## One-step Conversion of Furfural into 2-Methyltetrahydrofuran under Mild Conditions

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One-step direct conversion of biomass-derived furfural to 2methyltetrahydrofuran was realized under atmospheric pressure over a dual solid catalyst based on two-stage-packed Cu– Pd in a reactor; this is the first report that one-step conversion of furfural resulted in high yield of 2-methyltetrahydrofuran (97.1%) under atmospheric pressure. This strategy provided a successive hydrogenation process, which avoids high H<sub>2</sub> pressure, uses the reactor efficiently, and eliminates the product-separation step. Therefore, it could enhance the overall efficiency as a result of low cost and high yield.

Currently, the development and utilization of the biomassbased carbon resources is vitally critical for the sustainable production of transportation fuels and chemical substan-

ces.<sup>[1-3]</sup> Biomass-based synthesis of 2-methyltetrahydrofuran (2-MTHF) has gained significant attention as an approved gasoline additive with excellent combustion properties, as a versatile new-style solvent with broad application in organic chemistry and in the commercial resin industry, and also as an important medical intermediate.<sup>[4,5]</sup> Generally, 2-MTHF is derived from lignocellulose, which is a promising biomass-based alternative in the search for environmentally benign synthesis strategies.<sup>[6,7]</sup> The conversion of lignocellulose into 2-MTHF is achieved by a multistep conversion, including an acid-catalyzed hydrolysis of lignocellulose (pentose) to furfural, followed by hydrogenation-deoxygenation of furfural to 2-methylfuran (2-MF) and further hydrogenation of 2-MF to 2-MTHF in several separated reaction systems (Scheme 1).<sup>[8-11]</sup> For the conversion of lignocellulose into furfural (the first step reaction for the conversion of lignocellulose to 2-methyltetrahydrofuran), a high yield of furfural was achieved over various catalysts,

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|     | Supporting Information for this article is available on the WWW under<br>http://dx.doi.org/10.1002/cssc.201500178.    |

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and the process was commercialized.<sup>[8,12–14]</sup> However, the following two steps faced several problems, that is, limited largescale production of 2-MTHF [including the direct conversion of furfural to 2-MTHF necessitating a high H<sub>2</sub> pressure (>8.0 MPa)] and the multi-step conversion requiring multicomponent catalysts, at least two different reactors, and the isolation systems for the intermediates.<sup>[15,16]</sup> In a patent, it was reported that the conversion could also be realized by a two step conversion of furfural, for which two reactors and two catalysts are required.<sup>[7]</sup> In the first reactor, furfural was converted into 2-MF, then the crude product 2-MF was isolated and purified through a separation system. Following the second step, hydrogenation was performed in another reactor with the purified intermediate 2-MF as feed (reactant). Although this pro-



Scheme 1. Synthesis pathways of 2-methyltetrahydrofuran through the conversion of lignocellulose.

cess could avoid high  $H_2$  pressures, it would consume a great deal of energy and material and reduce the yield of the overall process. Thus, it would produce some negative effects on the economy of the 2-MTHF industry.

To the best our knowledge, there are only few reports on the one-step conversion of furfural to 2-MTHF in a reactor under atmospheric pressure. Especially high  $H_2$  pressure and the multiple reaction systems are the reasons limiting the large-scale production of 2-MTHF via biomass conversion because the whole process is difficult to control and requires a great deal of energy to complete, thus reducing the overall efficiency and yield of hydrogenation reaction.



Herein, a new continuous process is realized for the synthesis of 2-MTHF via the direct conversion of furfural under mild conditions that avoids the use of multiple reactors. We designed a successive process for the synthesis of 2-MTHF under atmospheric pressure, in which the conversion of intermediates can be controlled efficiently on the basis of the nature of the functional groups in furfural and especially through the method of packing the reactor with the catalyst. Interestingly, when the continuous fixed-bed reactor was fed with pure furfural, the yield of desired product 2-MTHF was high (up to 97.1%) for an optimized packing of the dual solid catalysts Cu-Pd under atmospheric pressure. From the perspective of energy consumption, this technology is also economical and greatly reduces the cost of product separation as the products are automatically isolated in the two-phase oil-water-based system (low solubility of 2-MTHF in water; Figure S1 in the Supporting Information). Furthermore, we also performed a detailed investigation of the performance of various catalysts and the influence of reaction conditions on the synthesis of 2-MTHF.

The hydrogenation process from furfural to 2-MTHF was investigated in a continuous fixed-bed reactor over various catalysts (Figure S2 and Table 1). Furfural possesses both C=C and C=O bonds and is a type of  $\alpha,\beta$ -unsaturated compound, which was treated as a good model compound for studying the selective hydrogenation of C=C and C=O bonds. Therefore, the selective conversion of functional groups from furfural plays an important role in the field of biomass conversion.<sup>[17]</sup> Crucially, the conversion of furfural to 2-MTHF demands the hydrogenation-deoxygenation of the --CH=O bonds and the hydrogenation of the C=C bonds in the furan ring (Scheme 1). Generally, Cu-based catalysts are superior to some conventional hydrogenation catalysts in the hydrogenation-deoxygenation of the -CH=O bonds,<sup>[18,19]</sup> and Ni/Pd-based catalysts play a significant role in the selective hydrogenation of C=C bonds.<sup>[20,21]</sup> Therefore, Cu/Ni/Pd-based catalysts might be excellent catalysts for the direct conversion of furfural to 2-MTHF. However, the reduction temperature of Cu and Ni metals is discordant, so Cuand Pd-based catalysts would be the better choice for the successive hydrogenation of furfural to 2-MTHF. Our previous work suggested that Cu/SiO<sub>2</sub> catalyst performs excellently in the hydrogenation-deoxygenation of the C=O bonds in furfural (Figure S2).<sup>[22]</sup> Herein, we investigated the operation of Cubased (copper phyllosilicate =  $Cu_2Si_2O_5(OH)_2$ ) and Pd-based (Pd/SiO<sub>2</sub>) catalysts; the results indicated that both Cu<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>2</sub> and Pd/SiO<sub>2</sub> had a poor selectivity towards the desired product 2-MTHF (Table 1, entries 1 and 2). For  $Cu_2Si_2O_5(OH)_2$ , the main product was 2-MF (yield = 84.6%) above 170°C, which derived from the hydrogenation-deoxygenation of the --CH=O bonds in furfural and exhibited an outstanding hydrogenation ability of the --CH=O bonds (Figure S3). However, on Pd/SiO<sub>2</sub>, the major products were tetrahydrofurfuryl alcohol at low temperature and furan at high temperature, which derived from the hydrogenation of the C=C bonds and the breaking of C-C bands in furfural (the breaking of furan ring and --CH=O; Figure S4). To verify the outstanding hydrogenation performance of Pd/SiO<sub>2</sub> for the C=C bonds, 2-MF was used as a reactant on Pd/SiO<sub>2</sub> as only C=C bonds exist in 2-MF, which could be efficiently converted into 2-MTHF with a 98.6% selectivity (Table 1, entry 3). These results verified that the Cu-based catalyst performed well in the hydrogenationdeoxygenation of the -CH=O bonds whereas the Pd-based catalyst efficiently hydrogenated the C=C bonds. Afterwards, the bimetallic CuPd (supported on SiO<sub>2</sub>) catalyst was synthetized and tested for the direct conversion of furfural into 2-MTHF. Unfortunately, CuPd/SiO<sub>2</sub> had a high selectivity for 2-MF and furfuryl alcohol due to the conversion of the --CH=O bonds (Table 1, entry 4), suggesting that the hydrogenation of the --CH=O bonds is superior to that of the C=C bonds of the furan ring in furfural. Based on the above results, we designed an integral process using two-stage packing of Cu<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>2</sub> and Pd/SiO<sub>2</sub> as catalysts (dual solid Cu-Pd catalysts) in a reactor, which depends mainly on the good catalytic performance of the Cu-based catalyst in the synthesis of 2-MF and the subse-

| Table 1. The hydrogenation of furfural over various catalysts. <sup>[a]</sup> |       |            |                   |      |      |          |        |  |  |
|---|-------|------------|-------------------|------|------|----------|--------|--|--|
| Catalysts   | Conv. |            | Selectivity [%]   |      |      |          |        |  |  |
|   | [%]   | $\bigcirc$ | $\langle \rangle$ | O OH | ОН   | THF + FU | others |  |  |
| Cu <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>2</sub>              | 94.4  | 0.8        | 84.6              | 0.1  | 5.4  | 0        | 9.1    |  |  |
| Pd/SiO <sub>2</sub>   | 99.3  | 0.4        | 0.1               | 1.3  | 12.9 | 84.8     | 0.5    |  |  |
| Pd/SiO <sub>2</sub> <sup>[b]</sup>  | 88.9  | 98.6       | 0                 | 0    | 0    | 0        | 1.4    |  |  |
| CuPd/SiO <sub>2</sub> <sup>[c]</sup>  | 88.7  | 1.6        | 66.1              | 20.9 | 4.7  | 0.1      | 6.6    |  |  |
| $Cu_2Si_2O_5(OH)_2 + Pd/SiO_2^{[d]}$  | 97.5  | 85.5       | 4.1               | 0.3  | 9.8  | 0        | 0.3    |  |  |
| $Pd/SiO_2 + Cu_2Si_2O_5(OH)_2^{[e]}$  | 99.5  | 1.6        | 43.4              | 0    | 21   | 28.9     | 5.1    |  |  |
| $Cu_2Si_2O_5(OH)_2 + Pd/SiO_2^{[f]}$  | 99.1  | 14.9       | 65.6              | 0.8  | 12.9 | 1.2      | 4.6    |  |  |

[a] Reaction conditions: atmospheric pressure, 170 °C,  $H_2/furfural (molar ratio) = 29$ , weight hourly space velocity (WHSV) = 0.19 h<sup>-1</sup>,  $Cu_2Si_2O_3(OH)_2 = 1.5$  g, Pd/SiO\_2 = 1.5 g, FU: furan, THF: tetrahydrofuran, others: 2-potanone (2-PO), 2-pentanol (2-PL), 1-pentanol (1-PL), tetrahydrofurfural, furfural polymers. [b] Reactant is 2-MF. [c] CuPd bimetal catalyst: palladium was impregnated on Cu phyllosilicate precursor. [d] The upper reactor was packed with Cu phyllosilicate as catalyst, and the bottom reactor was packed with Pd/SiO<sub>2</sub> as catalyst. [e] The upper reactor was packed with Pd/SiO<sub>2</sub> as catalyst, and the bottom reactor was packed with Cu phyllosilicate as catalyst, and the bottom reactor was packed with Cu phyllosilicate as catalyst, and the bottom reactor was packed with Cu phyllosilicate as catalyst. [f] Cu phyllosilicate and Pd/SiO<sub>2</sub> catalysts were mechanically mixed.

quent C=C bond hydrogenation of 2-MF to 2-MTHF on  $Pd/SiO_2$  (Scheme S1).

Notably, the method of packing of the dual solid Cu-Pd catalyst significantly affected the hydrogenation sequence of the -CH=O and C=C bonds and further influences product selectivity. It was discovered that when the upper of reactor was packed with Cu<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>2</sub> and catalyst and Pd/SiO<sub>2</sub> was at the bottom of the reactor, a 85.5% selectivity to 2-MTHF was obtained (Table 1, entry 5). Contrarily, when Pd/SiO<sub>2</sub> catalyst was in the upper part of the reactor, tetrahydrofurfuryl alcohol and tetrahydrofuran were selectively ob-

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tained through the hydrogenation of the C=C bonds and the breaking of C-C bonds (Table 1, entry 6). To further illustrate the importance of the packing method of the catalysts,  $Cu_2Si_2O_5(OH)_2$  and Pd/SiO<sub>2</sub> catalysts were mechanically mixed, and it was found that the selectivity reaction to 2-MTHF was much lower than for two-stage packing of the dual solid Cu-Pd catalyst (Table 1, entry 7). The molar ratio of H<sub>2</sub>/furfural (mol/mol) was also investigated in our system. When the molar ratio of H<sub>2</sub>/furfural was 29, the selective formation of 2-MTHF was the highest (Figure S5), which might be ascribed to the number of activated hydrogen atoms on the catalyst surface.

Sitthisa et al.<sup>[23]</sup> and Zhang et al.<sup>[24]</sup> reported that Pd-based catalysts could hydrogenate the C=C and C=O bonds at low temperature but would eliminate the C=O bonds (through the breaking of C-C bonds) from furfural at high temperature. In this work, we also investigated in detail the catalytic performance of copper phyllosilicate and Pd/SiO<sub>2</sub> at different reaction temperatures using furfural as feed (Figures S3 and S4), and the result is in accordance with the former reports. Therefore, it was considered that the reaction temperature is vitally important for the hydrogenation-deoxygenation of the -CH= O bonds and the hydrogenation of the C=C bonds on the different metals. At low temperature, the Cu-based catalyst was responsible for the hydrogenation of the -CH=O bonds, but was hardly active for the breaking (deoxygenation) of the -CH=O bonds. Similarly, Pd/SiO<sub>2</sub> performed well in the hydrogenation of the C=C and -CH=O bonds at low temperature, with the main product being tetrahydrofurfuryl alcohol. Nakagawa and Tomishige<sup>[25]</sup> also reported that the yield of 2,5-bis (hydroxymethyl) tetrahydrofuran obtained from the hydrogenation of the --CH=O and C=C bonds in 5-hydroxymethyl-2-furaldehyde reached 96% over a co-impregnation of Ni/Pd catalyst. Contrarily, at high temperature, Cu-based catalysts promoted the breaking (deoxygenation) of the -CH=O bonds, which is advantageous for the selective conversion of furfural into 2-MF.<sup>[18,23]</sup> However, the high reaction temperature is unfavorable for the hydrogenation of C=C bonds over the Pdbased catalyst as a result of side reactions occurring, such as the formation of furan and tetrahydrofuran, which stemmed from the breaking of C-C bonds (Figure 1). It was discovered that the best reaction temperature was 180°C, at which the selectivity towards 2-MTHF formation reached up to 93.3%. Moreover, a decrease in selectivity at a higher temperature

100 100 90 90 Selectivities to products (%) % 80 80 **Conversion of furfural** 70 70 Furfural conversion (%) 60 60 2-MF Selectivity(%) 2-MTHF Selectivity(%) 50 50 2-PO+2-PL+1-PL Selectivity(%) 40 40 THFA Selectivity(%) 30 30 20 20 10 10 0 0 160 170 190 200 180

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**Figure 1.** Influence of reaction temperature on catalytic performance of Cu–Pd dual solid catalysts. Reaction conditions: atmospheric pressure, H<sub>2</sub>/Furfural=29, WHSV=0.19 h<sup>-1</sup>, the upper of reactor: Cu<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>2</sub>=1.5 g, the bottom of reactor: Pd/SiO<sub>2</sub>=1.5 g, THFA: tetrahydrofurfuryl alcohol.

Temperature (°C)

2.0 g Pd/SiO<sub>2</sub> at the bottom of the reactor. This is related to the number of active sites and the different selectivities of the different metals for the conversion of functional groups in furfural. Furfural was first converted to 2-MF over Cu<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>2</sub> in the upper part of the reactor and then further converted to 2-MTHF over Pd/SiO<sub>2</sub> catalyst at the bottom of reactor. When the number of Pd sites is too small for the complete hydrogenation of the C=C bonds, the intermediate 2-MF could not be completely converted into 2-MTHF. It was found that 2-MF selectivity was roughly 23.4% at 0.5 g packing of Pd/SiO<sub>2</sub> (Table 2, entry 1). On the other hand, when there are not enough Cu sites (0.5 g  $Cu_2Si_2O_5(OH)_2 + 2.5$  g Pd/SiO<sub>2</sub>), furfural could be not completely converted to 2-MF, which is then further transformed to other products, such as furan and tetrahydrofuran, by the breaking of the C-C bonds in furfural in (Table 2, entry 4). Therefore, a suitable packing mass of the two-stage catalyst is extremely important for improving the selectivity of desired product 2-MTHF.

In summary, a highly efficiency process for the synthesis of 2-methyltetrahydrofuran (2-MTHF) from biomass-derived furfural was achieved by means of a two-stage packing of a dual solid Cu–Pd catalyst under atmospheric pressure. Compared

(200 °C) was related to the formation of undesired by-products, such as pentanol and pentanone, which were formed through the hydrogenolysis of 2-MF and 2-MTHF.<sup>[26]</sup>

Furthermore, the packing mass of the two-stage catalysts was investigated (Table 2 by varying the catalyst mass, and the yield of 2-MTHF was as high as 97.1% over 1.0 g  $Cu_2Si_2O_5(OH)_2$  catalyst in the upper part of the reactor and

Table 2. The effect of packing mass on product selectivity over dual solid catalysts based on two-stage-packed Cu–Pd.<sup>[a</sup> Packing mass [g+g] Conv. Selectivity [%]  $(Cu_2Si_2O_5(OH)_2 + Pd/SiO_2)$  $\mathsf{THF} + \mathsf{FU}$ [%] others 99.1 68.6 23.4 0.8 2.5 + 0.56.5 0.6 0.1 1.5 + 1.598.4 93.3 4.7 0 0.4 0 1.6 0 0 100 97.1 1.4 0.6 0.9 1.0 + 2.00.5 + 2.5100 76.1 21.2 0.5 0 1.0 1.2 [a] Reaction conditions: atmospheric pressure, T = 180 °C, H<sub>2</sub>/furfural = 29, WHSV = 0.19 h<sup>-1</sup>, the upper reactor was packed with Cu<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>2</sub> as catalyst, the bottom reactor was packed with Pd/SiO<sub>2</sub> as catalyst.

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with the single reaction process, this strategy provided a successive hydrogenation process by avoiding a high H<sub>2</sub> pressure, by using the reactor efficiently, and by eliminating the product-separation step. Therefore, it could enhance the overall efficiency, resulting in low cost and high yield. Notably, 2-MTHF yield is high (up to 97.1% at atmospheric pressure and at 180°C), which is the highest value reported so far. In this successive process, the  $Cu_2Si_2O_5(OH)_2$  catalyst located in the upper part of the reactor was mainly responsible for the synthesis of 2-methylfuran (2-MF) through the hydrogenation–deoxygenation of the –CH=O bonds in furfural, whereas Pd/SiO<sub>2</sub> catalyst at the bottom of the reactor facilitated the subsequent hydrogenation of the C=C bonds from 2-MF. This strategy could also be widely applied to other cascade reactions.

## **Experimental Section**

Details about the preparation method of catalysts and the analysis method of products are provided in the Supporting Information. The one-step direct conversion of furfural to 2-MTHF was performed in a continuous fixed-bed reactor. The reactor (600 mm long, 12 mm i.d.) was packed with a suitable amount of catalysts (20-40 mesh), which were located in the thermostat segment of the fixed-bed reactor. Before reaction, 5% (v/v) H<sub>2</sub>/N<sub>2</sub> was introduced into the reactor to reduce the catalysts by increasing the temperature from 25 to 270°C at a rate of 2°Cmin<sup>-1</sup> and then keeping it at 270 °C for 3 h. After reduction, distilled furfural was continuously pumped to a preheater using a HPLC pump, and the preheater was kept at 140 °C to prevent condensation of vaporized furfural. At the same time, pure H<sub>2</sub> (99.99%) was introduced into the top of the preheater using a mass-flow controller. Thereafter, at atmospheric pressure, vaporized furfural and H<sub>2</sub> were mixed before introducing the mixture into the reactor to perform the hydrogenation. The final products were condensed and collected in a gas-liquid separator.

The particle morphology and crystal size were analyzed using a JEM-1011 electron microscope operating at 80 kV. The reducibility of the catalysts was determined by means of H<sub>2</sub>-temperature programmed reduction, which was performed using an Auto Chem II2920 (Mircromeritics, USA). Temperature-programmed desorption of NH<sub>3</sub> (NH<sub>3</sub>-TPD) was performed on the same instrument as H<sub>2</sub>-TPR (Supporting Information).

## Acknowledgements

This work was supported by the Major State Basic Research Development Program of China (973 Program) (No.2012CB215305).

**Keywords:** biomass conversion · copper · deoxygenation · hydrogenation · palladium

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Received: February 3, 2015 Published online on ■■ ■, 0000

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