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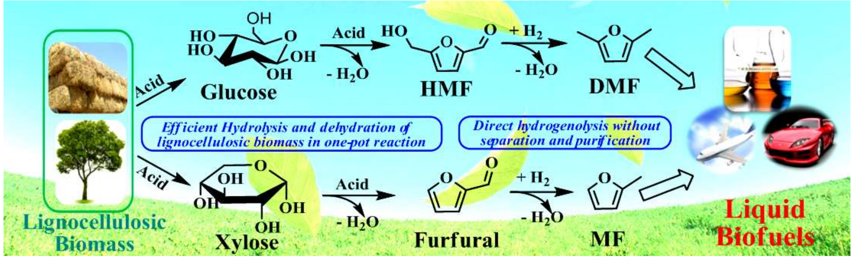

Furan derivatives, directly generated from lignocellulosic biomass, were efficiently upgraded into renewable liquid biofuels without complicated separation and purification processes for them.

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Efficient catalytic conversion of lignocellulosic biomass into renewable liquid biofuels *via* furan derivatives

Jianjian Wang, Xiaohui Liu, Bicheng Hu, Guanzhong Lu*, and Yanqin Wang*

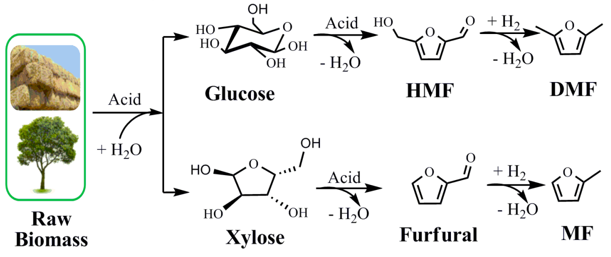
Efficient production and sequential utilization of furan derivatives will provide a promising approach towards achieving renewable liquid biofuels from biomass. This study aims to investigate the simultaneous production of furfural and 5-(hydroxymethyl)furfural (HMF) from biomass and further upgrade of them into biofuels. Firstly, furfural and HMF are obtained together with high yields from a mixture of C5 (xylose) and C6 (glucose) sugars, or from lignocellulosic biomass, such as birch, cornstalk, pine, bagasse, and poplar in a tetrahydrofuran (THF)/H_2O-NaCl biphasic system under mild conditions. The co-existence of C5/C6 sugars or impurities in lignocellulosic biomass has little influence on the simultaneous production of furfural and HMF. Then, the generated furfural and HMF in the upper organic phase are directly used as substrates without extra separation and purification processes, and efficiently upgraded to 2-methylfuran (MF) and 2,5-dimethylfuran (DMF), both of which are considered as promising renewable liquid biofuels with high-energy content. Hence, the seamless integration of lignocellulosic biomass into renewable liquid biofuels will accelerate our society moving towards a renewable transportation economy by utilizing cheap feedstocks, mild reaction conditions, and cost abatement in separation and purification.

Introduction

Over the past decades, coal, natural gas, and petroleum have played dominant roles as sources for energy and chemicals.[1] In future it will be difficult to meet the growing market demands with the now-renewable of gas and petroleum resources.[2] Meanwhile, the increasing cost of these fossil fuels and concerns about their environmental impact are accelerating the transition to a biomass-based economy, since biomass is an abundant and carbon-neutral renewable energy resource for the promising production of liquid biofuels and value-added chemicals.[3]

Generally, the effective utilization of lignocellulosic biomass requires the sufficient utilization of both hemicellulose and cellulose, consisting primarily of C5 (xylose) and C6 (glucose) sugars, respectively.[4] Great efforts have been devoted to design novel solid acid catalysts to selectively transform these two sugars into the platform intermediates, furfural and 5-(hydroxymethyl)furfural (HMF), since both of them are considered as promising options to replace fossil fuel-based organics for the production of valuable biofuels and chemicals.[5] However, the simultaneous conversion of xylose and glucose by single solid acid catalyst are complicated, since xylose can be directly converted into furfural over Brönsted acid sites and glucose should firstly isomerize to fructose over Lewis acid sites followed by the dehydration of generated fructose into HMF on Brönsted acid sites.[6] Using lignocellulosic biomass as feedstocks, such solid acid catalyst must be strong enough to break β-1,4-glycosidic bonds and depolymerize them into water-soluble sugars. Laosiripojina *et al.* have reported a process for lignocellulose conversion in hot compressed water (HCW) catalyzed by zirconium-based catalysts at 473-673 K, but the yields of furfural and HMF were much lower (< 35%).[7] Zhao *et al.* have obtained satisfactory yields of furfural (23-31%) and HMF (45-52%) from corn stalk, rice straw and pine wood in ionic liquids (ILs) with the presence of $CrCl_3$ under microwave irradiation.[8] However, ILs were not suitable for large scale applications due to their high cost and deactivation by small amounts of water, and their separation from the reaction mixture was still a problem. Recently, Schüth and co-workers have reported that the acid-catalyzed depolymerization of solid lignocellulosic biomass completely overcame the problems posed by the recalcitrance of lignocellulose driven by mechanical forces, and solid lignocellulose was converted to water-soluble oligosaccharides (WSO).[9] In biphasic reactors, high yields of furfural (> 70%) and HMF (> 50%) can be obtained from these generated WSOs under mild conditions. However, a certain amount of inorganic acid (*e.g.*, HCl) should be added into the pre-treatment process of solid lignocellulose, and the recycling of ($AlCl_3$) from the biphasic reactor was still a problem.

On the other hand, furfural and HMF were often used as platform compounds for the production of valuable liquid biofuels.[10] So, it would be much more promising and beneficial to directly convert the generated furfural and HMF into liquid biofuels in situ and avoid their complicated separation and purification processes, and thereby decrease the cost of the final products and whole reaction system for biomass utilization. Among the potential biofuel components, 2-methylfuran (MF) and 2,5-dimethylfuran (DMF), obtained from furfural and HMF via hydrogenolysis reactions (as shown in Scheme 1), are highly attractive due to their unique properties.[11] Compared with bio-ethanol, they exhibited better lubricity, higher energy density, higher boiling point and low solubility in water. Moreover, the purification energy consumption of MF and DMF is only one-third of bio-ethanol,[12] and the energy carrier can be preserved fully for the MF and DMF approach as well.[13] All of these advantages make MF and DMF promising substitutes for gasoline and bio-ethanol. Mascal *et al.* have reported that 5-(chloromethyl)furfural with high yields from sugars and pre-treated cellulose can be used as an important platform compound for the production of biofuel candidates or additives, such as 5-(ethoxymethyl)furfural and DMF by reacting with ethanol and hydrogen.[14] However, a certain amount of HCl should be involved in such process, and these chlorine-substituted compounds would lower the activities of hydrogenation catalysts. On the other hand, MF and DMF can be directly produced from the simultaneous hydrogenation of the generated furfural and HMF. Dumesic *et al.* have developed a catalytic strategy for the production of DMF from fructose.[11a] Firstly, as high as 66% HMF yield was obtained in a biphasic system at 180 ºC catalyzed by HCl. Then the upper organic phase was subjected to evaporation of water and HCl to obtain pure HMF. Finally, the collected HMF was converted to DMF over CuRu/C catalyst with about 71% DMF yield. In this approach, fructose was used as feedstock for HMF production and the evaporation process was necessary to purify HMF from the reaction mixture. Meanwhile, the CuRu/C catalyst for hydrogenolysis reactions was affected to some extent by the presence of chloride ions. Very recently, Dumesic *et al.* reported that HMF in the biomass-derived solvents can be directly converted to DMF without the separation process for HMF, but low yield of DMF (about 46%) was obtained by using RuSn/C as the catalyst at 200 ºC.[10] Liu *et al.* have presented an effective process for dehydration of xylose and glucose to furfural and HMF in a biphasic system, and the sequential conversion of furfural and HMF to MF and DMF, respectively. The highest yields could reach 61.9 mol% (for MF) and 60.3 mol% (for DMF) catalyzed by Ru/C under the optimal experimental conditions by starting with neat HMF and furfural in pure n-butanol. But, when furfural and HMF in the upper organic phase separated from the dehydration step was directly used as the substrate, the target products of MF and DMF could not be detected, indicating that the purification process of upper organic phase containing furfural and HMF was still necessary.[13]



Scheme 1 Conversion of lignocellulosic biomass to furfural and HMF and then direct upgrading of them into liquid biofuels.

In our previous work, satisfactory yields of HMF (above 50%) were achieved by using glucose-based carbohydrates, such as glucose, sucrose, starch or cellulose as substrates catalyzed by a Sn-Mont catalyst through the successful isomerization step of glucose to fructose before the dehydration process.[15] Then we adopted the early transition metal oxides (e.g., CoO_x) to break the C-O bond,[16] and the generated HMF from fructose was directly converted to DMF with high yield (final yield, 75.1%) on Ru/Co_3O_4 catalyst.[17] However, as mentioned above, the activities for the simultaneous conversion of the mixture of C5 and C6 sugars, or even lignocellulosic biomass into furfural and HMF over solid acid catalysts were not high (about 51-66% yield for furfural and 20-35% yield for HMF).[13,18] Especially, direct hydrogenolysis of furfural and HMF in reaction mixture into MF and DMF were rarely reported. Hence, in this context, we firstly investigated the effective conversion of C5 sugars into furfural by this Sn-Mont catalyst in a biphasic system under mild conditions, and then investigated the simultaneous conversion of the mixture of C5 and C6 sugars with the analogous ratios in the lignocellulosic biomass into furfural and HMF. Subsequently, we investigated the direct production of furfural and HMF from lignocellulosic biomass, such as birch, cornstalk, pine, bagasse, and poplar. Finally, we collected the upper organic phase containing furfural and HMF from the biphasic system, and investigated the direct conversion of furfural and HMF in the separated organic phase into MF and DMF, avoiding the complicated separation or purification processes typically required for furfural and HMF.

Results and discussion

Direct dehydration of xylose and glucose to furan derivatives

C6 sugars, including glucose, glucose-united disaccharides (sucrose and cellobiose) and polysaccharides (starch and cellulose) can be directly converted into HMF by using single Sn-Mont as the catalyst in a THF/H_2O-NaCl biphasic system.[15] In that process, Lewis acid sites on the Sn-Mont catalyst were favorable for the isomerization of glucose to fructose, and Brönsted acid sites were responsible for direct hydrolysis of di-/poly-saccharides to glucose and dehydration of generated fructose to HMF. As we know, C5 sugars, such as xylose usually can also be converted into furfural over acid sites. Hence, we initially investigated whether the acid sites on Sn-Mont catalyst were active enough for conversion of xylose into furfural. It was found that xylose also can be converted to furfural catalyzed by Sn-Mont in the THF/H_2O-NaCl biphasic system, and the selectivity and yield of furfural were up to 55.8 and 55.5% at 160 °C for 2 h, respectively. Especially, when doubled the xylose concentration to 33.3 wt.% to enlarge the production of furfural, the selectivity and yield of furfural were still high (52.5 and 52.4%, respectively) at the same reaction conditions.

From the above results, we can see that xylose also can be efficiently converted into furfural using Sn-Mont catalyst in this biphasic system. Thus, such catalyst could directly convert the mixture of xylose and glucose into furan derivatives (furfural and HMF) in the same conditions. Hence, we investigated the simultaneous conversion of xylose and glucose with different weight ratios catalyzed by Sn-Mont and it was seen that the mixture of xylose and glucose could be fully converted with single Sn-Mont as the catalyst in one reactor, indicating Lewis acid sites on Sn-Mont catalyst could isomerize glucose to fructose and Brønsted acid sits were able to convert xylose and generated fructose to furfural and HMF. Moreover, the co-existence of two sugars almost did not affect each other, and the yields of furfural and HMF were about 50 and 65% (as shown in Fig. 1), respectively. For example, using a mixture of xylose and glucose (20:50, wt.%) as the substrate, the yields of furfural and HMF were 59.4 and 71.4%, respectively. Increasing or reducing reaction temperature would increase the rate of side-reactions or lower down the rate of xylose conversion, resulting in the low selectivities to furfural and HMF. These results were very promising to lead us to directly convert diverse lignocellulosic biomass into furan derivatives by using Sn-Mont as the catalyst in one-pot biphasic system.

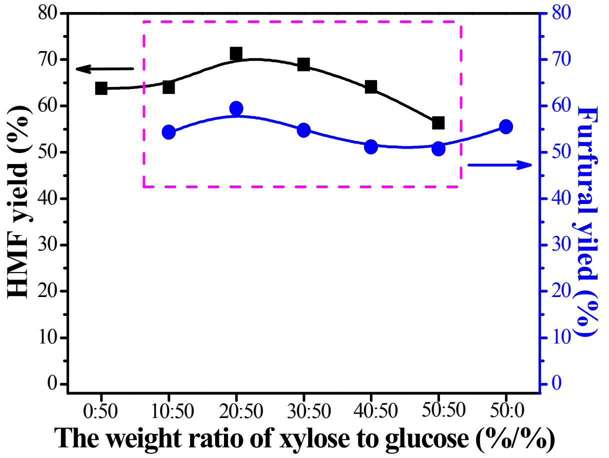


Fig. 1 The yields of HMF and furfural achieved with different weight ratios of xylose to glucose using Sn-Mont as a catalyst in THF/H_2O-NaCl biphasic system. All reactions were conducted at 160 °C for 2 h. The total amount of substrate (0.2 g), Sn-Mont (0.1 g), water saturated with NaCl (1 mL), and organic solvent (5 mL) were put into a 50 mL stainless-steel autoclave.

Generally, conversion of xylose was easier than that of glucose, and the yield of furfural was higher than that of HMF at the same conditions. Dumesic *et al.* presented that the yields of furfural and HMF were about 80% and 15% from the mixed xylose and glucose catalyzed by the H-mordenite in GVL solvent, due to the partial glucose conversion to furfural.[6e] The yield of furfural was about three times higher than that of HMF from lignocellulosic biomass (such as corn stover, pine wood and poplar) by using $AlCl_3·6H_2O$ as the catalyst in a biphasic reactor.[6f] Even though these lignocellulosic biomass were pre-treated by mechanical forces to generate the water-soluble oligosaccharides, the yields of HMF were still 10% lower than that of furfural catalyzed by $AlCl_3·6H_2O$ in a biphasic reactor using alkylphenolic solvents as the extracting phase. However, in our work, the current yield of HMF was always higher than that of furfural at various weight ratios of xylose to glucose (Fig. 1). Meanwhile, the yields of furfural were always below 60% over Sn-Mont catalyst at different reaction temperatures or times (Fig. S1). It could be due to the low amount of acid sites on the Sn-Mont catalyst (Brönsted site: 218.2 μmol/g; Lewis site: 104.2 μmol/g. Both were determined by pyridine-adsorbed FT-IR at 200 °C), since higher concentration of acid sites, especially Brönsted acid sits would benefit the selective conversion of xylose into furfural.[6e] Combined with another solid acid developed in our group, mesoporous niobium phosphate ($NbOPO_4$) with the similar ratio of Brönsted to Lewis sites and higher amount of acid sites (Brönsted site: 531.5 μmol/g; Lewis site: 276.9 μmol/g) as a co-catalyst,[19] the yield of furfural increased from 59.4% to 76.8% with the yield of HMF nearly unchanged (68.6%) from the mixture of xylose and glucose (20:50, wt.%) at the same reaction conditions. Such furfural yield can be comparable to that obtained from 2 wt.% xylose in expensive GVL solvents using H-mordenite as catalyst.[6e] On the other hand, the yields of furfural/HMF were just 69.2/56.7% or 43.8/69.8% catalyzed by single Sn-Mont or $NbOPO_4$ catalyst with doubled dosage (0.2 g) at the same reaction conditions. It indicated that the remarkable performances of $NbOPO_4$ and Sn-Mont catalyst may be attributed to the synergic effect between them in the biphasic system, that is, the higher amount of acid sites of $NbOPO_4$ was favourable for xylose conversion to furfural, and the Lewis sites of Sn-Mont were effective for glucose conversion to HMF. It also can be seen that increasing the dosage of single catalyst, the yields of furfural and HMF decreased, which might be due to the decomposition of products or the inevitable formation of polymers (*e.g.*, humins).[20] Besides, the stability of mixed catalysts was confirmed as well, and the yields of furfural and HMF almost did not decrease even after six recycles (about). Meanwhile, mixed catalysts did not suffer from leaching of active sites into the reaction mixture, and the leaching of tin or niobium in the aqueous phase was negligible (< 1% detected by ICP-AES). Almost no measurable amounts of chlorinated compounds were observed in the organic layer, suggesting that chloride ions did not transfer into the organic phase or react with generated intermediates and products. Therefore, by the combination of Sn-Mont with $NbOPO_4$ as the co-catalyst, the xylose fraction can be further utilized, and then the mixture of C5 and C6 sugars was efficiently converted to furfural and HMF in one-pot reactor under mild conditions.

Conversion of lignocellulosic biomass to furan derivatives

Encouraged by the high-yield production of furfural and HMF through the simultaneous transformation of different weight ratios of xylose and glucose, the conversion of raw lignocellulosic biomass was also investigated under the same reaction conditions (Table 1). It can be seen that these lignocellulosic biomasses also can be efficiently converted by the mixed solid acid catalyst as well, and the molar yields of furfural/HMF from birch, cornstalk, pine, bagasse, and poplar were 64.8/23.3, 80.5/44.1, 54.2/58.2, 54.5/27.2, and 52.7/22.6%, respectively. The lignin contents or inorganic salt ions (e.g, sulfur and chlorine) in raw lignocellulosic biomass had little influence on the activity of mixed catalysts. Even using un-milled cornstalk as substrate, the yields of furfural and HMF were still high, about 71.7/33.5% after 8 h (Table 1, Entry 3). No xylose or glucose could be detected in the aqueous phase, indicating that these lignocellulosic biomass could be fast depolymerized and then the generated C5 and C6 sugars were effectively converted into furfural and HMF, respectively. The by-products, such as formic acid and levulinic acid (from the rehydration of HMF or furfural) were also observed in the conversion of these lignocellulosic biomass samples. However, their yields were low, and the major by-products were humins. The stability of this mixed catalyst was excellent, and the yields of furfural and HMF were about 76.8/39.7% from cornstalk in the fifth recycle (Entry 4). The slight drop in activity of the mixed catalyst was likely due to the occupancy of active sites on mixed catalysts by insoluble by-products (*e.g.*, humins), since the leaching of active sites was negligible (< 1%) detected by ICP-AES.

On the other hand, in contrast with the production of furfural, the molar or mass yields of HMF were clearly dependent on different lignocellulosic biomass. The yield of HMF from pine was twice than that from bagasse even with the similar content of cellulose fraction, which may be due to the different structures and complicated network of bonds in this lignocellulosic biomass.[21]

Table 1 The yields of furfural and HMF obtained from various sources of lignocellulosic biomass.[a]

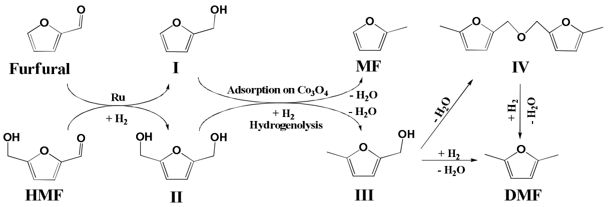
		The molar yield /%[b]		The mass yield /%[c]		
Entry	Sample	furfural	HMF	furfural	HMF	Total
1	birch	64.8	23.3	9.1	10.2	19.3
2	cornstalk	80.5	44.1	8.8	13.1	21.9
3[d]	cornstalk	71.7	33.5	7.9	10.0	17.9
4[e]	cornstalk	76.8	39.7	8.4	11.8	20.2
5	pine	54.2	58.2	4.2	19.6	23.8
6	bagasse	54.5	27.2	11.5	9.8	21.3
7	poplar	52.7	22.6	7.8	10.6	18.4

[a] Reaction conditions: biomass (0.2 g), Sn-Mont (0.1 g), $NbOPO_4$ (0.1 g), water saturated with NaCl (1 mL), THF (5 mL), reaction temperature 160 °C, and reaction time 2 h. [b] The molar yield of furfural was based on a hemicellulose content of 19.3, 15.1, 10.3, 29.2, and 20.4% (by weight), and yield of HMF from birch, cornstalk, pine, bagasse, and poplar was based on a cellulose content of 56.1, 38.0, 43.2, 46.2, and 60.3% (by weight), respectively. The compositions of lignocellulosic biomass were adapted from ref.[22] according to the procedures of the Van Soest method. [c] The mass yields of furfural and HMF were only calculated from the organic phase. [d] Un-milled cornstalk was used as substrate for 8 h. [e] The solid acid catalysts was used for fifth recycle.

Direct upgrading of the furan derivatives in THF phase into liquid biofuels

As mentioned above, furfural and HMF were often used as important platform compounds, and it will be promising and important to integrate their production with subsequent upgrading into liquid biofuels (*e.g.*, MF and DMF), realizing the goals of partial replacement of the non-renewable fossil fuels to meet with the urgent demand for the rapid development of economy.[5b,10,23] Based on this purpose, we collected the upper organic phase containing the generated furfural and HMF from the mixture of xylose and glucose (20:50, wt.%) and investigated the direct hydrogenolysis of furfural and HMF in organic phase over Ru/Co_3O_4 catalyst without extra separation and purification processes.

HMF had been efficiently converted to DMF using Ru/Co_3O_4 as catalyst in THF solvent at mild conditions (130 °C and 0.7 MPa of H_2 pressure, Table 2, Entry 1). Altering with other high boiling-point solvents, such as sec-butylphenol, excellent yield (75%) still can be obtained over this Ru/Co_3O_4 catalyst at the same reaction conditions. It was found that Ru particles were favourable for H_2 activation and hydrogenation reactions, and CoO_x species as an early transition metal oxide played a key role in the cleavage of C-O bond.[17,24] The hydrogenolysis of HMF passed through three steps: 1) hydrogenation of HMF to bis(hydroxymethyl)furan (II); 2) hydrogenolysis of II into 2-hydroxymethyl-5-methylfuran (III); 3) hydrogenolysis of III to DMF. Besides, little amount of 5,5'-(oxybis(methylene))bis(2-methylfuran) (IV) was formed through the etherification of III as well (Scheme 2). Here, as shown in Entry 2, this Ru/Co_3O_4 catalyst also displayed excellent performances for simultaneous hydrogenolysis of furfural and HMF in collected organic phase, and both of them can be fully converted under mild conditions (130 °C with 0.7 MPa of H_2 pressure). But the yields of MF and DMF were low, about 47.9 and 39.6%, respectively and a certain amount of intermediates, such as I (furfuryl alcohol, 51.3%), II (29.3%), III (22.4%) and IV (8.2%) formed, which may be due to the presence of water in the organic phase (ca. 3%). Following further increases to 170 °C and 1.0 MPa, these intermediates can be further converted and the yields of MF and DMF increased, up to 92.5 and 90.8% (Entry 3), respectively, indicating that furfural and HMF in the upper THF phase can be directly converted and upgraded into MF and DMF without complicated separation and purification processes. Even obtained from lignocellulosic biomass, such as birch, cornstalk, pine, bagasse, and poplar, furfural and HMF in the organic phase can be converted to MF and DMF with high yields (Entry 5-9), about 92.6/89.2, 92.3/90.4, 92.0/90.1, 90.9/89.6, and 92.7/88.8%, respectively, indicating the robustness of Ru/Co_3O_4 catalyst and also realizing the goal of production of liquid biofuels from the lignocellulosic biomass. In addition, this catalyst was also stable, and the yield of MF and DMF only decreased slightly after being used three times (Entry 4). The Ru particles were still highly dispersed and did not sinter after the reaction, since no reflections of Ru particles appeared in the XRD pattern (Fig. S2).



Scheme 2 Proposed catalytic reaction pathway for the conversion of furfural and HMF into MF and DMF over 3.5 wt.% Ru/Co_3O_4 catalyst.

These results are very promising since they show that the mixture of C5 and C6 sugars, even lignocellulosic biomass can be directly and efficiently converted to the liquid biofuels or additives of gasoline (MF and DMF) with high selectivity and yield through combination the hydrolysis and dehydration step with subsequent hydrogenolysis step together under mild conditions, avoiding the complicated and energy-intensive separation and purification processes for the platform compounds furfural and HMF.

Conclusions

In the industrial production, avoiding extra separation and purification steps for platform compounds would be promising and beneficial, and thereby decreases the energy-consumption and cost of the production of renewable liquid biofuels from lignocellulosic biomass. Here, we described an efficiently catalytic process for converting lignocellulosic biomass into biofuels with high-energy content through integrating the production of furan derivatives (furfural and HMF) with sequential upgrading process. High yield of furfural and HMF can be firstly obtained from the mixtures of C5 and C6 sugars or even from lignocellulosic biomass in a biphasic system under mild conditions. Then the generated furfural and HMF in the upper organic phase were directly upgraded into renewable liquid biofuels, avoiding their complicated separation and purification processes. Nearly all of furfural and HMF in the THF phase were converted, and the yields of MF and DMF were both above 90%. Finally, the catalytic systems, including the hydrolysis step, dehydration reaction, and hydrogenolyisis process, have been shown to be robust, and solid catalysts can be recycled repeatedly without loss of activities. The seamless integration of lignocellulosic biomass into renewable liquid biofuels will accelerate our society moving towards a renewable transportation economy by utilizing cheap feedstocks, catalyst reusability, mild reaction conditions, and cost abatement in separation and purification.

Table 2 Results of the direct conversion of the generated furfural and HMF in upper THF phase into MF and DMF.[a]

					Products		Others			
Entry	Temp. (°C)	P_{H2} (MPa)	$C_{Furfural}$ (%)[b]	C_{HMF} (%)[b]	Y_{MF} (%)[c]	Y_{DMF} (%)[c]	I (%)	II (%)	III (%)	IV (%)
1[d]	130	0.7	-	> 99	-	93.5	-	-	1.6	4.7
2	130	0.7	> 99	> 99	47.9	39.6	51.3	29.3	22.4	8.2
3	170	1.0	> 99	> 99	92.5	90.8	6.7	0.9	3.0	4.6
4[e]	170	1.0	> 99	> 99	91.4	88.9	8.2	1.3	2.7	6.8
5[f]	170	1.0	> 99	> 99	92.6	89.2	6.5	0.8	2.5	7.2
6[g]	170	1.0	> 99	> 99	92.3	90.4	6.8	0.5	3.2	6.0
7[h]	170	1.0	> 99	> 99	92.0	90.1	7.6	0.7	3.2	6.1
8[i]	170	1.0	> 99	> 99	90.9	89.6	8.3	0.7	2.8	6.5
9[j]	170	1.0	> 99	> 99	92.7	88.8	6.9	1.1	3.4	6.5

[a] Reaction conditions: 0.1 g of Ru/Co_3O_4, 3 mL of organic phase from the dehydration reaction using the mixture of xylose and glucose (20:50, wt.%) as the substrate, 3.4 mL of THF, 24 h, 0.1 mL of tridecane (internal standard compound). All catalysts were reduced before used in the reaction. [b] Calculated on the actual amount of furfural or HMF in 3 mL of THF phase (approximately containing 16.69 and 36.57 mg of furfural and HMF). [c] Calculated as: (the mole of generated MF or DMF)/(the mole of furfural or HMF). [d] Adapted from ref.[17]. [e] The collected catalyst was used in the third run. [f-j] The upper THF phases containing furfural and HMF were obtained from birch, cornstalk, pine, bagasse, and poplar, respectively.

Experimental

Reagents

5-(Hydroxymethyl)furfural (HMF), MF, DMF, and levulinic acid (LA) were purchased from Alfa Aesar Chemical Reagent Company. Furfural, NaCl, xylose, and glucose were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The lignocellulosic biomass, such as birch, cornstalk, pine, bagasse, and poplar were dried at 100 °C for 1 day, smashed and milled at 800 rpm for 1 day, and then sized above 60 meshes before use. The contents of hemicellulose and cellulose in this lignocellulosic biomass were accorded to that presented by Zhang *et al.*[22] Tetrahydrofuran (THF) was chemical pure solvents and purchased from Shanghai Chemicals Company. All reagents were used as supplied without further purification.

Catalyst preparation

Sn-Mont catalyst was synthesized by ion-exchanged method. 3 g of Ca-Mont and an aqueous solution of $SnCl_4 \cdot 5H_2O$ was mixed and stirred at 50 °C for 24 h. The collected clay was filtered and washed with water until the filtrate was neutral (pH = 7). Finally, this catalyst was dried at 100 °C overnight, followed by being ground to powder in a mortar with a pestle and stored in a glass bottle. In order to further improve the conversion of xylose in the mixed sugars or hemicellulose in the lignocellulosic biomass, another solid acid catalyst of $NbOPO_4$ was used as the co-catalyst, which was water-tolerant and used in the aqueous phase dehydration of xylose and fructose.[19] Typically, 1.32 g (0.01 mol) of diammonium hydrogen phosphate was dissolved in 20 mL water and then the pH was adjusted to 2 using phosphoric acid. With vigorous stirring, 20 mL of 0.5 M niobiumtartrate (pH = 2) was added to the above solution. Then the mixed solution was dropped into the aqueous solution of cetyltrimethyl ammonium bromide (CTAB) which was previously prepared by dissolving 1.0 g of CTAB in 13 mL of distilled water. The pH value of the final solution was about 2. This mixture was stirred for additional 60 min at 35 °C, and then the transparent solution was aged in a Teflon-lined autoclave for 24 h at 160 °C. After cooling down, the solid was filtered, washed with distilled water and then dried at 50 °C. Finally, the $NbOPO_4$ sample was obtained by calcination at 500 °C for 5 h in air.

The hydrogenolysis of furfural and HMF in the organic phase was catalyzed by a Ru/Co_3O_4 catalyst, which was prepared by the co-precipitation method from an aqueous solution of ruthenium trichloride and cobalt nitrate ($Ru/(Ru + Co_3O_4) = 3.5$ wt.%, solution A) and a basic solution (NaOH and Na_2CO_3, solution B). Firstly, an aqueous solution (100 mL) containing 0.045 mol of $Co(NO_3)_2 \cdot 6H_2O$ and 0.001 mol of $RuCl_3 \cdot 3H_2O$ (solution A) and another aqueous solution (100 mL) containing 0.13 mol of NaOH and 0.065 mol of Na_2CO_3 (solution B) were added dropwise into 250 mL of deionized water at room temperature under vigorous stirring to maintain the pH value around 10.8. Then the mixture was aged at 80 °C for 24 h under magnetic stirring. After cooling down to room temperature, the solid precipitate was collected by centrifugation and washed several times with deionized water until the pH value of the filtrate was neutral (pH = 7). The resulting Ru/Co_3O_4 catalyst was obtained after drying at 100 °C and calcined at 500 °C for 4 h with a ramp of 2 $°C \cdot min^{-1}$. Then the obtained material was reduced at 200 °C with flowing H_2 in a tube furnace for 2 h with a ramp of 2 $°C \cdot min^{-1}$ before use as a catalyst. The final Ru loading in the calcined catalyst determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) was 3.2 wt.%, approximately in agreement with the initial designed content.

Hydrolysis of xylose and lignocellulosic biomass

Hydrolysis of xylose: the reaction was conducted in a stainless steel autoclave (50 mL) heated with a temperature-controlled heating jacket. 0.2 g of xylose, 0.1 g of Sn-Mont, and solvent (5 mL of organic solvent and 1 mL of water saturated with NaCl) were charged in the sealed autoclave equipped with a magnetic stirring bar at around 400 rpm. Nitrogen (N_2) gas was used for purging air outside the reactor and keeping a certain pressure to prevent solvent boiling. Co-hydrolysis of xylose and glucose: 0.2 g of xylose and glucose with different weight ratios, 0.1 g of Sn-Mont, and solvent (5 mL of organic solvent and 1 mL of water saturated with NaCl) were put in the reactor. Hydrolysis of lignocellulosic biomass: 0.2 g of milled lignocellulosic biomass, 0.1 g of Sn-Mont, and solvent (5 mL of organic solvent and 1 mL of water saturated with NaCl) were charged in the sealed autoclave.

After reaction, the reactor was cooled down to room temperature in cool water, and the reaction medium itself was separated into two phases, the upper organic phase and the lower aqueous phase. After dilution with THF and water, the upper organic phase and the lower aqueous phase were taken for analysis by HPLC, respectively. The used catalyst in the aqueous phase were collected by centrifugation, washed with water and ethanol, and dried at 100 °C overnight for a new cycle.

The analysis of furfural and HMF in the upper organic phase was carried out by means of an HPLC apparatus (Agilent 1260) equipped with an Ultraviolet Detector (Agilent G 1314B) by using an XDB-C18 column (Eclipse USA, 5 um, 4.6×250 mm) operated at 45 °C. The maximum absorption wavelengths for furfural and HMF were 274 and 282 nm, respectively. In order to quantify the content of furfural and HMF together, 254 nm was selected in this work and the values of linearity coefficient were 0.997 and 0.999, respectively. The mobile phase was a mixture of methanol and water (20:80, v/v) with a flow rate of 0.6 $mL \cdot min^{-1}$. The analysis of the lower aqueous phase was conducted on an HPLC apparatus (Agilent 1200) equipped with a Refractive Index Detector (Agilent G 1362A) by using a Bio-Rad Aminex HPX-87H sugar column operated at 80 °C. The mobile phase was pure water with a flow rate of 0.8 $mL \cdot min^{-1}$. All the main products were quantified based on the external standard and their structures were confirmed by GC-MS. An auto-sampler (Agilent G1329A) was used to enhance the reproducibility.

Conversion of monosaccharide (C, mol%), yield (Y, mol%) and selectivity (S, mol%) of products were defined as follows:

$$\textit{monosaccharide conversion} = \frac{\textit{moles of monosaccharide reacted}}{\textit{moles of starting monosaccharide}}$$

$$\textit{product yield} = \frac{\begin{array}{c}\textit{moles of product produced both in organic}\\ \textit{phase and aqueous phase}\end{array}}{\textit{moles of starting monosaccharide}}$$

$$\textit{product selectivity} = \frac{\textit{product yield}}{\textit{monosaccharide conversion}}$$

In addition, the soluble polymers and insoluble by-products (*e.g.*, humins) were not quantified, due to their difficulties to be detected on HPLC or GC-MS.

For lignocellulosic biomass, the yields of furfural and HMF were defined as follows:

$$\textit{furfural yield} = \frac{\begin{array}{c}\textit{moles of furfural produced both in organic}\\ \textit{phase and aqueous phase}\end{array}}{\textit{moles of pentose units in lignocellulosic biomass}}$$

$$\textit{HMF yield} = \frac{\begin{array}{c}\textit{moles of HMF produced both in organic}\\ \textit{phase and aqueous phase}\end{array}}{\textit{moles of hexose units in lignocellulosic biomass}}$$

Direct hydrogenolysis of furfural and HMF in the separated organic phase

In a typical experiment for the hydrogenolysis of the generated furfural and HMF, 3 mL of the separated organic phase, 0.1 g of 3.5 wt.% Ru/Co_3O_4 catalyst, 3.4 mL of THF and 0.1 mL of tridecane (internal standard) were placed in a stainless steel autoclave (50 mL) equipped with a magnetic stirring bar. The system was pressurized with H_2 before heating with a temperature-controlled heating-jacket. After the reaction, the reactor was rapidly cooled down in cool water. The solid catalyst was collected by filtration for the next usage, and the filtrate was taken for analysis. The structure characteristics and quantification of the products were conducted using gas chromatography-mass spectrometry (GC-MS). The conversion of HMF and yield of DMF were based on the internal standard method.

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Notes and references

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