODS

2.1. Materials. Cellulose (50 μm), glucose monohydrate, HMF (99%), DMF (99%), 5-MF (98%), 5-MFA (97%), DHMF (99%), HXD (99%), Pd/C (with a noble metal loading of 5%), Pt/C (with a noble metal loading of 5%), and Ru/C (with a noble metal loading of 5%) were all purchased from Aladdin Reagents company (China). THF (99.5%), H₂SO₄ (98%), and the metal salts used in this study were all analytically pure grade. All reagents were used without further purification.

2.2. Conversion of Cellulose into HXD. The catalytic conversion of cellulose and HMF into HXD was proceeded in one parallel screening plant containing four stainless steel reactors with a volume of 35 mL. In a typical process, 0.5 g of cellulose, 0.15 g of Al₂(SO₄)₃·18H₂O, 0.05 g of Pd/C, 4 mL of H₂O, 7 mL of THF and one magnetic stir bar were loaded into each reactor. The reactors were sealed and purged with hydrogen four times and then pressurized to a final pressure of 2 MPa at room temperature. Then, the reactors were put into a thermal conductive plate, heated to 190 °C, and held for 60 min under stirring (1000 rpm). After completion, the reactors were taken out and cooled down to room temperature using water. Then, the reaction mixture in each reactor was taken out and diluted by ethanol for analysis.

2.3. Quantitative Analysis Methods. The quantitative analysis of 5-MF, 5-MFA, DMF, and HXD was proceeded on a gas chromatograph (GC9790Plus, Fuli Instrument company) equipped with a FID detector and an KB-1 column (50 m × 0.32 mm × 1.00 μm). The concentration of these compounds was determined by the internal standard method, with ethyl levulinate as the internal standard substance. The vaporization temperature was set as 250 °C and the detection temperature was 300 °C. The column temperature was kept at 50 °C for 3 min and then heated to 240 °C with a rate of 20 °C/min.

The HMF concentration in the reaction mixture was analyzed by means of high-performance liquid chromatography (HPLC) equipped with an UV detector (with the wavelength

of 254 nm) and a Zorbax SB-C18 column, using water–methanol (40:60, v/v) as the mobile phase at a flow rate of 0.5 mL/min.

2.4. Calculation of Conversion and Yield. The conversion of cellulose was calculated by the weight difference of dried solid contents before and after the reaction, assuming the weight of the solid catalyst was constant.

$$\text{Conversion (\%)} = \frac{m_{\text{cellulose}} + m_{\text{catalyst}} - m_{\text{residue}}}{m_{\text{cellulose}}}$$

The product yield was determined on a carbon basis by following equation

$$\text{yield (\%)} = \frac{C \times V/M}{m_{\text{cellulose}}/162}$$

C denotes the concentration of the product in the reaction solvent, *V* denotes the volume of the reaction system, and *M* denotes the molar mass of each product. The number 162 is the molar mass of the cellulose unit.

3. RESULTS AND DISCUSSION

3.1. Influence of H₂O/THF Ratio on Conversion of HMF into HXD. As is known to all, the hydrogenolysis of HMF needs a metal catalyst, and the hydrolytic furan ring-opening of the furanic intermediates (5-MFA and DMF) is catalyzed by an acidic catalyst.^{28,29} In this study, Al₂(SO₄)₃ was employed as an acidic catalyst because Al₂(SO₄)₃ could generate strong Brønsted acid (H⁺) and Lewis acid ([Al(OH)₂]⁺) in aqueous solution.^{37,43} Pd/C was also employed here because of its excellent activity on catalyzing the hydrogenolysis of HMF.^{44–46}

In the beginning, we studied the influence of the H₂O/THF ratio on conversion of HMF into HXD. As shown in Table 1, the H₂O/THF ratio showed a significant impact on the conversion of HMF into HXD. With a low H₂O/THF ratio of 1/10, the yield of HXD was only 26.1%, accompanied by the total yield of furanic compounds reached over 60% (Table 1, entry 1). The low yield of HXD and the high yield of furanic compounds indicated that the hydrolytic ring-opening of the furanic intermediates could not proceed with low H₂O content. With the increase in the H₂O/THF ratio from 1/10 to 4/7, the yield of HXD increased from 26.1 to 82.8%, accompanied by the decrease in the total yield of the furanic compounds from over 60% to below 15% (Table 1, entry 2–4). The increase in the yield of HXD and the decrease in the yield of furanic compounds with the increase of H₂O/THF ratio were ascribed to the fact that the increase in H₂O content

Table 2. Conversion of Furanic Intermediates Into HXD^a

entry	reactant	solvent		catalyst		conversion (%)	yield (%)		
		H ₂ O (mL)	THF (mL)	Al ₂ (SO ₄) ₃ ·18H ₂ O (g)	Pd/C (g)		HXD	DMF	S-MFA
1	DMF	4	7	0.15	0.05	52.2	43.5		
2	S-MFA	4	7	0.15	0.05	93.8	83.7	7.4	
3	S-MF	4	7	0.15	0.05	100	50.4		0
4	DMF	4	7	0.15	0	100	98.4		
5	DMF	0	11	0.15	0.05	8.6	0		
6	S-MFA	0	11	0.15	0.05	100	4.8	92.4	
7	S-MF	0	11	0.15	0.05	100	2.6	63.2	11.9
8	DMF	11	0	0.15	0.05	41.7	11.5		
9	S-MFA	11	0	0.15	0.05	100	3.6	0	
10	S-MF	11	0	0.15	0.05	100	9.1	0	0
11	DMF	4	7	0	0.05	12.7	3.5		
12	S-MFA	4	7	0	0.05	70.4	13.7	30.9	
13	S-MF	4	7	0	0.05	100	5.2	40.6	8.4

^aReaction conditions: 0.3 g of reactant, 190 °C, 60 min, 2.0 MPa H₂.

could accelerate the hydrolytic ring-opening reaction. However, further increasing the H₂O/THF ratio to over 5/6 leads to the decrease in the yield of HXD and the increase in the yield of unknown byproducts (Table 1, entry 5–7), which should be due to the fact that the high H₂O content in the reaction system could cause the hydrolytic ring-opening of HMF and DHMF. When H₂O was used as the sole reaction solvent, the yield of HXD decreased to only 8.2%, accompanied by the formation of over 79% of unknown byproducts (Table 1, entry 8). The byproducts should be the humins, levulinic acid, and HHD formed by hydrolytic ring-opening of HMF and DHMF.^{28,29,47}

The influence of the H₂O/THF ratio on the conversion of HMF into HXD could be explained by the fact that the H₂O/THF ratio could influence the reaction activity of the hydrolytic ring-opening of the furanic intermediates. As shown in Figure 1, the furanic intermediates (DHMF, S-MF, S-MFA, and DMF) all could undergo hydrogenation to form downstream furanic or THF derivatives^{27,44,48,49} or undergo hydrolytic ring-opening reaction to form non-furanic products such as levulinic acid, HXD, and HHD.^{21,47,50–52} With a low H₂O/THF ratio of 1/10 and 2/9, the hydrolytic furan ring-opening of the furanic intermediates was inactive, thus the furanic intermediates (S-MFA and DMF) could not undergo hydrolytic ring-opening reaction to form HXD.^{44,48,49} With the increase in the H₂O/THF ratio of the reaction system, the hydrolytic furan ring-opening of DMF and S-MFA was accelerated; thus, the HXD became the main product. However, further increasing the H₂O/THF ratio of the reaction system could lead to the DHMF and HMF, which underwent hydrolytic ring-opening reaction before they can undergo hydrogenolysis; thus, the levulinic acid or HHD became the main product.^{21,47,50,51} In fact, it has been widely reported that hydrogenolysis of HMF in water favors the production of HHD instead of HXD.⁵³ Thus, only with a proper H₂O/THF ratio of 4/7, the HMF, DHMF, and S-MF could preferentially undergo hydrogenolysis to form S-MFA and DMF, while the S-MFA and DMF could preferentially undergo hydrolytic ring-opening reaction; thus, the HXD became the main product from HMF.

In brief, the Al₂(SO₄)₃ combined with Pd/C could efficiently catalyze the conversion of HMF into HXD with a high yield of 82.8% in the H₂O–THF reaction mixture. The H₂O content

in the reaction system played a critical role in hydrolytic ring-opening of these furanic intermediates.

3.2. Mechanism Study on the Conversion of HMF into HXD. To gain a deep insight into the reaction mechanism of conversion of HMF into HXD in the H₂O–THF co-solvents, we further studied the conversion of the furanic substrates (S-MF, S-MFA, and DMF) in the H₂O–THF reaction system.

In the beginning, we studied the conversion of these furanic substrates in the optimized reaction system (4 mL of H₂O, 7 mL of THF, 0.15 g of Al₂(SO₄)₃·18H₂O, and 0.05 g of Pd/C). Under such a condition, the yield of HXD from DMF, S-MFA, and S-MF were 43.5, 83.7, and 50.4%, respectively (Table 2, entry 1–3). Obviously, the yield of HXD obtained from S-MFA was higher than those from DMF and S-MF, which was in accord with several previous literature.^{22,23,40} The higher yield of HXD from S-MFA could be due to the fact that the hydroxymethyl group of S-MFA could promote the ring-opening reaction activity.^{22,23,40} Based on the abovementioned results, we proposed that S-MFA may play a more crucial role compared to DMF during the formation of HXD from HMF in the H₂O–THF co-solvents. Interestingly, the conversion of DMF and the yield of HXD in the absence of Pd/C (Table 2, entry 4) were all significantly higher than those in the presence of Pd/C (entry 1), suggesting that the Pd/C may suppress the hydrolytic ring-opening of DMF. Considering that the furan ring of DMF has an electron-donating effect, we proposed that DMF can be strongly attached to the surface of Pd/C;⁴⁰ thus, the hydrolytic ring-opening of DMF was restrained in the presence of Pd/C.

Then, we studied the conversion of these furanic substrates with THF or H₂O as the sole solvent (Table 2, entry 5–7). When THF was employed as the sole reaction media, the yields of HXD from all these furanic substrates were quite low, which was ascribed to the fact that the hydrolytic furan ring-opening reaction could not proceed without H₂O, as mentioned above. One interesting result was that the conversion of DMF was only 8.6% (Table 2, entry 5), indicating that DMF was rather stable in THF, even with the presence of Al₂(SO₄)₃ and Pd/C. Thus, we proposed that Pd/C could not catalyze the over-hydrogenation of DMF into 2,5-dimethyltetrahydrofuran (DMTHF). On the other hand, DMF became the main product from S-MFA and S-MF (Table 2, entry 6–7), indicating that Pd/C combined with Al₂(SO₄)₃ is

Table 3. Influence of Acid and Noble Metal on the Conversion of Cellulose Into HXD^a

entry	acid	metal	yield (%)				
			HMF	5-MF	5-MFA	DMF	HXD
1		5% Pd/C	0	2.9			10.3
2	Al ₂ (SO ₄) ₃ ·18H ₂ O	5% Pd/C	0	10.9	1.3	2.6	79.2
3	AlCl ₃	5% Pd/C	0	14.3	2.4	4.2	62.6
4	Fe ₂ (SO ₄) ₃ ·xH ₂ O	5% Pd/C	0	12.8	2.7	3.8	39.0
5	FeCl ₃ ·6H ₂ O	5% Pd/C	0	8.7	2.3	4.1	47.5
6	SnCl ₄ ·5H ₂ O	5% Pd/C	0	12.7	2.8	4.2	70.7
7 ^b	H ₂ SO ₄	5% Pd/C	0	8.2	1.9	3.4	73.4
8	Al ₂ (SO ₄) ₃ ·18H ₂ O	5% Pt/C	0	14.7	1.7	4.3	64.6
9	Al ₂ (SO ₄) ₃ ·18H ₂ O	5% Ru/C	0	12.4	1.6	3.9	39.2
10 ^c	Al ₂ (SO ₄) ₃ ·18H ₂ O		45.7	0	0	0	0

^aReaction condition: 0.5 g of cellulose, 0.15 g of acidic salt, 0.05 g of noble metal catalyst, 4 mL of H₂O, 7 mL of THF, 2.0 MPa H₂, 190 °C, 1 h. ^b20 μL H₂SO₄ was used. ^cReaction condition: 2 mL of H₂O, 8 mL of THF, 190 °C, 1 h.

quite efficient in the process of hydrogenolysis of the side chain of these furanic intermediates. However, when H₂O was employed as the sole solvent, the selectivity of HXD from all these furanic reactants was also quite low (Table 2, entry 8–10), which could be explained by the fact that the stability of HXD and these furanic substrates in acidic aqueous solution was much lower than that of THF.³⁸ Thus, we proposed that the role of THF in the reaction system was to improve the stability of HXD and furanic intermediates.

In order to reveal the role of Al₂(SO₄)₃, we also studied the conversion of these furanics in the H₂O–THF co-solvents without Al₂(SO₄)₃. Under such a condition, when DMF was used as feedstock, the conversion of DMF (12.7%) and the yield of HXD (3.5%) were all much lower than those in the presence of Al₂(SO₄)₃ (Table 2, entry 11 vs entry 1), indicating that Al₂(SO₄)₃ played an important role in hydrolytic ring-opening of DMF. When 5-MF and 5-MFA were employed as reactants, the total yields of HXD and DMF were also obviously lower than those obtained in the presence of Al₂(SO₄)₃ (Table 2, entry 12–13 vs entry 2–3), suggesting that Al₂(SO₄)₃ also played a critical role in the hydrogenolysis of 5-MFA and 5-MF.

In short, the abovementioned results indicated that H₂O, THF, Al₂(SO₄)₃, and Pd/C all played a critical role in conversion of HMF into HXD. H₂O and Al₂(SO₄)₃ were all necessary for the hydrolytic furan ring-opening of DMF and 5-MFA. The Pd/C combined with Al₂(SO₄)₃ could efficiently catalyze the hydrogenolysis of the furanic intermediates without causing over-hydrogenation of the furan ring. The function of THF was to improve the stability of HXD and these furanics in the reaction system and suppress the hydrolytic ring-opening of HMF and DHMF.

3.3. Conversion of Cellulose into HXD. Inspired by the high yield of HXD from HMF shown above and the previous research advance on the conversion of cellulose into HMF in H₂O–THF co-solvents,³⁷ we further studied the one-pot conversion of cellulose into HXD in the H₂O–THF co-solvents, catalyzed by homogeneous acidic catalysts (Al₂(SO₄)₃·18H₂O, anhydrous AlCl₃, Fe₂(SO₄)₃·xH₂O, FeCl₃·6H₂O, SnCl₄·5H₂O, and H₂SO₄) combined with noble metal catalysts (Pd/C, Pt/C, and Ru/C).

First, we screened the acidic catalyst for conversion of cellulose into HXD, within Pd/C as a hydrogenation catalyst (Table 3, entry 1–7). As shown, when no acidic catalyst was added, the yield of HXD was only 10.3%, which was ascribed to the fact that the hydrolysis of cellulose could not proceed

without an acidic catalyst.³⁷ In contrast, the addition of the acidic catalysts into the reaction system greatly increased the yields of HXD. For the reaction systems with Al₂(SO₄)₃, AlCl₃, Fe₂(SO₄)₃, FeCl₃, SnCl₄, and H₂SO₄ as a catalyst, the yields of HXD from cellulose were 79.2, 62.6, 39.0, 47.5, 70.7, and 73.4%, respectively, indicating that the catalytic performance of these acidic salts followed the order of Al₂(SO₄)₃ > H₂SO₄ > SnCl₄ > AlCl₃ > FeCl₃ > Fe₂(SO₄)₃. The excellent performance of Al₂(SO₄)₃ and SnCl₄ on conversion of cellulose into HXD was in accord with their excellent catalytic activity on conversion of cellulose into HMF.³⁷ Interestingly, the H₂SO₄ combined with Pd/C also showed excellent performance on conversion of cellulose into HXD, which should be due to the fact that H₂SO₄ could catalyze the conversion of cellulose into HMF and catalyze the conversion of furanic intermediates (5-MFA and DMF) into HXD.^{54,55} The better performance of Al₂(SO₄)₃ than H₂SO₄ was ascribed to the fact that Al₂(SO₄)₃ could undergo hydrolysis to form [Al(OH)₂]⁺ and H₂SO₄ in the H₂O–THF mixture, in which [Al(OH)₂]⁺ could catalyze isomerization of glucose into fructose (one crucial step for conversion of glucose into HMF).^{37,43} It should be noted that the yield of HXD obtained from cellulose (79.2%) in the H₂O–THF reaction system was much higher than that of HMF (generally below 55%),^{37,56} indicating that HXD was more suitable as the platform chemical than HMF from biomass.

The catalytic performances of the other noble metals (Pt/C and Ru/C) on conversion of cellulose into HXD were also explored (Table 3, entry 8–9). As shown, the yields of HXD from cellulose in the presence of Pt/C and Ru/C were 64.6 and 39.2%, respectively, all of which were lower than that of Pd/C (79.2%). The results were in accord with that reported by Yu et al., who also found that Pt/C and Ru/C were all less active than Pd/C for conversion of cellulose into HXD.¹⁰ The lower HXD selectivity of Pt/C was ascribed to its higher activity for the hydrogenation of the furan ring (which will lead to the hydrogenation of DMF to DMTHF).¹⁰ Besides, the lower HXD selectivity of the Ru/C catalyst can be rationalized by its higher activity for the hydrogenation of glucose into polyols such as sorbitol, mannitol, and erythritol.¹⁰

In brief, the abovementioned results confirmed that Al₂(SO₄)₃ combined with Pd/C is more efficient than other combinations for conversion of cellulose into HXD in the H₂O–THF co-solvents.

3.4. Influence of Catalyst Dosage. As mentioned above, Al₂(SO₄)₃ in the reaction system plays the role of catalyzing

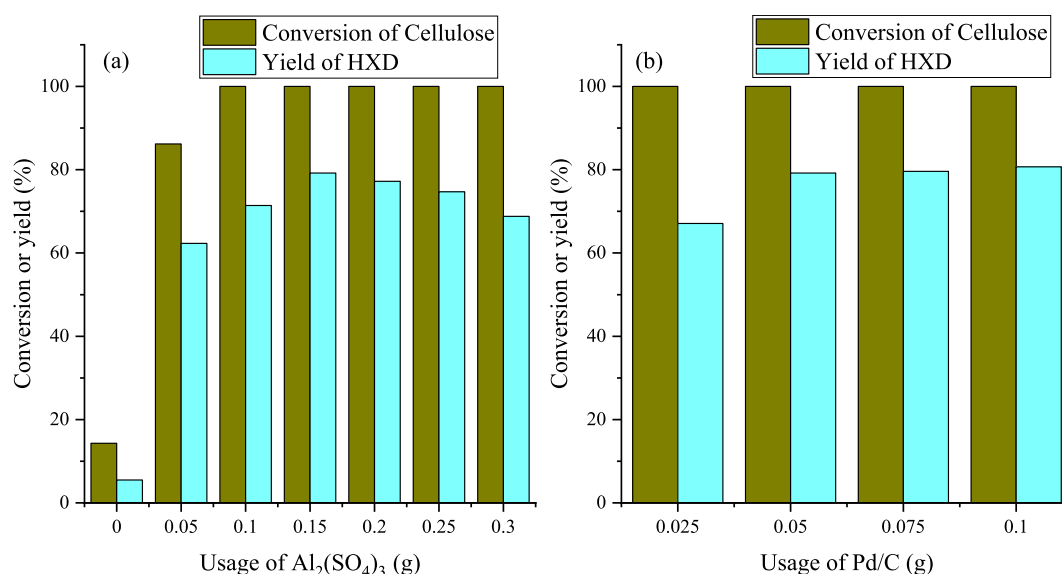


Figure 2. Influence of (a) usage of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and (b) usage of Pd/C on the yield of products from cellulose. Reaction conditions: 0.5 g of cellulose, 0.15 g of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, 0.05 g of Pd/C, 4 mL H_2O , 7 mL of THF, 2.5 MPa H_2 , 190 °C, 60 min.

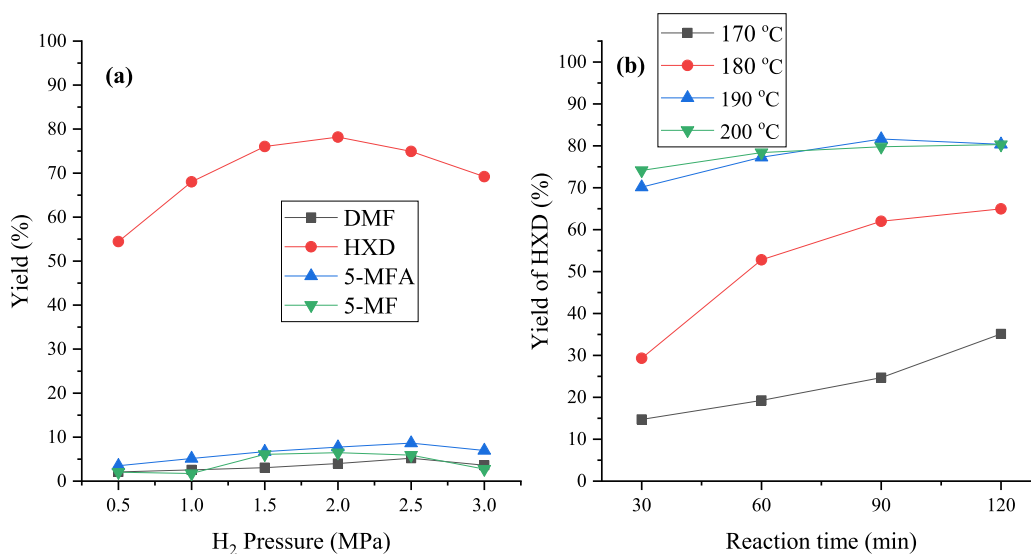


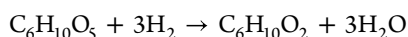
Figure 3. Influence of (a) H_2 pressure and (b) reaction temperature and time on the yield of products from cellulose. All reaction conditions were kept identical except for the one that was varied when necessary: 0.5 g of cellulose, 0.15 g of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, 0.05 g of Pd/C, 4 mL H_2O , 7 mL of THF, 2.0 MPa H_2 , 190 °C, 60 min.

the conversion of cellulose into HMF, and Pd/C plays the role of catalyzing the hydrogenolysis of HMF into the 5-MFA and DMF. Thus, we further studied the influence of the usage of $\text{Al}_2(\text{SO}_4)_3$ and Pd/C on the yield of HXD from cellulose. As shown in Figure 2a, with the increase of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ usage from 0.05 to 0.15 g, the yield of HXD increased from 63.2 to 79.2%, which was ascribed to the fact that the increase in the usage of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ could promote the conversion of cellulose into HMF and the conversion of 5-MFA and DMF into HXD. Further increase in the usage of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ to 0.2 g led to the decrease in HXD yield to 76.8%, which was ascribed to the fact that the excess $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ could promote the hydrolytic ring-opening of HMF and DHMF into byproducts such as levulinic acid, HHD, and humin.

Figure 2b shows the influence of Pd/C usage on the conversion of cellulose to HXD. With the increase of Pd/C

usage from 0.025 to 0.05 g, the yield of HXD increased from 67.1 to 79.2%, which was ascribed to the fact that the increasing Pd/C could accelerate the hydrogenolysis of HMF and DHMF.⁴⁰ Further increasing the usage of Pd/C to 0.1 g only slightly increased the HXD yield to 80.7%, indicating that the HXD yield was not sensitive with the Pd/C usage in range between 0.05 and 0.1 g. A further increase in the usage of Pd/C could lead to a further increase in the yield of HXD, but pursuing the high yield of HXD by increasing the usage of Pd/C is not feasible because of the high cost of Pd/C.

3.5. Optimization of Other Reaction Parameters. The influence of other reaction parameters (H_2 pressure, reaction temperature, and time) was further studied. As shown in Figure 3a, relatively low HXD yield of 54.4% was obtained under low H_2 pressure of 0.5 MPa. According to the following equation, conversion of per mole unit of cellulose into HXD could consume 3 moles of H_2 .



Thus, totally converting the 0.5 g of cellulose ($\sim 3.1 \times 10^{-3}$ mol glucose unit) into HXD would consume around 9.3×10^{-3} mol H_2 . On the other hand, the volume of H_2 in the reactor was only around 24 mL, so the pressure of 9.3×10^{-3} mol H_2 was around 0.86 MPa, which indicated that around 0.86 MPa H_2 in the reactor was enough for totally conversion 0.5 g of cellulose into HXD. Thus, the relatively low HXD yield obtained under low H_2 pressure of 0.5 MPa was ascribed to the shortage of the H_2 in the reaction system. With the increase of the H_2 pressure from 1.0 to 2.0 MPa, the yield of HXD increased from 68.1 to 79.2%, which should be due to the fact that the increase of H_2 pressure could accelerate the hydrogenolysis of HMF into furanic intermediates (5-MFA and DMF). However, further increasing the H_2 pressure to 2.5 MPa led to the slight decrease of the HXD yield to 74.8%, which should be due to the fact that the excess H_2 pressure could lead to the over-hydrogenation of the furanic intermediates into THF derivatives.⁴⁰

Figure 3b shows the reaction temperature (170–200 °C) and time (30–120 min) on the yield of HXD from cellulose. At the low temperature of 170 °C, the yield of HXD was always below 25%, which was ascribed to the fact that the temperature of 170 °C was insufficient for $\text{Al}_2(\text{SO}_4)_3$ to catalyze the hydrolysis of cellulose.³⁷ With the increase of the reaction temperature to 180 °C, the peak yield of HXD significantly increased to 65.0%, which clearly confirmed that the cellulose-to-HXD process is favored at elevated temperature. For the reaction temperature of 190 and 200 °C, the peak yields of HXD were 80.1 and 80.3%, respectively, indicating that the reaction temperatures of 190–200 °C were suitable for conversion of cellulose to HXD.

The reaction time showed less significant influence on the yield of HXD from cellulose. As shown in Figure 3b, at the reaction temperatures of 190 and 200 °C, the yields of HXD have reached over 60% with 30 min, and the yields of HXD all reached around 80% with reaction time of 60 min, indicating that the conversion of cellulose into HXD was quite fast under such conditions. Further extending the reaction time led to slight decrease in the yield of HXD, which was ascribed to the further hydrogenation of HXD.

As shown above, the high HXD yield of 80.3% was obtained from cellulose in the H_2O –THF co-solvents, with $\text{Al}_2(\text{SO}_4)_3$ and Pd/C as a co-catalyst. The yield of HXD obtained here was obviously higher than that of 24–35% obtained in water with ZrW or $[\text{Ni}@\text{NC} + \text{H}_3\text{PO}_4]$ as a catalyst,^{41,42} and slightly higher than that of 64.2% obtained in the H_2O – CH_2Cl_2 co-solvents with $[\text{HCl} + \text{Pd}/\text{C}]$ as a catalyst.⁹ Compared with the work of conversion of cellulose in H_2O – CH_2Cl_2 co-solvents with $[\text{HCl} + \text{Pd}/\text{C}]$ as catalysts, the catalyst $\text{Al}_2(\text{SO}_4)_3$ employed here is safer for transportation and storage, and the solvent THF can be formed from renewable biomass resource,⁵⁷ making the process reported here more feasible for commercial.

Little humin was formed during the process, and the carbon balance reached almost 100%. As has been reported previously, humin was formed by aldol condensation of the α -carbonyl aldehydes such as 3-deoxyglucosone (formed by dehydration of glucose) and 2,5-dioxo-6-hydroxyhexanal (formed by hydrolytic ring-opening of HMF).^{31,32} We proposed that these α -carbonyl aldehydes could not be formed under the

hydrogenation condition, because of which little humin was formed.

3.6. Conversion of Other Feedstocks into HXD. The applicability of the catalytic reaction system on the other carbohydrates was further explored. Figure 4 shows the yield of

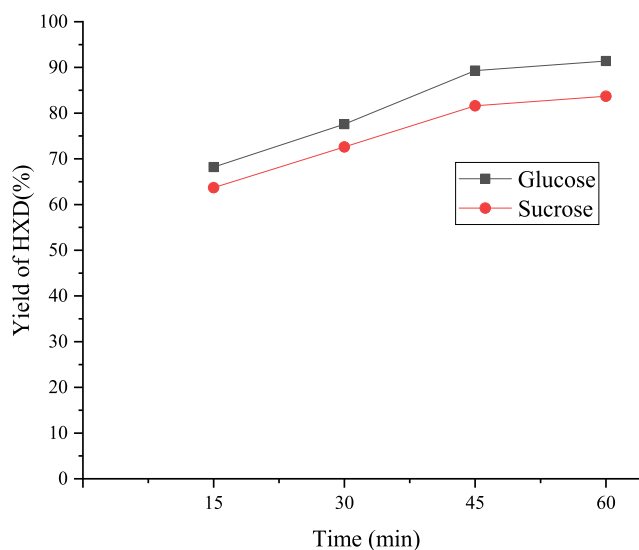


Figure 4. Yield of HXD from glucose and sucrose varied with reaction times. Reaction conditions: 0.5 g of reactant, 0.15 g of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, 0.05 g of Pd/C, 4 mL of H_2O , 7 mL of THF, 200 °C, 2.0 MPa H_2 .

HXD from glucose and sucrose obtained at 200 °C, with reaction times of 15, 30, 45, and 60 min. In only 15 min, the yields of HXD from glucose and sucrose had reached 68.2 and 63.7%, respectively, indicating that the catalytic reaction system was also quite efficient with these carbohydrates as feedstocks. Obviously, the yield of HXD from glucose was higher than that from sucrose, which should be due to the fact that the conversion of sucrose into HXD involved the extra reaction step of hydrolysis of sucrose into glucose and fructose. The peak HXD yields from glucose and sucrose were 91.4 and 83.7%, respectively, suggesting that the reaction system with those carbohydrates as feedstock also have great application prospect.

4. CONCLUSIONS

The one-pot selective conversion of cellulose into HXD with high yield of 80.3% was achieved in H_2O –THF co-solvents, with $\text{Al}_2(\text{SO}_4)_3$ combined with Pd/C as a catalyst. The excellent performance of the reaction system was ascribed to the fact that the $\text{Al}_2(\text{SO}_4)_3$ could efficiently catalyze the conversion of cellulose into HMF, and the Pd/C combined with $\text{Al}_2(\text{SO}_4)_3$ could efficiently catalyze the hydrogenolysis of HMF into furanic intermediates 5-MFA and DMF without causing the over-hydrogenation of the furanic intermediates. The $\text{H}_2\text{O}/\text{THF}$ ratio of the reaction system could influence the conversion of cellulose into HXD by altering the reactivity of the hydrolytic ring-opening of the furanic intermediates. $\text{Al}_2(\text{SO}_4)_3$ also played a crucial role in hydrolytic ring-opening of the furanic intermediates.

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Notes

The authors declare no competing financial interest.

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