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Conversion of Xylose to Furfuryl Alcohol and 2-Methylfuran in a Continuous Fixed-Bed Reactor

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An efficient process was designed for the synthesis of furfuryl alcohol and 2-methylfuran from xylose using a continuous fixed-bed reactor over a catalyst combining Hβ zeolite and Cu/ZnO/Al_2O_3 in γ-butyrolactone (GBL)/water as solvent. The cooperative effect of Hβ zeolite and GBL facilitated the dehydration of xylose and enhanced largely the furfural yield. The production of furfuryl alcohol and 2-methylfuran can be simply tuned by changing the hydrogenation temperature for furfural over the Cu/ZnO/Al_2O_3 catalyst. The yield for furfuryl alcohol reached 87.2% at 150 °C whereas a yield of 86.8% was achieved for 2-methylfuran at 190 °C.

With the growing requirement of fuels and chemicals, the strategies to cope with the depletion of fossil resources and environment pollution become increasingly important.[1] The utilization of biomass resources is considered as a beneficial solution due to their renewable and abundant nature.[2] One of the key strategies for biomass utilization is to convert the biomass-derived carbohydrates to platform chemicals, followed by the transforming of these platform chemicals to fuels and fine chemicals.[3] Among the various pathways for carbohydrate conversions, the conversion of xylose to furfural and the subsequent hydrogenation of furfural have been identified as a promising route in industry.[4]

As one of the top-value platform chemicals, furfural is the feedstock for many valuable chemicals, including furfuryl alcohol (FFA), 2-methylfuran (2-MF), tetrahydrofurfuryl alcohol, and 2-methyltetrahydrofuran.[5,6] More than 50% of furfural is consumed to produce FFA, which is an important monomer in the polymer industry.[7] 2-MF is considered as a promising liquid fuel as it has several excellent properties such as comparable energy density, better knock suppression ability, and lower aldehyde emission.[8] The current industrial production processes of FFA and 2-MF from biomass resources contain several steps. Specifically, furfural is produced from the dehydration of pentose (xylose) in hemicellulose over mineral acid catalysts and the further hydrogenation of the carbonyl bond (C=O) in furfural yields FFA; 2-MF, on the other hand, can be obtained through the hydrogenolysis of FFA (Scheme 1). Compared with the multi-step process, the efficient conversion of xylose to FFA or 2-MF using a one-step method is promising as it is more economical and the energy-intensive separation of furfural is not necessary. Although many efforts have been made to improve the efficiencies of the separate steps in the multi-step process, those to enhance the efficiencies of the direct conversion of xylose to FFA and 2-MF are scarce. Particularly, the controllable production of FFA and 2-MF from xylose still remains a challenge. Perez and Fraga investigated the one-pot production of FFA from xylose over combined Pt/SiO_2 and sulfated ZrO_2 catalysts in a batch reactor, and a considerable yield of 51% for FFA was obtained.[7] Ordomsky et al. reported the dehydration of xylose and the consecutive furfural hydrogenation over Amberlyst-15 and a Ru/C catalyst, and the main product was tetrahydrofurfuryl alcohol with a selectivity of 50% at a xylose conversion of 32%.[9] Several problems are faced for the direct conversion of xylose using a batch reactor. One problem is that besides contacting with the first catalyst (the acid catalyst), xylose molecules have equal possibilities to contact with the second catalyst, that is, the hydrogenation catalyst. In this case, xylose is readily converted into xylitol over the hydrogenation catalyst, which cannot be converted to furfural.[9] Another problem is that a longer reaction time is usually required in the batch reactor compared with that in the continuous reactor, which would inevitably promote the side reactions between xylose, xylose dehydration intermediates ,and FFA.[10] All these problems would lead to a complexity in the product distribution and a large reduction in the yield for the overall process. It would be, therefore, more desirable but highly challenging to develop a more efficient process to produce FFA and 2-MF directly from xylose with improved overall yield under mild reaction conditions.

Herein, an efficient process was designed to produce FFA and 2-MF from xylose under mild conditions. The efficient production of FFA and 2-MF can be realized through the utilization of a continuous fixed-bed reactor system over a catalyst utilizing a combination of acidic Hβ zeolite and Cu/ZnO/Al_2O_3 in a mixture of γ-butyrolactone (GBL)/water as solvent. The production of FFA and 2-MF can be simply tuned by changing the hydrogenation temperature for furfural. Interestingly, a co-

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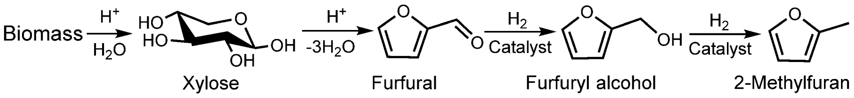


Scheme 1. Conversion of biomass to FFA and 2-MF.

operative effect of Hβ zeolite and GBL was observed, which facilitated the dehydration of xylose to furfural and consequently enhanced largely the overall efficiency of the process. A high yield of 87.2% for FFA was obtained at 150 °C and 0.1 MPa H_2 whereas a yield of 86.8% for 2-MF was achieved at 190 °C and 0.1 MPa H_2.

Initially, we selected zeolites as the solid acid catalysts for the dehydration of xylose because of their high hydrothermal stability and easy recovery. The conversion of xylose into furfural over various zeolites was investigated in a fixed-bed reactor (Table 1). Furfural yields were low over HZSM-5 and H-Mordenite whereas higher yields were obtained over HY and Hβ. Particularly, a high yield of 87.6% for furfural was achieved over Hβ. Compared with other zeolites, HY and Hβ have more acid sites (Table S1 and Figures S2 and S3 in the Supporting Information) and larger pores, which facilitated the dehydration of xylose into furfural.[11] Especially, Hβ can catalyze efficiently the isomerization of xylose to xylulose at its Lewis acid sites.[12] Xylulose was dehydrated more readily into furfural over the Brønsted acid sites relative to xylose, which favored the high selectivity of furfural.[13]

Table 1. Dehydration of xylose to furfural.[a]

Entry	Catalyst	Solvent	Xylose conversion [%]	Furfural yield [%]
1	Hβ[b]	GBL/water	99.8	87.6
2	HY	GBL/water	99.9	59.5
3	HZSM-5	GBL/water	99.9	24.9
4	H-Mordenite	GBL/water	99.9	17.5
5[c]	Hβ[d]	water	99.8	18.5
6[c]	Hβ	methanol/water	99.9	21.3
7[c]	Hβ	ethanol/water	99.9	26.5
8[c]	Hβ	1,4-dioxane/water	99.9	50.3

[a] 150 °C, 0.1 MPa H_2, WHSV (xylose) = 0.023 h^{-1}, H_2 feed: 25 mL min^{-1} and pressure 0.1 MPa, 5 g zeolite catalyst, xylose concentration for each run: 5 wt%, water content in organic solvent/water mixture: 20 wt%. [b] Carbon balance: 87.7%. [c] 2 MPa, H_2 feed: 300 mL min^{-1}; XRD patterns of various zeolites are shown in Figure S1 in the Supporting Information. [d] Carbon balance: 19.1%.

In the acid-catalyzed dehydration of sugars, the catalytic efficiency not only relies on the acidic properties of catalysts but also on the solvents.[14,15] The yield of furfural was low (< 20%) when using water as the solvent (Table 1, entry 5), implying a negative effect of water on xylose dehydration. Therefore, several organic solvents including methanol, ethanol, 1,4-dioxane, and GBL were selected as the solvent (Table 1, entries 1, 6–8) to improve the catalytic efficiency of xylose dehydration and the selectivity toward furfural. It was observed that the furfural yield increased in these organic solvent/water mixtures. Particularly, the highest yield of furfural was obtained using GBL/water as solvent. In addition, the loss of furfural in water and GBL/water was also explored. A considerable loss for furfural (36.7%) was observed in water whereas the degradation of furfural into humins occurred much less in GBL/water (see Table S2 in the Supporting Information). This implied that the GBL/water mixture reduced furfural degradation during xylose dehydration, which facilitated a higher selectivity to furfural. However, the presence of water is inevitable in the reaction as it is required to dissolve xylose and is a product of xylose dehydration.[16] Therefore, the effect of water content in GBL/water on the dehydration reaction was investigated (Table 2, entries 1–5). The furfural yield reached a high level when the water content was in the range of 10–20%, and decreased drastically when the water content exceeded 30%. The effect of reaction temperature on the reaction was also studied (Table 2, entries 6–8). The furfural yield increased with increasing reaction temperature, with the suitable temperature being 150 °C.

Table 2. Effects of water content and reaction temperature on the dehydration of xylose.[a]

Entry	T [°C]	Water content [wt%]	Xylose conversion [%]	Furfural yield [%]
1	150	10	99.4	82.6
2	150	20	99.9	87.6
3	150	30	99.9	77.3
4	150	40	99.6	41.3
5	150	50	99.9	35.6
6	130	20	89.4	65.6
7	140	20	99.9	77.3
8	160	20	99.9	86.6

[a] WHSV (for xylose) = 0.023 h^{-1}, H_2 feed: 25 mL min^{-1}, 0.1 MPa H_2, 5 g zeolite catalyst for each run, xylose concentration for each run: 5 wt%.

The stability for Hβ was further investigated. The yield of furfural decreased considerably after a time on stream of 162 h, implying the deactivation of zeolite catalyst (Figure 1). In addition, a mass loss was observed using thermogravimetric (TG) analysis for the used Hβ (Figure S4, the Supporting Information) and the color of the used Hβ changed from black into white after TG analysis. These results indicated that the observed mass loss can be ascribed to the removal of the carbon deposits on the used Hβ. Therefore, Hβ used for 162 h was recalcined (recovered) in air at 550 °C for 2 h and again used for the reaction. The furfural yield on the recycled Hβ reached the same level as the fresh counterpart, implying that

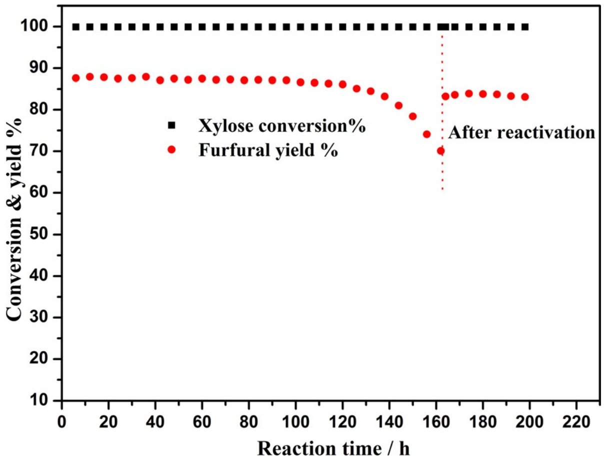


Figure 1. Stability of Hβ zeolite. Conditions: weight hourly space velocity (WHSV) of xylose = 0.023 h^{-1}, H_2 feed rate 25 mL min^{-1} and pressure 0.1 MPa, 5 g Hβ zeolite catalyst, xylose concentration 5 wt %, water concentration 20 wt %, GBL concentration 75 wt %.

the activity of Hβ can be recovered by the reactivation in air (Figure 1).

As xylose can be efficiently converted to furfural over Hβ, a metal catalyst is required for the hydrogenation of produced furfural to FFA and 2-MF. Our previous study shows that the non-noble Cu/ZnO/Al_2O_3 catalyst has a high activity and selectivity for the hydrogenation of furfural and hydrogenolysis of FFA.[17,18] Hence, the direct conversion of xylose into FFA or 2-MF was investigated over a combination of Hβ and ternary CuO/ZnO/Al_2O_3 as the catalyst systems (Figure 2). As can be seen in Table 3, the products included FFA, furfural, 2-MF, and γ-valerolactone. A considerable amount of furfural (26.5 %) was obtained when the mass ratio of Hβ to CuO/ZnO/Al_2O_3 was 2.5, indicating that the amount of active sites present in the Cu catalyst were not enough for the hydrogenation of furfural. Therefore, we increased the amount of CuO/ZnO/Al_2O_3 catalyst to enhance the capability for furfural hydrogenation. The FFA yield increased with increasing the amount of Cu catalyst, and a yield of 87.2 % for FFA was achieved when the mass ratio of Hβ to CuO/ZnO/Al_2O_3 was 1. This yield, to our best of knowledge, was the highest in literature concerning the direct conversion of sugars to FFA. With a further increase in the amount of CuO/ZnO/Al_2O_3, both the FFA and 2-MF yields did not change. This result indicated that the reaction temperature was insufficient for the hydrogenolysis of FFA to 2-MF, and a higher reaction temperature (> 150 °C) was necessary for the efficient conversion of furfural to 2-MF. Therefore, the reaction temperature for the hydrogenation of furfural over Cu/ZnO/Al_2O_3 was further increased. A gradual increase in the yield of 2-MF was observed, which was accompanied by a gradual reduction in the FFA yield on further increasing the reaction temperature. The yield of 2-MF reached nearly 90 % whereas only traces of FFA were detected at 190 °C. This result clearly demonstrated the excellent efficiency of the integrated technology proposed herein for the direct conversion of xylose to 2-MF.

In summary, an efficient integrated process was designed for the direct conversion of xylose to furfuryl alcohol (FFA) and 2-methylfuran (2-MF) over a combined Hβ zeolite and Cu/ZnO/Al_2O_3 catalyst in a continuous fixed-bed reactor using γ-butyrolactone (GBL)/water as the solvent. The cooperative effect of Hβ zeolite and GBL facilitated the dehydration of xylose to furfural, leading to a high furfural yield. Hβ zeolite deactivated by carbon deposits could be recovered by reactivation in air, and the recycled Hβ zeolite reached a similar activity for the dehydration of xylose in comparison with the fresh counterpart. By controlling the reaction temperature for the hydrogenation of furfural over Cu/ZnO/Al_2O_3, the product distribution can be conveniently tuned from FFA to 2-MF. A high yield was achieved for FFA (87.2 %) at 150 °C, and a yield of 86.8 % was achieved for 2-MF at 190 °C.

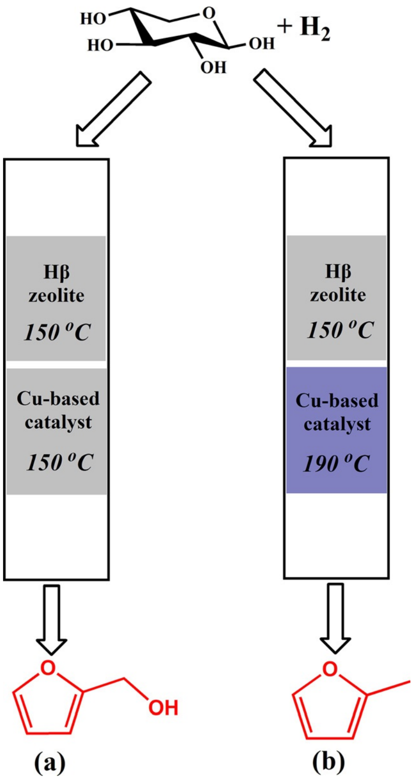
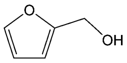
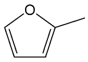
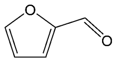
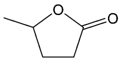


Figure 2. Direct conversion of xylose to (a) FFA and (b) 2-MF in a fixed-bed reactor.

Experimental Section

The conversion of xylose to furfural, FFA, and 2-MF were performed in a continuous fixed-bed reactor. The reactor (600 mm long, 12 mm i.d.) was packed with the catalysts (20–40 mesh), which were located in the thermostat segment of the fixed-bed reactor. Before the reaction, CuO/ZnO/Al_2O_3 was pre-reduced in situ using a stream of 10 % H_2/N_2 (60 mL min^{-1}) under 250 °C for 2 h. The reaction solution (xylose in GBL/water) was continuously pumped to the reactor using a HPLC pump. In addition, a stream of pure H_2 was introduced from the top of the reactor using a mass-flow controller. The final products were condensed and collected in a gas–liquid separator. The conversion of xylose was analyzed using HPLC [Agilent 1260 equipped with a Shodex SH-1821 capillary column (300 mm × 8 mm × 0.6 μm) and a refractive index detector].

Table 3. Conversion of xylose to FFA and 2-MF.[a]

Entry	$H\beta/CuO/ZnO/Al_2O_3$ ratio [$g\,g^{-1}$]	T [°C]	Xylose conversion [%]	Yield [%]			
							
1	2.5:1	150	99.4	59.3	0.4	26.5	0.2
2	2:1	150	99.9	68.1	0.6	18.9	0.4
3	1:1	150	99.9	87.2	1.1	0.2	1.5
4	1:2	150	99.6	86.9	1.5	trace	2.6
5[b]	1:1	170	99.9	40.6	45.2	trace	1.2
6[b]	1:1	180	99.9	19.3	68.5	trace	2.6
7[b]	1:1	190	99.9	0.1	86.8	trace	1.9

[a] WHSV (xylose) = 0.023 h^{-1}, H_2 feed: 25 mL min^{-1}, 0.1 MPa H_2, 5 g zeolite catalyst, xylose concentration: 5 wt%, water concentration: 20 wt%, GBL concentration: 75 wt%; all Cu-based catalysts were pretreated with 10% H_2/N_2 at 250 °C for 2 h in situ before the reactions. [b] The reaction temperature for the xylose dehydration over Hβ zeolite was 150 °C; the stability of $CuO/ZnO/Al_2O_3$ is shown in Figure S5 in the Supporting Information.

The temperature of the capillary column and the detector was 50 °C. The mobile phase was diluted sulfuric acid (pH 2) at a flow rate of 0.6 mL min^{-1}. The yields of all products were analyzed by GC [Agilent 7890 equipped with a DB-INNOWAX capillary column (30 m × 0.32 mm × 0.5 μm) and a flame ionization detector (FID) detector]. The FID detector temperature and injection temperature was 250 °C. The injecting sample size was 0.2 μL, and the split ratio was 50. Standard solutions were used to obtain the calibration curves to calculate the concentrations of the compounds by the external standard method.

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Keywords: γ-butyrolactone · fixed-bed reactor · furfural · heterogeneous catalysis · xylose

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