ACS Sustainable Chemistry & Engineering

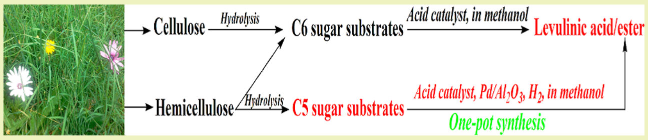
Research Article

pubs.acs.org/journal/ascecg

One-Pot Synthesis of Levulinic Acid/Ester from C5 Carbohydrates in a Methanol Medium

Xun Hu, Yao Song, Liping Wu, Mortaza Gholizadeh, and Chun-Zhu Li*

Fuels and Energy Technology Institute, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia



ABSTRACT: A process for direct conversion of xylose to methyl levulinate and levulinic acid has been developed in this study. A methanol medium, solid acid catalyst Amberlyst 70, and hydrogenation catalyst Pd/Al_2O_3 were used to direct xylose to follow the designed route to the target products. The methanol medium can prevent the hydrogenation of xylose to xylitol via the transformation of xylose into methyl xylosides. Amberlyst 70 catalyzes the dehydration of methyl xylosides into furfural, while Pd/Al_2O_3 catalyzes the hydrogenation of furfural into furfuryl alcohol. The hydrolysis/methanolysis of furfuryl alcohol over Amberlyst 70 produces levulinic acid/ester. Among these steps, the hydrogenation of furfural is the one determining the overall selectivity from xylose to levulinic acid/ester. The ideal hydrogenation catalyst needs to be selective to hydrogenate only the carbonyl group of furfural but not the furan rings.

KEYWORDS: *C5 carbohydrates, Acid-catalyzed conversion, Hydrogenation, Furfural, Levulinic acid*

■ INTRODUCTION

Cellulose and hemicelluloses are the major components of abundantly available biomass and are the feedstock for value-added chemicals and biofuels.[1−4] Via hydrolysis, cellulose produces mainly glucose, and glucose can be further converted to levulinic acid, the building block for chemical diversity and biofuels production.[5−10] Via hydrolysis, hemicellulose produces sugar monomers with an abundance of C5 sugars such as xylose.[11,12] Although C6 sugars and C5 sugars share many similarities, they have quite different destinies via further hydrolysis, producing levulinic acid[13−19] and furfural,[20,21] respectively. If the C5 sugars could also be directly converted into levulinic acid, then both cellulose and hemicellulose, which account for roughly 2/3 of biomass content,[22] could be converted into the same product, levulinic acid. This will significantly promote the efficiency for levulinic acid production from biomass and also diversify the utilizations of C5 sugars as the feedstock for value-added chemicals.

Although production of levulinic acid from C6 sugars has been intensively investigated, to the best of our knowledge, the one-pot conversion of C5 sugars such as xylose to levulinic acid/ester has not been explored yet. In theory, xylose can be converted into levulinic acid but via several separate steps. The first step is the dehydration of xylose to furfural.[23,24] Furfural is then separated and transformed into furfuryl alcohol via a gas-phase hydrogenation step.[25,26] The followed acid catalysis of furfuryl alcohol in water produces levulinic acid,[27] while in alcohols produces levulinic esters.[28] These separate steps involve heterogeneous and/or homogeneous catalysis, liquid-phase and gas-phase reactions, and also the separation of reaction intermediates such as furfural and furfuryl alcohol via distillation or other ways. These multiprocesses are complex and energy intensive, which could significantly increase the cost in the production of levulinic acid from xylose.

In this study, a simple one-pot synthesis of levulinic acid/ester from xylose and ribose in alcohols has been developed. The concept combines the multiple acid catalysis and hydrogenation steps into one. As is detailed in Scheme 1, the carbonyl group of xylose is first protected from hydrogenation by transformation of xylose into methyl xylosides. Methyl xylosides then dehydrate to furfural and its acetal, which are then hydrogenated to furfuryl alcohol, and the followed acid catalysis produces levulinic acid/ester. There is no need to separate furfural and furfuryl alcohol in the overall process. The multistep acid-catalyzed reactions and the one-step hydrogenation reaction occur simultaneously, which is a simple and effective way to directly produce levulinic acid/ester from C5 carbohydrates.

■ EXPERIMENTAL SECTION

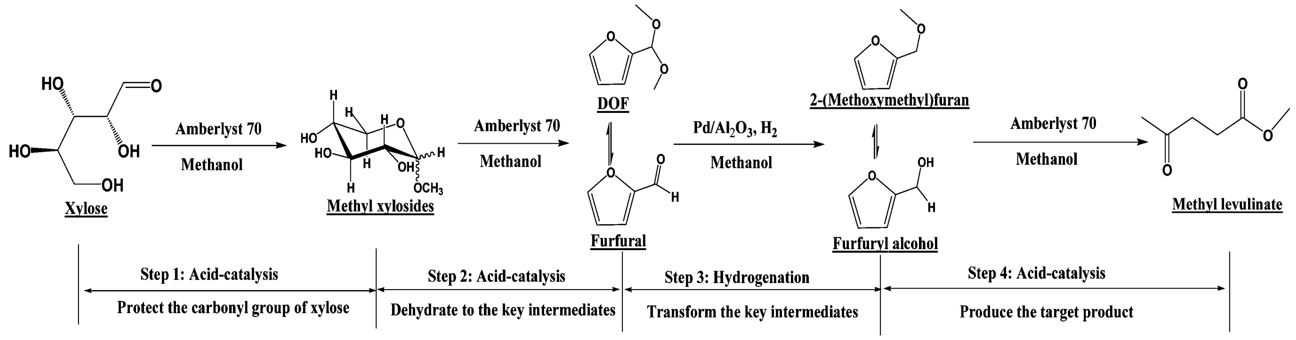
Materials. The reagents and the standards for GC/MS were analytical grade and were obtained from Sigma Aldrich, LC Scientific, Inc. (Canada), Merck Australia, and Carbosynth Limited (U.K.), respectively. Amberlyst 70 is a commercial acidic resin catalyst and was used directly in this study. The noble metal-based catalysts with a reduced form were obtained from Sigma and were used without further reduction. The metal loading is 5 wt %. $Ni-Mo-S/Al_2O_3$ and $Co-Mo-S/Al_2O_3$ catalysts are commercial catalysts and were obtained from Eurecat in France. The catalysts can be used directly without prereduction. The unsupported copper catalysts were obtained by direct reduction of the copper oxide powder purchased from Sigma in autoclave at 250 °C for 120 min.

Experimental Procedure. All the experiments were performed in a 130 mL Hastalloy batch autoclave reactor (Autoclave Engineers, Division of Snap-Tite, Inc.). In a typical run, xylose, Amberlyst 70, the hydrogenation catalyst, and methanol were mixed and loaded into

Received: July 11, 2013
Revised: September 4, 2013
Published: September 10, 2013

ACS Publications © 2013 American Chemical Society

Scheme 1. Proposed Reaction Pathways for the Conversion of Xylose to Levulinic Ester in Methanol with Acid and Hydrogention Catalysts



reactor at room temperature. The xylose loaded in all the runs can totally dissolve in the alcohols used. The specific reaction conditions are detailed in the footnotes of the tables. After checking leakage, the reactor was purged with nitrogen for several times, and then the temperature was increased to the setting one under autogenerated vapor pressure in 20 min. The vapor pressure at 165 °C is typically about 20 bar. Hydrogen was fed immediately after the reaction temperature reaching the setting temperature, and the total pressure was maintained at 70 bar for 120 min. No sample was taken during the run. After finishing the experiment, the liquid samples were separated via filtration for further analysis.

Analytical Methods. Products were analyzed using an Agilent GC-MS (6890 series GC with a 5973 MS detector) with a capillary column (HP-INNOWax) (length: 30 m; internal diameter: 0.25 mm; film thickness: 0.25 μm of cross-linked polyethylene glycol). GC-MS was calibrated with the injection of the standards with different concentrations. A respond factor K_R can be obtained via the equation: [Peak area] = K_R [Concentration of the standard] to calculate concentration of that compound in samples. The concentration of the compound in the sample must be in the range of that of the standards. The detailed operating procedures of GC-MS can be found in the literature.[29] A derivatization method was used to measure concentration of the xylose, generally following the procedures in the literature.[30] Yields of all the products are reported on molar basis in this study.

RESULTS AND DISCUSSION

Importance of Reaction media. Table 1 shows the formation of levulinic acid/ester from xylose/ribose versus temperatures and reaction mediums. Xylose can be converted into methyl levulinate at 140 °C in methanol with Amberlyst 70 (A70) and Pd/Al_2O_3 catalysts. However, the dehydration of methyl xylosides at this temperature is slow. Approximately 20% of the methyl xylosides is still unconverted at the end (run 1 in Table 2), but furfural, the dehydration product from methyl xylosides, is present with negligible concentration. Apparently, it is a minor intermediate. Once furfural was formed, it was converted immediately. The presence of a small amount of furfural in the reaction medium is favorable as furfural is prone to polymerize in the acidic environment.

In run 4 at 175 °C, the total yields of methyl levulinate and levulinic acid reach about 27%. Xylose was converted completely, and no xylitol was detected at the end, proving the protection of the carbonyl group of xylose from hydrogenation in methanol. However, the increase in reaction temperature to 190 °C leads to a significant decrease in levulinic acid/ester formation. One of the main reasons for the decrease in levulinic acid/ester production is the water formed (concentration in reaction medium: 44 wt %) via intermolecular etherification of methanol. The presence of this large amount of water shifts the reaction equilibrium between methyl levulinate and levulinic acid to the acid direction and, more importantly, promotes the side reactions. The further experiments (runs 7 and 8, Table 1) using methanol/water and pure water as reaction mediums prove the negative effects of water. The total yields of levulinic acid/ester are about 9.9% in methanol/water, while they decrease further to about 2.3% in pure water, which is substantially lower than that in pure methanol.

Table 1. Yields of Methyl Levulinate (MLE) and Levulinic Acid (LA) versus Reaction Temperature and Reaction Medium[a]

				yields (%)	
entry	reactants	solvents	T (°C)	MLE	LA
run 1	xylose	methanol	140	17.5	1.2
run 2	xylose	methanol	155	22.8	2.6
run 3	xylose	methanol	165	21.6	3.4
run 4	xylose	methanol	175	21.5	5.4
run 5	xylose	methanol	190	12.6	6.6
run 6[b]	xylose	methanol	165	22.9	3.5
run 7	xylose	methanol/water[c]	165	6.2	3.3
run 8	xylose	water	165	0	2.3
run 9	xylose	ethanol	165	17.7[d]	2.5
run 10	ribose	methanol	165	20.9	3.1

[a] Reaction conditions: Xylose loading: 9.1 wt %. Catalysts: A70 (9.1 wt %) + Pd/Al_2O_3 (9.1 wt %). Residence time = 120 min. P = 70 bar. [b] During run 6, H_2 was fed at beginning. [c] Mass ratio of methanol to water is 1:1. [d] Yield is the that of ethyl levulinate.

In a water medium, xylose can be easily hydrogenated to xylitol,[31] which will not be able to continue to dehydrate to furfural, as is shown in Scheme 2. Xylitol was detected in run 8 (not quantified), proving the hydrogenation of xylose in the water medium. Moreover, in water, the cross-polymerization of xylose and furfural also leads to the low yields of levulinic acid/ester. In a methanol medium, the conversion of xylose into methyl xylosides prevents the conversion of xylose into xylitol, which is an essential step to direct xylose following the designed routes to levulinic acid/ester. Methanol is quite reactive with xylose in the presence of an acid catalyst. In run 6 (Table 1), hydrogen was fed before heating the reactants, while similar yields of levulinic acid/ester are obtained, which proves that in methanol hydrogenation of xylose is effectively suppressed. Methanol not only protects the carbonyl group of xylose but also alleviates the polymerization of furfural and xylose.[32] In ethanol (run 9), xylose is correspondingly converted into ethyl levulinate, a fuel and fragrance

Table 2. Yields of Products Other than Methyl Levulinate and Levulinic Acid[a]

		distribution of the intermediates/products				
entry	typical reaction conditions	MAXP	MBXP	furfural	DOF	cyclopentanone
run 1	xylose, Pd/Al_2O_3 + A70, 140 °C	12.3	8.1	0.6	0.3	1.3
run 2	xylose, Pd/Al_2O_3 + A70, 155 °C	0.7	0.5	0.2	0.07	3.5
run 3	xylose, Pd/Al_2O_3 + A70, 165 °C	0.06	0.1	0	0	5.0
run 4	xylose, Pd/Al_2O_3 + A70, 175 °C	0.06	0.1	0	0	6.1
run 5	xylose, Pd/Al_2O_3 + A70, 190 °C	0.3	0.6	0	0	6.6
run 6	H_2 feeding at beginning	0	0	0.04	0	4.2
run 7	xylose, methanol/water	0.2	0.2	0.08	0	2.1
run 8	xylose, water	0	0	0.1	0	2.2
run 9	xylose, ethanol	0	0	0	0	2.9
run 10	ribose, methanol	0	0	2.1	0.03	3.9
run 11	only Pd/Al_2O_3	0	0	0.06	0	0
run 12	only A70, 0 min	34.4	25.3	15.3	7.4	0
run 13	only A70, 30 min	20.6	14.9	28.8	8.2	0
run 14	only A70, 60 min	7.7	5.9	29.4	4.4	0
run 15	only A70, 90 min	2.6	1.9	19.7	1.9	0
run 16	only A70, 120 min	0.9	0.7	12.0	0.3	0
run 17	Pd/Al_2O_3, A70, 30 min	5.4	3.6	0.7	0.4	2.5
run 18	Pd/Al_2O_3, A70, 60 min	0.9	0.7	0.3	0.1	3.8
run 19	methyl xylosides	—	—	0	0	5.0
run 20	furfural, Pd/Al_2O_3 + A70	0	0	0	0	1.8
run 21	furfural, Pd/Al_2O_3	0	0	0	0	0
run 22	2-furylmethanol, Pd/Al_2O_3 + A70	0	0	0	0	0
run 23	2-furylmethanol, A70	0	0	0	0	0
run 24	xylose loading: 4.8 wt %	0	0	0	0	3.3
run 25	Pd/Al_2O_3 loading: 4.5 wt %	0.2	0.1	0.1	0.03	6.6
run 26	A70 loading: 4.5 wt %	0.3	0.2	0	0	3.9
run 27	Pd/C, 190 °C	0	0	0	0	12.8
run 28	Pd/C, 155 °C	10.4	7.1	0	0	5.4
run 29	Pt/C, 165 °C	0	0	0	0	10.3
run 30	Ru/C, 165 °C	0.1	0.1	0	0	0
run 31	$Ni{-}Mo{-}S/Al_2O_3$ with ZnO, 165 °C	1.2	0.7	2.6	0.7	0.7
run 32	$Co{-}Mo{-}S/Al_2O_3$ with ZnO, 165 °C	1.1	0.6	0.6	0.2	1.0
run 33	$Co{-}Mo{-}S/Al_2O_3$ without ZnO, 165 °C	0.03	0.02	0.03	0	3.2
run 34	unsupported Cu, 165 °C	0	0	0	0	0

[a] Abbreviations: MAXP for methyl α-D-xylopyranoside; MBXP for methyl β-D-xylopyranoside; DOF for 2-(dimethoxymethyl)-furan.

additives.[33,34] Other C5 carbohydrates such as ribose (run 10) could also be converted into levulinic acid/ester despite its different steric structure with that of xylose.

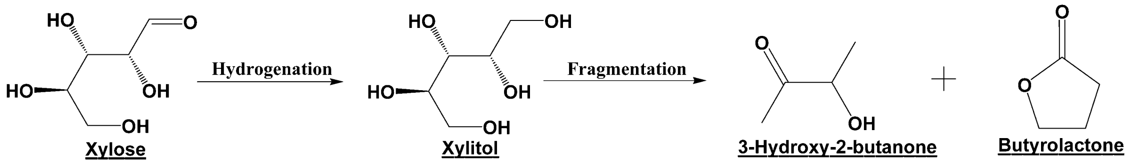
Importance of Pd/Al_2O_3 and A70 Catalysts. Table 3 shows catalytic roles of Pd/Al_2O_3 and A70 catalysts in the conversion of xylose to levulinic acid/ester. With only Pd/Al_2O_3, the acid-catalyzed reactions rarely happen, and the dominant reactions are hydrogenlysis and fragmentation, as shown in Scheme 2. A trace amount of furfuryl alcohol was detected, but it cannot further go to levulinic acid despite the alumina support in Pd/Al_2O_3 may have some weak acidic sites. In addition, a small amount of xylitol was also detected. In the absence of A70, xylose cannot be effectively converted to methyl xylosides. Consequently, the hydrogenation of xylose happened. Over only A70 (runs 12−16), the acid-catalyzed reactions dominate, and methyl levulinate formation is negligible. Furfural is the main product. Without the hydrogenation catalyst, furfural cannot be hydrogenated to furfuryl alcohol. It has nowhere to go, and with the prolonged reaction time, polymerization is its destiny.

Over A70 and Pd/Al_2O_3, polymerization and hydrogenation of furfural are competitive and occur in parallel. The hydrogenation of furfural substantially reduced concentrations of furfural in the reaction medium and consequently suppress the polymerization of furfural. As shown in run 17 in Table 2, over A70 and Pd/Al_2O_3, the yields of furfural is only 0.7%, which is significantly lower than that (28.8%) with only A70 in run 13. The low concentration of furfural indicates that the hydrogenation of furfural proceeds very quickly, which helps to suppress the cross-polymerization of furfural with the intermediates from the dehydration of xylose. In addition, methyl xylosides yields in run 17 over A70 and Pd/Al_2O_3 is about 9% (Table 2), which is also significantly lower than that (about 35%) in run 13 over only A70. This result indicates that the hydrogenation of furfural also facilitates the further dehydration of methyl xylosides to furfural. Methyl xylosides are the only major intermediates in the conversion of xylose to levulinic acid. Clearly, the dehydration of methyl xylosides to furfural is the rate-determining step, and others such as the hydrogenation of furfural to furfuryl alcohol and the following conversion of furfuryl alcohol to levulinic acid/ester proceeds quite quickly.

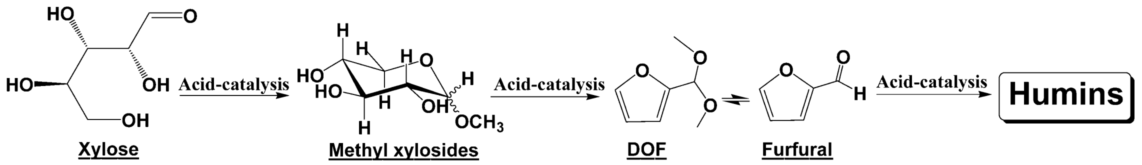
As shown in Scheme 1, the one-pot synthesis of methyl levulinate involves four steps with methyl xylosides, furfural, and furfuryl alcohol as the reaction intermediates. In each step, some side reactions such as polymerizations and undesirable

Scheme 2. Reaction Pathways of Xylose in Water and in Methanol with Dual or Single Catalyst

a. Water medium. Catalysts: Pd/Al_2O_3 + Amberlyst 70.



b. Methanol medium. Catalyst: only Amberlyst 70.



c. Methanol medium. Catalyst: only Pd/Al_2O_3.

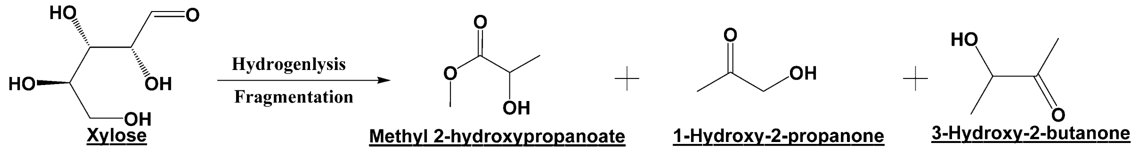


Table 3. Yields of Methyl Levulinate and Levulinic Acid versus Catalysts and Reaction Time[a]

			yields (%)	
entry	catalysts	reaction time (min)	MLE	LA
run 11	Pd/Al_2O_3	120	0	0
run 12	A70	0	0	0
run 13	A70	30	0.1	0
run 14	A70	60	0.3	0.7
run 15	A70	90	0.5	0.6
run 16	A70	120	0.6	0.6
run 17	Pd/Al_2O_3 + A70	30	18.2	1.5
run 18	Pd/Al_2O_3 + A70	60	19.6	2.0

[a] Reaction conditions: xylose loading, 9.1 wt %; T = 165 °C; P = 70 bar.

hydrogenations may be involved, leading to the loss of levulinic acid/ester formation. To understand the loss from each step, acid treatment and/or hydrogenation of each reaction intermediate was performed subsequently.

Side Reactions in the Conversion of Xylose. Table 4 shows the catalytic conversion of methyl xylosides, furfural, and furfuryl alcohol over A70 and/or Pd/Al_2O_3 catalysts. Methyl xylosides gave similar yields of levulinic acid/ester to that from xylose, indicating that methanolysis of xylose to methyl xylosides does not contribute to the loss of levulinic acid/ester from xylose. Methanolysis of xylose to methyl xylosides is a very efficient and selective step.[35] However, from xylose or methyl xylosides to furfural is always accompanied with polymerization.[36] For example, the maximum yields of furfural and its acetal in run 13 is about 36% (Table 2). Thus, in run 20 with furfural as the starting reactant, high yields of levulinic acid/ester were expected. However, furfural gave similar yields of levulinic acid/ester to that from xylose or methyl xylosides. Polymerization is one side reaction as the high initial concentration of furfural favors polymerization. Another very important side reaction is the deep hydrogenation of furfural and furfuryl alcohol.

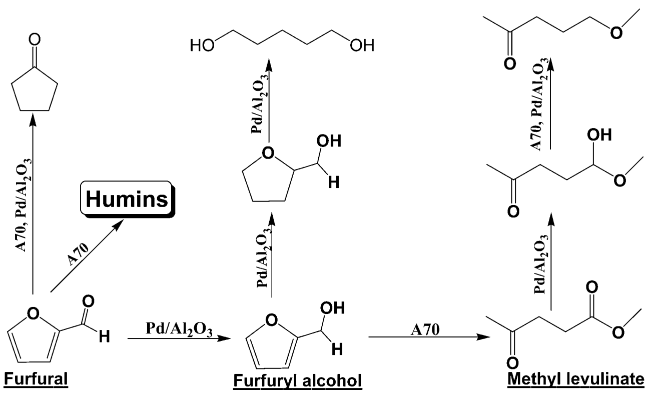
Ideally, furfural is expected to be hydrogenated to furfuryl alcohol and then follow the acid catalysis step to levulinic acid/ester. However, over Pd/Al_2O_3, furfural has many ways to go, as shown in Scheme 3. The hydrogenation of furfural over only

Table 4. Yields of Methyl Levulinate and Levulinic Acid with Different Starting Reactants[a]

			yields (%)	
entry	reactants	catalysts	MLE	LA
run 19	methyl xylosides	Pd/Al_2O_3 + A70	21.5	2.8
run 20	furfural	Pd/Al_2O_3 + A70	23.1	2.4
run 21	furfural	Pd/Al_2O_3	0.1	0
run 22	2-furylmethanol	A70	80.2	11.7
run 23	2-furylmethanol	Pd/Al_2O_3 + A70	26.5	3.3

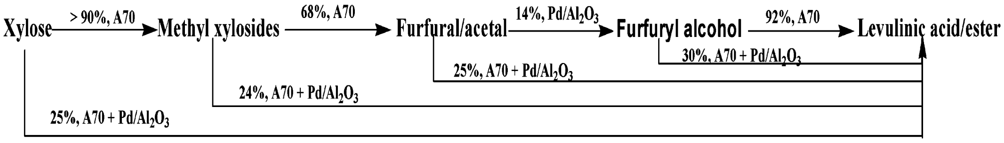
[a] Reaction conditions: loading of starting material, 9.1 wt %; T = 165 °C; residence time = 120 min; P = 70 bar.

Scheme 3. Typical Side Reactions in the Conversion of Xylose/Furfural to Methyl Levulinate[a]



[a] All the products presented in this scheme were identified with GC/MS.

Scheme 4. Yields of Levulinic Acid/Ester with Different Starting Reactants[a]



[a]Reaction conditions: loading of starting material, 9.1 wt %; T = 165 °C; residence time = 120 min; P = 70 bar.

Pd/Al_2O_3 (run 21) shows that the yield of the targeted furfuryl alcohol is about 14%, and yields of levulinic acid/ester are negligible. Tetrahydro-2-furanmethanol, the fully hydrogenated compound from furfural, is the dominant product. In addition, methyl levulinate also undergoes further hydrogenation to 5-methoxy-2-pentanone (Scheme 3), which is another side reaction. Furfuryl alcohol can be selectively converted into levulinic acid/ester with the yield as high as about 92% over only A70 (run 22). However, over A70 and Pd/Al_2O_3 catalysts, the yields of levulinic acid/ester from furfuryl alcohol decrease to about 30% (run 23, Table 4), which is caused by the deep hydrogenation of furfuryl alcohol to tetrahydro-2-furanmethanol. This result is similar to that from furfural to levulinic acid/ester in Run 20. The yields of levulinic acid/ester from xylose and each reaction intermediate are summarized in Scheme 4. Apparently, hydrogenation of the furan rings in furfural and in furfuryl alcohol is one major reason for the loss of levulinic acid/ester production from xylose, furfural, and/or furfuryl alcohol.

The hydrogenation catalyst is supposed to hydrogenate only the carbonyl group of furfural, but the noble metal catalyst employed is too active to be selective. Thus, the choice of hydrogenation catalyst is crucial to achieve high yields of levulinic acid/ester. In literature, the yield of furfural from xylose with a concentration of 2 wt % is roughly 70%.[37] Furfural can be selectively hydrogenated to furfuryl alcohol in vapor phase,[25] while the yield of levulinic acid from furfuryl alcohol is about 70%.[38] On the basis of this data, the overall yield of levulinic acid from these multiple separate steps is about 49%. In this study, the yield of levulinic acid/ester from xylose in a one-pot reaction reaches about 27% in run 4 by variation of reaction temperatures. Other reaction parameters were further optimized, aiming to suppress the side reactions.

Effect of Typical Reaction Parameters. Table 5 shows the effects of xylose, Pd/Al_2O_3, and A70 loadings on the formation of levulinic acid/ester. The production of levulinic acid/ester does not improve much with the lower initial xylose loading in run 24. The lower xylose loading may help to alleviate the polymerization but could not suppress the deep hydrogenation reactions. Reducing A70 loading to half in run 25 also is not effective to suppress the undesired hydrogenation reactions. Conversely, the lower A70 loading slows down the acid-catalyzed reactions, and consequently, furfural and 2-furylmehanol would have more chances to be fully hydrogenated. The production of levulinic acid/ester is only improved with lower Pd/Al_2O_3 loading in run 26, with the yields increasing to about 32%. The low Pd/Al_2O_3 loading is unfavorable for the deep hydrogenation and correspondingly promotes levulinic acid/ester formation. As presented above, the roles of hydrogenation catalyst are crucial to selectively produce levulinic acid/ester. Thus, a range of other hydrogenation catalysts were further evaluated.

Table 5. Yields of Methyl Levulinate and Levulinic Acid versus Xylose and Catalyst Loadings[a]

				yields (%)	
entry	xylose loading (wt %)	Pd/Al_2O_3 loading (wt %)	A70 loading (wt %)	MLE	LA
run 24	4.8	9.1	9.1	24.7	2.7
run 25	9.1	4.5	9.1	28.4	3.6
run 26	9.1	9.1	4.5	18.6	1.4

[a]Reaction conditions: T = 165 °C; residence time = 120 min; P = 70 bar.

Catalytic Behaviors of Other Hydrogenation Catalysts. Table 6 shows levulinic acid/ester yields over A70 and different hydrogenation catalysts. Pd/C is very active for the undesired hydrogenation reactions at 190 °C. Only a small amount of furfural can make their way to furfuryl alcohol and then to methyl levulinate (run 27). The yield of cyclopentanone, a byproduct from hydrogenation, reaches 12.7%. Moreover, the abundance of 5-methoxy-2-pentanone, the hydrogenation product from methyl levulinate, is six times higher over Pd/C than over Pd/Al_2O_3. Even at a lower temperature of 155 °C, Pd/C is still active enough for hydrogenation but not selective enough for hydrogenation of furfural to furfuryl alcohol. Similarly, Pt/C also shows excessive hydrogenation activity, forming a significant amount of cyclopentanone and other hydrogenation products. Ru/C shows high activity for hydrogenlysis of the C−C bonds of xylose, forming the various complex fragments. Xylose has little chance to be converted into furfural or levulinic acid/ester (Run 30).

Table 6. Yields of Methyl Levulinate and Levulinic Acid versus Hydrogenation Catalysts[a]

			yields (%)	
entry	hydrogenation catalysts	T (°C)	MLE	LA
run 27	Pd/C	190	4.9	1.4
run 28	Pd/C	155	7.8	0.9
run 29	Pt/C	190	5.3	1.2
run 30	Ru/C	190	0.1	0.2
run 31	$Ni-Mo-S/Al_2O_3$[b]	190	1.2	0.1
run 32	$Co-Mo-S/Al_2O_3$[b]	190	1.1	0.1
run 33	$Co-Mo-S/Al_2O_3$[c]	190	6.5	0.6
run 34	unsupported Cu	190	1.5	0.3

[a]Reaction conditions: xylose loading, 9.1 wt %; catalysts, A70 (9.1 wt %) + hydrogenation catalyst (9.1 wt %); residence time = 120 min; P = 70 bar. [b]ZnO was used to capture the H_2S generated by the catalysts. [c]ZnO was not used in this run.

$Ni-Mo-S/Al_2O_3$ and $Co-Mo-S/Al_2O_3$ catalysts (runs 31 and 32) were also employed as the hydrogenation catalysts due to their mild activity at the low temperatures. However, during heating, these two catalysts release H_2S, which is very corrosive to the autoclave, so zinc oxide was added to fix the H_2S generated. However, zinc oxide reacted with the acidic A70, preventing the occurrence of acid-catalyzed reactions. The further experiment without zinc oxide shows an improvement of levulinic acid/ester formation, but the yields are still low (run 33). Copper-based catalysts are reported to be very active for the hydrogenation of furfural to furfuryl alcohol.[38] However, the unsupported copper catalyst was not active as expected in the liquid phase. The low specific area and low reaction temperature, which is limited by the maximum operating temperature of A70 (190 °C), may be responsible for the low activity.

Pd/Al_2O_3 is the most active one among the hydrogenation catalysts explored, but Pd/Al_2O_3 is still too active to be selective. The hydrogenation catalysts are the key to achieve the high yields of levulinic acid/ester. The suitable catalyst must be selective to hydrogenate the carbonyl group of furfural but not the furan ring. In addition, the reaction intermediates have to migrate between A70 and Pd/Al_2O_3 to go through the multiple steps to form levulinic acid/ester. A lot of side reactions occurred simultaneously, competing for the formation of the targeted products. Thus, a bifunctional catalyst with both acidic sites for the acid-catalyzed reactions and the metallic sites for hydrogenation reactions is preferred.

■ CONCLUSION

To summarize, xylose could be directly converted into levulinic acid/ester via a one-pot synthesis involving multiple acid-catalyzed steps and one hydrogenation step. The methanol medium plays an important role to protect the carbonyl group of xylose from hydrogenation, while both the acid catalyst and hydrogenation catalyst have to work together to make xylose follow the designed routes to levulinic acid/ester. Deep hydrogenation of the furan rings in furfural and furfuryl alcohol is the main side reaction. The key to selectively produce levulinic acid/ester is that the hydrogenation catalyst must be selective to hydrogenate only the carbonyl group of furfural but not the furan rings. The choice or the development of the hydrogenation catalysts is the key for selective conversion of xylose to levulinic acid/ester.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: (+) 61 8 9266 1131. Fax: (+) 61 8 9266 1138. E-mail: chun-zhu.li@curtin.edu.au.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project is supported by the Commonwealth of Australia under the Australia−China Science and Research Fund as well as Curtin University of Technology through the Curtin Research Fellowship Scheme.

■ REFERENCES

(1) Serrano-Ruiz, J. C.; Dumesic, J. A. Catalytic routes for the conversion of biomass into liquid hydrocarbon transportation fuels. *Energy Environ. Sci.* **2011**, *4*, 83−99.

(2) Huber, G. W.; Corma, A. Synergies between bio- and oil refineries for the production of fuels from biomass. *Angew. Chem., Int. Ed.* **2007**, *46*, 7184−7201.

(3) Chheda, J. N.; Huber, G. W.; Dumesic, J. A. Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals. *Angew. Chem., Int. Ed.* **2007**, *46*, 7164−7183.

(4) Mohan, D.; Pittman, C. U., Jr.; Steele, P. H. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy Fuels* **2006**, *20*, 848−889.

(5) Girisuta, B.; Janssen, L. P. B. M.; Heeres, H. J. Kinetic study on the acid-catalyzed hydrolysis of cellulose to levulinic acid. *Ind. Eng. Chem. Res.* **2007**, *46*, 1696−1708.

(6) Lin, H.; Strull, J.; Liu, Y.; Karmiol, Z.; Plank, K.; Miller, G.; Guo, Z.; Yang, L. High yield production of levulinic acid by catalytic partial oxidation of cellulose in aqueous media. *Energy Environ. Sci.* **2012**, *5*, 9773−9777.

(7) Vyver, S. V.; Geboers, J.; Jacobs, P. A.; Sels, B. F. Recent advances in the catalytic conversion of cellulose. *ChemCatChem* **2011**, *3*, 82−94.

(8) Zhang, L.; Xu, C.; Champagne, P. Overview of recent advances in thermo-chemical conversion of biomass. *Energy Convers. Manage.* **2010**, *51*, 969−982.

(9) Weingarten, R.; Conner, W. C.; Huber, G. W. Production of levulinic acid from cellulose by hydrothermal decomposition combined with aqueous phase dehydration with a solid acid catalyst. *Energy Environ. Sci.* **2012**, *5*, 7559−7574.

(10) Shen, J.; Wyman, C. E. Hydrochloric acid-catalyzed levulinic acid formation from cellulose: Data and kinetic model to maximize yields. *AIChE J.* **2012**, *58*, 236−246.

(11) Ormsby, R.; Kastner, J. R.; Miller, J. Hemicellulose hydrolysis using solid acid catalysts generated from biochar. *Catal. Today* **2012**, *190*, 89−97.

(12) Enslow, K. R.; Bell, A. T. The kinetics of Brønsted acid-catalyzed hydrolysis of hemicellulose dissolved in 1-ethyl-3-methylimidazolium chloride. *RSC Adv.* **2012**, *2*, 10028−10036.

(13) Mascal, M.; Nikitin, E. B. High-yield conversion of plant biomass into the key value-added feedstocks 5-(hydroxymethyl)-furfural, levulinic acid, and levulinic esters via 5-(chloromethyl)furfural. *Green Chem.* **2010**, *12*, 370−373.

(14) Zhao, H.; Holladay, J. E.; Brown, H.; Zhang, Z. C. Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural. *Science* **2007**, *316*, 1597−1600.

(15) Young, J.; Chan, G.; Zhang, Y. Selective conversion of fructose to 5-hydroxymethylfurfural catalyzed by tungsten salts at low temperatures. *ChemSusChem* **2009**, *2*, 731−734.

(16) Chheda, J. N.; Román-Leshkov, Y.; Dumesic, J. A. Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono-and poly-saccharides. *Green Chem.* **2007**, *9*, 342−350.

(17) Qi, X.; Watanabe, M.; Aida, T. M.; Smith, R. L., Jr. Efficient catalytic conversion of fructose into 5-hydroxymethylfurfural in ionic liquids at room temperature. *ChemSusChem* **2009**, *2*, 944−946.

(18) Benoit, M.; Brissonnet, Y.; Guélou, E.; Vigier, K. D. O.; Barrault, J.; Jérôme, F. Acid-catalyzed dehydration of fructose and inulin with glycerol or glycerol carbonate as renewably sourced co-solvent. *ChemSusChem* **2010**, *3*, 1304−1309.

(19) Vigier, K. D. O.; Benguerba, A.; Barrault, J.; Jérôme, F. Conversion of fructose and inulin to 5-hydroxymethylfurfural in sustainable betaine hydrochloride-based media. *Green Chem.* **2012**, *14*, 285−289.

(20) Lange, J.-P. Biofuels, Lignocellulose conversion: An introduction to chemistry, process and economics. *Biofuels. Bioprod. Biorefin.* **2007**, *1*, 39−48.

(21) Lima, S.; Pillinger, M.; Valente, A. A. Dehydration of D-xylose into furfural catalysed by solid acids derived from the layered zeolite Nu-6(1). *Catal. Commun.* **2008**, *9*, 2144−2148.

(22) Berndes, G.; Hoogwijk, M.; Broek, R. The contribution of biomass in the future global energy supply: a review of 17 studies. *Biomass Bioenergy* **2003**, *25*, 1−28.

(23) Lange, J.-P.; Heide, E.; Buijtenen, J.; Price, R. Furfural—A promising platform for lignocellulosic biofuels. *ChemSusChem* **2012**, *5*, 150−166.

(24) Marcotullio, G.; Jong, W. D. Chloride ions enhance furfural formation from D-xylose in dilute aqueous acidic solutions. *Green Chem.* **2010**, *12*, 1739−1746.

(25) Nagaraja, B. M.; Padmasri, A. H.; Raju, B. D.; Rao, K. S. R. Vapor phase selective hydrogenation of furfural to furfuryl alcohol over Cu−MgO coprecipitated catalysts. *J. Mol. Catal. A: Chem.* **2007**, *265*, 90−97.

(26) Wu, J.; Shen, Y.; Liu, C.; Wang, H.; Geng, C.; Zhang, Z. Vapor phase hydrogenation of furfural to furfuryl alcohol over environmentally friendly Cu−Ca/SiO_2 catalyst. *Catal. Commun.* **2005**, *6*, 633−637.

(27) Maldonado, G. M. G.; Assary, R. S.; Dumesic, J.; Curtiss, L. A. Experimental and theoretical studies of the acid-catalyzed conversion of furfuryl alcohol to levulinic acid in aqueous solution. *Energy Environ. Sci.* **2012**, *5*, 6981−6989.

(28) Lange, J. P.; Graaf, W. D.; Haan, R. J. Conversion of furfuryl alcohol into ethyl levulinate using solid acid catalysts. *ChemSusChem* **2009**, *2*, 437−441.

(29) Hu, X.; Wu, L.; Wang, Y.; Mourant, D.; Lievens, C.; Gunawan, R.; Li, C.-Z. Mediating acid-catalyzed conversion of levoglucosan into platform chemicals with various solvents. *Green Chem.* **2012**, *14*, 3087−3098.

(30) Chen, C. C.; Mcginnis, G. D. The use of 1-methylimidazole as a solvent and catalyst for the preparation of aldononitrile acetates of aldoses. *Carbohydr. Res.* **1981**, *90*, 127−130.

(31) Mikkola, J.-P.; Salmi, T. Three-phase catalytic hydrogenation of xylose to xylitol—prolonging the catalyst activity by means of on-line ultrasonic treatment. *Catal. Today* **2001**, *64*, 271−277.

(32) Hu, X.; Lievens, C.; Li, C.-Z. Acid-catalyzed conversion of xylose in methanol-rich medium as part of biorefinery. *ChemSusChem* **2012**, *5*, 1427−1434.

(33) Windom, B. C.; Lovestead, T. M.; Mascal, M.; Nikitin, E. B.; Bruno, T. J. Advanced distillation curve analysis on ethyl levulinate as a diesel fuel oxygenate and a hybrid biodiesel fuel. *Energy Fuels* **2011**, *25*, 1878−1890.

(34) Huber, G. W.; Iborra, S.; Corma, A. Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering. *Chem. Rev.* **2006**, *106*, 4044−4098.

(35) Bishop, C. T.; Cooper, F. P. Glycosidation of sugars: I. Formation of methyl-D-xylosides. *Can. J. Chem.* **1962**, *40*, 224−232.

(36) Lima, S.; Antunes, M. M.; Fernandes, A.; Pillinger, M.; Ribeiro, M. F.; Valente, A. A. Catalytic cyclodehydration of xylose to furfural in the presence of zeolite H-Beta and a micro/mesoporous Beta/TUD-1 composite material. *Appl. Catal. A: Gen.* **2010**, *388*, 141−148.

(37) Gurbuz, E. I.; Wettstein, S. G.; Dumesic, J. A. Conversion of hemicellulose to furfural and levulinic acid using biphasic reactors with alkylphenol solvents. *ChemSusChem* **2012**, *5*, 383−387.

(38) Rao, R. S.; Baker, R. T. K.; Vannice, M. A. Furfural hydrogenation over carbon-supported copper. *Catal. Lett.* **1999**, *60*, 51−57.