ChemPubSoc Europe

DOI: 10.1002/cssc.201601122

CHEMSUSCHEM Full Papers

Catalytic Transfer Hydrogenation of Furfural to 2-Methylfuran and 2-Methyltetrahydrofuran over Bimetallic Copper–Palladium Catalysts

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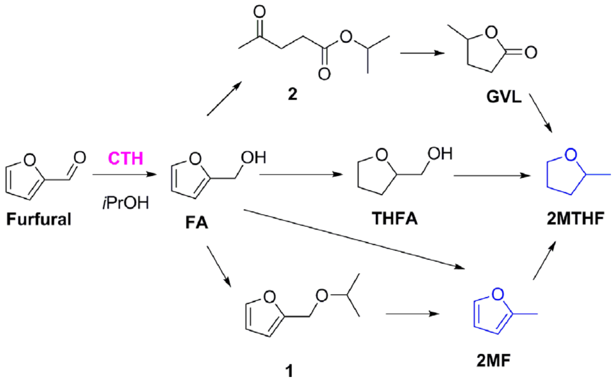
The catalytic transfer hydrogenation of furfural to the fuel additives 2-methylfuran (2-MF) and 2-methyltetrahydrofuran (2-MTHF) was investigated over various bimetallic catalysts in the presence of the hydrogen donor 2-propanol. Of all the as-prepared catalysts, bimetallic Cu-Pd catalysts showed the highest catalytic activities towards the formation of 2-MF and 2-MTHF with a total yield of up to 83.9% yield at 220 °C in 4 h. By modifying the Pd ratios in the Cu-Pd catalyst, 2-MF or 2-MTHF could be obtained selectively as the prevailing product. The other reaction conditions also had a great influence on the product distribution. Mechanistic studies by reaction monitoring and intermediate conversion revealed that the reaction proceeded mainly through the hydrogenation of furfural to furfuryl alcohol, which was followed by deoxygenation to 2-MF in parallel to deoxygenation/ring hydrogenation to 2-MTHF. Finally, the catalyst showed a high reactivity and stability in five catalyst recycling runs, which represents a significant step forward toward the catalytic transfer hydrogenation of furfural.

Introduction

The effective conversion of lignocellusic biomass into sustainable chemicals and fuels has gained much attention during the past few decades. As a result of the oxygen-rich nature of biomass-derived molecules, the selective removal of the oxygenated groups has become a primary challenge for the utilization of these molecules.[1] A variety of chemical reactions, which include dehydration, dehydrogenation, hydrogenation, hydrolysis, and hydrogenolysis, have been reported widely as versatile tools for the conversion,[2] for example, the conversion of oxygen-rich resources to platform molecules and their further upgrade to the desired value-added products. A representative example is the conversion of hemicellulose into, for example, 2-methylfuran (2-MF) and 2-methyltetrahydrofuran (2-MTHF) via the platform molecule furfural.[3] 2-MF and 2-MTHF are good liquid fuel additives with a high energy density, boiling point, and octane number and can be partly blended into gasoline for engines.[3] Additionally, they have numerous applications as solvents in organic/polymer chemistry and as chemical intermediates for drugs.[3] Although the dehydration of hemicellulose to furfural has been industrialized over various catalysts,[4] the conversion of furfural to 2-MF or 2-MTHF is still under development.

The hydrodeoxygenation (HDO) of furfural to 2-MF or 2-MTHF occurs mainly through the hydrogenation and hydrogenolysis of the C=O bonds in parallel to some tandem reactions as shown in the reaction network displayed in Scheme 1. Therefore, catalytic sites with excellent hydrogenation/hydrogenolysis abilities would be potential candidates for this conversion. To date, a variety of catalysts based on Cu,[5] Mo,[6] Pd,[7] Ru,[8] Pt,[9] Ni,[10] and others[11] have been applied successfully for this conversion in the presence of molecular hydrogen. Recently, the use of a hydrogen donor to replace molecular hydrogen has emerged as a green and cost-effective method (i.e., catalytic transfer hydrogenation; CTH) for the reductive upgrading of biomass-derived molecules such as levulinic acid/esters[12] and 5-hydroxymethylfurfural.[13] Numerous studies have been reported on the development of new efficient catalysts for these conversions. However, very few catalysts have been developed for the CTH of furfural. For example, Hermans et al.[14] used a Pd/Fe_2O_3 catalyst for the CTH of furfural in the presence of 2-propanol, however, only 40% yield of



Scheme 1. Reaction network of the hydrogenolysis of furfural.

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Supporting Information for this article can be found under: http://dx.doi.org/10.1002/cssc.201601122.

2-MF+2-MTHF was obtained. Vlachos et al.[15] reported the use of a Ru/C catalyst for the CTH of furfural in 2-propanol, which provided a higher 2-MF yield of 61 % at 180 °C after 10 h. Later, they demonstrated that a partially oxidized Ru/C (Ru/RuO_x/C) possessed a high reactivity toward the CTH of furfural because of the introduction of RuO_x Lewis acid sites and yielded 76 % 2-MF under the same reaction conditions.[16] Despite these advances, more efficient systems for the CTH of furfural are still highly desired.

In light of previous work, the search for active sites for the effective HDO of the aldehyde group and/or further ring hydrogenation has become the top priority for the CTH of furfural to 2-MF or 2-MTHF.[3] Generally, Cu-based catalysts are potential candidates toward the HDO of the aldehyde group to the methyl group, whereas Pd-based catalysts exhibit a good performance in the hydrogenation of the unsaturated C=O bond or the furan ring.[17] Therefore, a combination of these two metal sites in one catalyst may provide a multifunctional catalyst for the conversion of furfural.

Herein, we report the use of robust and efficient bimetallic Cu-Pd catalysts for the CTH of furfural to 2-MF and 2-MTHF in the presence of the hydrogen donor 2-propanol. By modifying the Cu/Pd ratio, either 2-MF or 2-MTHF could be obtained selectively as the major product under the optimized reaction conditions. The effect of the Cu/Pd ratio, support material, reaction temperature, and reaction time on the reaction conversion and product distribution was studied. Furthermore, a detailed investigation on the reaction mechanism and the synergy between Cu and Pd is also presented. Finally, the catalyst recycling ability was investigated.

Results and Discussion

Catalyst characterization

XRD patterns of the as-prepared metal catalysts and the ZrO_2 support are shown in Figure 1. The diffraction pattern of the support reveals the monoclinic phase of ZrO_2, which corresponds to JCPDF 37-1484. These peaks are still present in the patterns of the obtained catalysts without noticeable change. For 3Pd/ZrO_2, no characteristic peaks that correspond to Pd species were detected in the pattern, probably because of the superposition with the strong diffraction peaks of the ZrO_2 phase and the highly dispersed Pd particles, which was reported previously.[18] For 10Cu/ZrO_2, three new peaks were found at $2\theta = 43.3$, 50.5, and 74.2° that correspond to the (111), (200), and (220) planes of Cu^0, respectively. If Pd was coimmobilized on the support, the diffraction peaks became much weaker. For 10Cu-1Pd/ZrO_2, the diffraction peak of Cu^0 was still found but with a low intensity. A new weak peak at 42.9° was found. This new peak was between the (111) reflections of pure Cu ($2\theta = 43.3°$) and Pd ($2\theta = 40.1°$), which indicates the successful distribution of the Pd atoms in the Cu lattice by the formed Cu-Pd alloys and leads to a change of the original Cu–Cu lattice spacing and a shift of the diffraction peak.[19] This indicates that both Cu^0 and Cu-Pd alloy were present in the 10:1 Cu/Pd ratio catalyst. However, the diffraction peak of Cu disappeared in the 10:3 and 10:5 catalysts (magnified images are presented in the Supporting Information). The diffraction peak of the Cu-Pd alloy shifted continuously toward lower angles as the Pd content increased: $2\theta = 42.7$ and 42.5° for 10Cu-3Pd/ZrO_2 and 10Cu-5Pd/ZrO_2, respectively. This suggests a different composition of alloys in these two catalysts. Another important finding was that the diffraction peaks became much weaker compared to that in the pattern of the monometallic Cu catalyst, which indicates the better dispersion of Cu particles with the introduction of Pd by the formation of CuPd alloys and shows the advantages of a bimetallic catalyst over a monometallic catalyst in the dispersion of the metal sites.

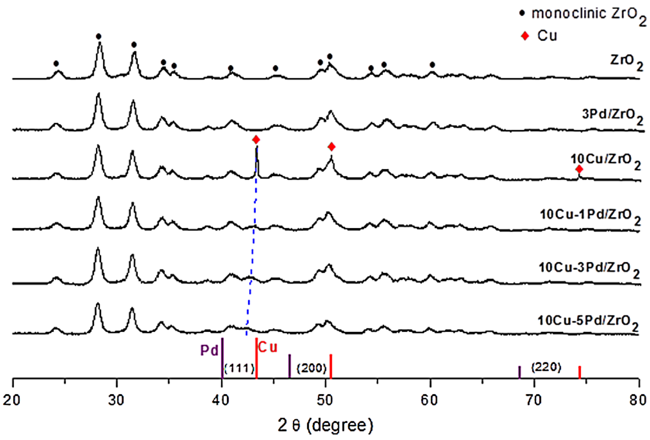


Figure 1. XRD patterns of the as-prepared catalysts.

A TEM image of the representative 10Cu-3Pd/ZrO_2 catalyst is presented in Figure 2. The metal particles were well dispersed on the supports with a mean size of 10.8 nm, which was smaller than that of the monometallic Cu/ZrO_2 catalyst (mean size of 13.2 nm; Figure S1). The introduction of Pd reduced the aggregation of Cu particles significantly during the preparation procedure, which resulted in a better dispersion and smaller sizes of the metal particles. This may be attributed to the interactions between the two metals, known as the geometric and stabilizing effect, and the addition of a second metal promoter alters the geometry of the particle size and improves the stability of the active metal sites by inhibiting metal sintering during the preparation or reaction.[20] A high-resolution trans-

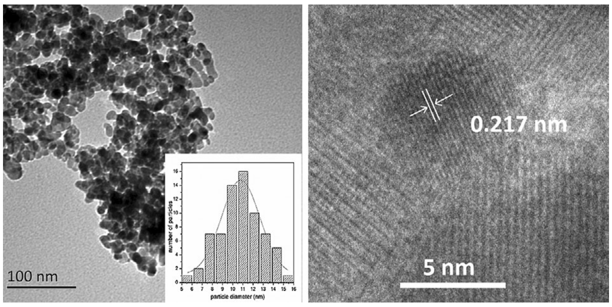


Figure 2. TEM (left) and HRTEM (right, Cu-Pd alloy domain) analysis of the 10Cu-3Pd/ZrO_2 catalyst. The inset shows the particle size distribution.

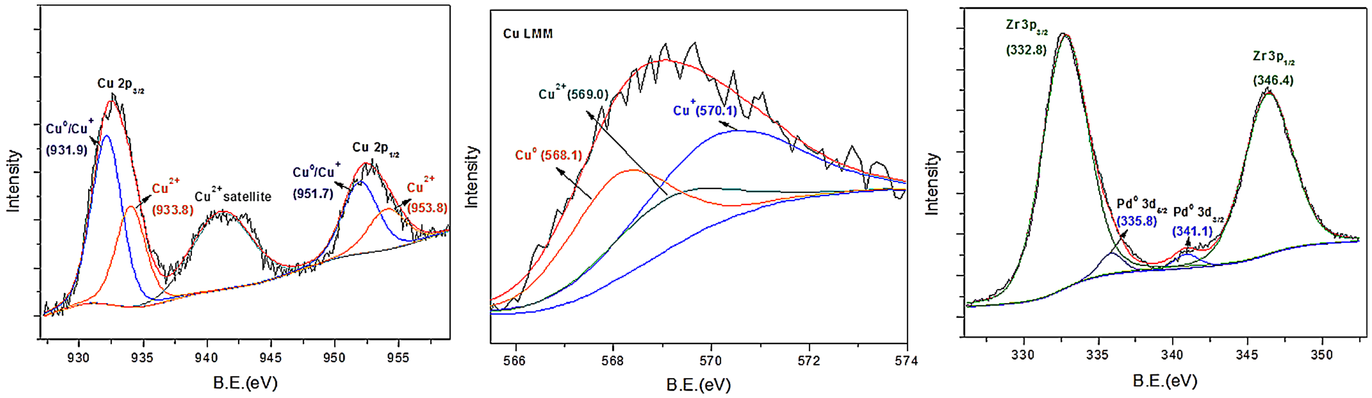


Figure 3. XPS spectra of the as-prepared 10Cu-3Pd/ZrO_2 catalyst: Cu 2p, Cu LMM, and Pd 3d level spectra.

mission electron microscopy (HRTEM) image of the 10Cu-3Pd/ZrO_2 catalyst was also recorded. The clear crystalline fringe of the selected domain was measured to be 0.217 nm, which corresponds to the (111) interplanar spacing of the face-centered cubic structure of the CuPd alloy.[20,21] This result agreed with the XRD results, which showed that the two metals formed an alloy particle in the as-prepared catalyst.

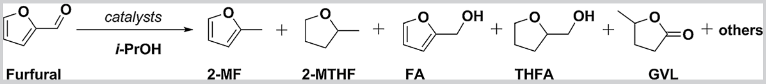
The chemical states of the metal particles of the Cu-Pd catalyst were further identified by using X-ray photoelectron spectroscopy (XPS). 10Cu-3Pd/ZrO_2 was selected as a representative catalyst for the XPS analysis, and the results are presented in Figure 3. Apart from the metal and alloy states of Cu particles as indicated by the XRD results, the oxidative states also exist in the catalyst. The Cu 2p$_{3/2}$ and Cu 2p$_{3/2}$ levels were fitted together with a fixed separation. In the Cu 2p$_{3/2}$ spectrum, the main peak at a binding energy (BE) of 930–935 eV was deconvoluted into two peaks that correspond to Cu^0/Cu^+ (BE = 931.9 eV) and Cu^{2+} (BE = 933.8 eV) species, respectively.[19,22] The satellite peak around BE = 941 eV was clear evidence of the existence of Cu^{2+} particles in the Cu-Pd catalysts. As the binding energies of Cu^0 and Cu^+ are very close, the Cu LMM spectrum was recorded to distinguish these two species. The peak was deconvoluted into three peaks at BE = 568.1, 569.0, and 570.1 eV, which were assigned to the Cu^0, Cu^{2+}, and Cu^+ species, respectively, consistent with values reported previously.[23] The percentages of the three components were calculated from their area peak ratios, which were approximately 44.2, 21.0, and 34.8 %, respectively. All three different valence Cu species were present in the as-prepared catalyst, which indicated that the catalyst was not fully reduced under our reaction conditions. The metal oxide may also contribute to the CTH reaction by providing more Lewis acid sites to facilitate the deoxygenation of the O atoms, as revealed by Panagiotopoulou and Vlachos.[16] The Pd 2d$_{5/2}$ and Pd 2d$_{3/2}$ peaks overlapped partially with the strong peak from Zr^{4+} in the Zr 3p$_{3/2}$ spectrum. After fitting, it can be seen that Pd existed mainly in the Pd^0 state, shown by peaks at BE = 335.8 and 341.1 eV, and no high-valance Pd was observed. This result suggested that most of the Pd particles were reduced to the metallic state under the specific catalyst reduction conditions. If we combine the XPS results with the XRD analysis, it could be found that both Cu and Pd were immobilized successfully and dispersed homogeneously on the support ZrO_2 in the form of Cu-Pd alloy and metal oxide states.

The textural properties of the catalysts are presented in Table S1. The support ZrO_2 has a moderate BET surface area of 109.18 m^2g^{-1}, a total pore volume of 0.34 cm^3g^{-1}, and an average pore diameter of approximately 12.47 nm. After the immobilization of the metals, all three parameters of the as-prepared catalysts decreased to some extent. With the increase of the Pd content at a fixed Cu loading, the BET surface area, total pore volume, and average pore size of the obtained catalysts decreased gradually (Table S1, entries 4–6). This may be caused by the slight collapse of the structure during the catalyst preparation and the blockage of the pores as more metal particles were incorporated into the ZrO_2 structure.

Catalyst screening for the CTH of furfural

The CTH of furfural was performed by using a batch reactor with 2-propanol as the solvent and the H donor. Initially, three different bimetallic catalysts (Cu-Ni, Cu-Ru, and Cu-Pd) with a fixed metal ratio of 10:3 were prepared and subjected to the CTH reaction to compare their reactivities in the CTH reaction. For the reactions with Cu-Ni or Cu-Ru, furfural was converted fully at 220 °C in 4 h but with low yields of the desired products 2-MF and 2-MTHF of 28.5 and 9.7 %, respectively (Table 1, entries 1–2). Furfuryl alcohol (FA), from the hydrogenation of furfural, was detected as the main byproduct of these reactions (33.8 and 36.3 %). Apart from that, only a small amount of byproducts [e.g., γ-verolactone (GVL), cyclopentanone, and 2-(isopropoxymethyl)furan (IPMF)] were detected. The mass balance of the two reactions was relatively low, which may be caused by the instability of FA at an elevated temperature, possibly by forming humins or polymers that cannot be detected by using GC.[24] Therefore, it can be inferred that the Cu-Ni and Cu-Ru catalysts only had limited deoxygenation ability to catalyze the cleavage of the C–OH bond of FA to produce 2-MF or 2-MTHF. Strikingly, if we used Cu-Pd as the catalyst, the CTH of furfural provided 82.3 % yield of 2-MF+2-MTHF, in which 2-MF was obtained as the major product in 61.9 % yield. THFA (2.9 %) and GVL (1.2 %) were also obtained as by-

Table 1. CTH of furfural with different catalysts.[a]



Entry	Catalyst	Conversion [%][b]	Yield[b] [%] 2-MF	2-MTHF	FA	THFA	GVL	others[c]	2-MF+2-MTHF	2-MF/2-MTHF	Mass balance[d]
1	$10Cu\text{-}3Ni/ZrO_2$	100	27.0	1.5	33.8	0	1.5	7.3	28.5	18.6	71.1
2	$10Cu\text{-}3Ru/ZrO_2$	100	8.6	1.1	36.3	0	4.6	8.9	9.7	7.8	59.5
3	$10Cu\text{-}3Pd/ZrO_2$	100	61.9	20.4	0	2.9	1.2	3.5	82.3	3.0	89.9
4	$10Cu\text{-}3Pd/Al_2O_3$	100	32.3	26.2	0	0.8	0	6.2	58.5	1.23	65.5
5	$10Cu\text{-}3Pd/SiO_2$	100	35.2	24.4	0	22.6	1.1	4.1	59.6	1.4	87.4
6	$10Cu\text{-}3Pd/ TiO_2$	100	61.2	5.6	0	0.9	1.9	10.2	66.8	10.9	79.8
7	$10Cu\text{-}5Pd/ZrO_2$	100	5.1	78.8	0	6.8	1.0	1.3	83.9	0.06	93.0
8	$10Cu\text{-}1Pd/ZrO_2$	98.5	63.6	11.4	0	1.5	4.5	3.8	75.0	5.6	84.8
9	$10Cu/ZrO_2$	98.9	31.4	7.0	38.7	0	0	7.5	38.4	4.5	84.6
10	$3Pd/ZrO_2$	97.2	0	33.5	0	0	0	15.3	33.5	0	48.8
11[e]	$10Cu/ZrO_2+3Pd/ZrO_2$	97.9	0	48.3	0	0	0	11.4	48.3	0	59.7

[a] Conditions: furfural 1 mmol, catalyst 120 mg, 2-PrOH 14 mL, 220 °C. [b] Determined by using GC. [c] Other products include cyclopentanone/cyclopentanol, 2-potanone and 2-(isopropoxymethyl)furan. [d] The mass balance was calculated based on the detected known products. [e] The catalyst loading was 120 mg+120 mg.

products (Table 1, entry 3), and the mass balance was 89.9 %. This indicates that the combination of Cu and Pd in the bimetallic catalyst was an appropriate choice for the CTH of furfural to produce 2-MF and 2-MTHF.

Other commercially available supports (Al_2O_3, SiO_2, and TiO_2) were employed in the preparation of Cu-Pd catalysts to compare their reactivities in the CTH of furfural. Moderate yields of the desired products 2-MF and 2-MTHF were obtained with the three catalysts, among which the TiO_2-supported catalyst showed the highest 2-M+2-MTHF yield (Table 1, entries 4–6), which was still lower than that of the catalyst with ZrO_2 as the support. Therefore, ZrO_2 was the best support for the CTH reaction. This may be explained by the special properties of zirconium oxides as reported previously for the CTH reaction.[25] Zirconium oxides helped the dissociation of H from the H donor and transferred it to the unsaturation through its acidic and basic sites by forming strong hydrogen-bonding or metal–oxygen interactions. In light of these previous results, we speculate that the acid–base sites of Zr support of our catalyst also assists the absorption of alcohols and participates in the dissociation of H from alcohols, which thereby promoted the reaction rate in addition to the Cu and Pd sites. This may be the key to the excellent performance of the ZrO_2-supported catalysts.

The influence of Pd on the CTH reaction was also investigated by varying the Pd loading at a fixed Cu loading. If $10Cu\text{-}5Pd/ZrO_2$ was used, a higher yield of 83.9 % of the 2-MF and 2-MTHF mixture was obtained under the same reaction conditions (Table 1, entry 7). Contrary to the reaction with $10Cu\text{-}3Pd/ZrO_2$, 2-MTHF was produced selectively as the main product (78.8 %) with only a 5.1 % yield of 2-MF. This may be caused by the increase of the Pd loading, which created more active sites for ring hydrogenation to facilitate the conversion of 2-MF to 2-MTHF. This was confirmed by the result with the catalyst that had a lower Pd loading: if $10Cu\text{-}1Pd/ZrO_2$ was used, 98.5 % furfural conversion was achieved with a 75.0 % yield of 2-MF+2-MTHF (Table 1, entry 8). Although the decrease of the Pd content led to a slight decrease in the product yield as compared to that of $10Cu\text{-}3Pd/ZrO_2$, the catalyst still maintained a high reactivity in the CTH reaction. Notably, the 2-MF/2-MTHF ratio increased from 3.0 to 5.6, which indicated that the ring hydrogenation of 2-MTHF was suppressed at a lower Pd loading. From the results of the catalysts with various Pd loadings, the selectivity to 2-MF increased along with the Pd loading, which was consistent with the previous discussion that the ring hydrogenation occurred mainly on the Pd sites.

To investigate out the role of Cu and Pd in the CTH reaction, monometallic Cu/ZrO_2 and Pd/ZrO_2 were prepared and tested in the CTH of furfural. If $10Cu/ZrO_2$ was used, only a 31.4 % yield of 2-MF and a 7.0 % yield of 2-MTHF was obtained (Table 1, entry 9) accompanied by a considerable amount of FA (38.7 %). This result shows clearly that the monometallic Cu catalyst had a HDO ability but cannot catalyze the cleavage of the C–OH bond efficiently under the specific CTH reaction conditions. Cu/ZrO_2 showed an inferior catalytic activity to the Cu-Pd bimetallic catalyst. This comparison further highlighted the necessity to employ Pd as a promoter to the catalyst. However, if Pd/ZrO_2 was used, only a 33.5 % yield of 2-MTHF was obtained without other detectable byproducts (Table 1, entry 10). Many of the products may underwent the C–C cracking reaction and decomposed to small molecules or gaseous products under the specific reaction conditions. It has been described previously that monometallic Pd had a strong hydrogenation ability that caused the cracking of C–C bonds easily at elevated reaction temperatures.[17,20] Therefore, the introduction of Cu to the Pd catalyst in an appropriate ratio can inhibit the strong hydrogenation ability of Pd, which thereby increases the reaction selectivity to the desired product. Based on these results, we can see that both the properties of the two metals were modified in the bimetallic catalyst, by the formation of alloys or mixed phases, to result in a more efficient catalyst than either of the single monometallic catalysts in the CTH of furfural. Additionally, the physical mixture of the two catalysts in the CTH of furfural only yielded 48.3% 2-MF+2-MTHF (Table 1, entry 11), which is much lower than that of the as-prepared bimetallic catalysts. Based on these result, we can infer that the synergism between the two metals is key to the high efficiency of the catalyst, either in the form of an alloy or the physical proximity between the two metals. The physical mixing cannot create the "interactions" between the two metals, which thereby lack the sufficient reactivity. Overall, the CTH of furfural to 2-MF and 2-MTHF was realized over the Cu-Pd bimetallic catalyst supported on ZrO_2 with high yields. By varying the metal loading, 2-MF or 2-MTHF could be obtained selectively as the major product.

Effect of the reaction temperature and catalyst loading

The effect of the reaction temperature on the CTH of furfural was investigated in the range of 160–240 °C, and the other reaction conditions were maintained (Figure 4). The reaction conducted at 160 °C provided a 27.6% yield of 2-MF+2-MTHF at 99.0% furfural conversion, accompanied by a 51.6% yield of FA. This result suggested the hydrogenation of the aldehyde group proceeded well under relatively mild conditions, however, the hydrogenolysis of the C–O group was difficult. As the reaction temperature increased, furfural was converted fully, FA was converted gradually, and the yield of 2-MF+2-MTHF increased continuously until it reached a maximum of 82.3% at 220 °C. This implied that the hydrogenolysis ability of the catalyst was promoted as the reaction temperature increased. The carbon balance also increased even at the full conversion of furfural, which may be caused by the absorption of furfural or FA on the surface of the catalyst that cannot be detected (Table S6). However, an excessively high temperature caused a decrease in the yield of 2-MF+2-MTHF (66.7%) and more byproducts were detected. The carbon balance decreased to 80.1% as some of the side products may undergo decomposition (Table S3). Therefore, a moderate reaction temperature of 220 °C was selected as optimal. Notably, the yield of 2-MTHF increased gradually over the entire reaction temperature range, which implies that the ring hydrogenation ability of the Cu-Pd catalyst increased as the reaction temperature increased.

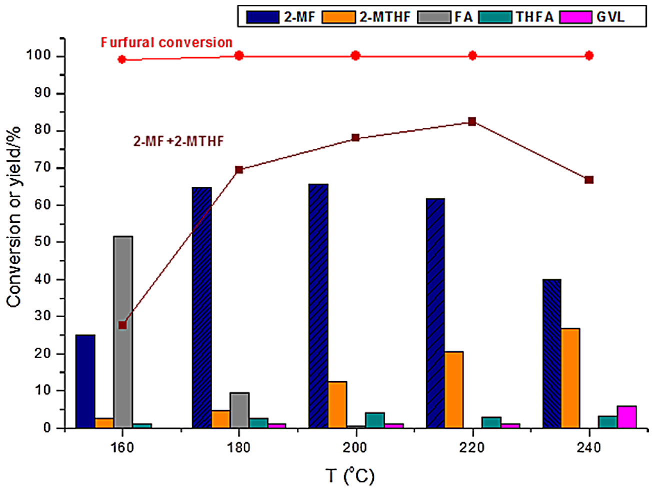


Figure 4. Influence of the reaction temperature on the product distribution. Conditions: furfural 1 mmol, catalyst 120 mg, 2-PrOH 14 mL, 4 h.

The influence of the catalyst loading on the product distribution was also investigated to assess its role in the CTH reaction. To reserve the starting material and intermediates, a milder temperature of 180 °C was used for the reaction (Table S2). The furfural conversion increased from 98.6 to 100%. During this stage, the yield of 2-MF increased continuously to reach the highest yield of 65.6% at 18.9 wt% catalyst loading, which remained almost unchanged at 21.7 wt% catalyst loading. At the same time, the yield of 2-MF also increased as the catalyst loading increased. An excessive catalyst loading did not further improve the yield of 2-MF+2-MTHF and decreased the reaction carbon balance (18.9 and 21.7 wt%). This phenomenon may be caused by side reactions in the presence of excessive active metal sites. In these catalytic runs, FA was present as the main intermediate, and its concentration decreased as the catalyst loading increased. This indicated that FA might be the key intermediate to the final product from furfural. In addition, the carbon balance of the reactions conducted at 180 °C was a little lower than that of the reactions conducted at under the optimized reactions. This may be caused by the lower reaction rate of furfural and FA at a lower reaction temperature. These two substrates undergo side reactions easily (to form humins or polymers) if they are exposed to the reaction medium for longer (Table S6).

Reaction pathway and proposed mechanism

FA and the other byproducts were identified by using GC–MS to give direct evidence of the CTH reaction mechanism. Hence, the product evolution with respect to reaction time was traced by using GC at a mild reaction temperature of 180 °C (Figure 5). During the heating of the reaction to the desired reaction temperature (15 min), 52.5% furfural was converted and FA was detected in 18.3% yield together with 2.3% yield of

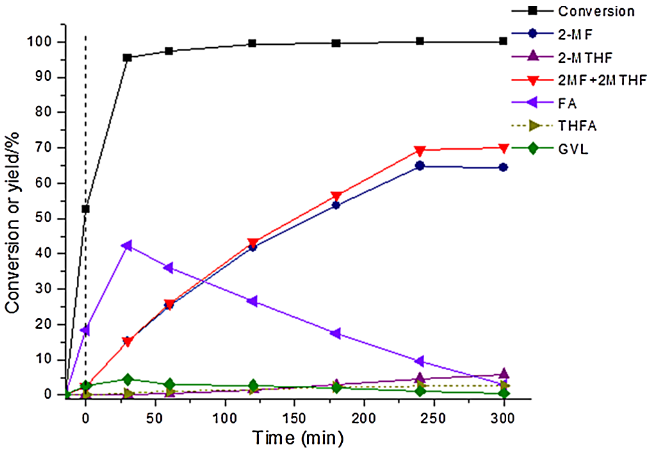
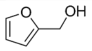
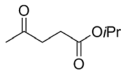
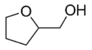
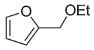
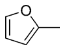
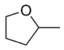
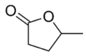


Figure 5. Time course of CTH with the 10Cu-3Pd/ZrO_2 catalyst. Conditions: furfural 1 mmol, catalyst 120 mg, 2-PrOH 14 mL, 180 °C.

2-MF and no 2-MTHF. The formation of other byproducts was negligible. As the reaction proceeded, furfural was converted quickly in 30 min and, at the same time, FA reached a maximum yield of 42.0%, which decreased gradually afterwards. The yields of 2-MF and 2-MTHF increased over the entire reaction time. The yield of 2-MF reached a maximum of 64.8% at 240 min and then it remained almost unchanged at 300 min. The yield of 2-MTHF increased continuously over the entire reaction time until it reached 5.8% at 300 min. From these results, it can be seen that furfural was converted quickly and FA was the main intermediate, the concentration of which first increased and then decreased in the reaction. During this stage, the concentration of GVL exhibited similar changes to FA in the reaction mixture, which indicated that GVL might also be an intermediate of this reaction (Table S4).

Table 2. CTH of the possible intermediates and products.[a]

Entry	Substrate	Conversion [%]	Yield[b] [%] 2-MF	2-MTHF	THFA	GVL	Mass balance
1		98.9	64.8	20.1	3.5	–	89.5
2		98.0	–	4.6	–	78.5	86.8
3		4.5	–	0	–	–	93.0
4		66.1	11.8	3.2	–	38.6	89.8
5		30.5/95.0[c]	–/–	18.6/84.0[c]	–/–	–/–	88.1/90.0[c]
6		9.0	–	–	–	–	92.3
7		12.0	–	2.8	–	–	90.8

[a] Conditions: substrate 1 mmol, 10Cu-3Pd/ZrO_2 120 mg, 2-PrOH 14 mL, 220 °C, 4 h. [b] Determined by using GC. [c] Pd/ZrO_2 (120 mg) as catalyst.

To further investigate the reaction pathways, possible intermediates as listed above were also subjected to the CTH reaction under the optimized reaction conditions. Furfuryl alcohol was first tested in the CTH reaction. 2-MF and 2-MTHF were obtained in 64.8 and 20.1% yield, respectively, which is similar to the results with furfural as the starting material (Table 2, entry 1). This is direct evidence of the furfural→FA→2-MF/2-MTHF reaction pathway of the CTH reaction, through hydrogenation, hydrogenolysis, and ring hydrogenation. In addition to this pathway, three other possible routes might also existed in the CTH reaction: 1) FA is alcoholyzed to isopropyl levulinate (IPL) with 2-propanol, then hydrogenated to GVL, and finally hydrodeoxygenated to 2-MTHF; 2) FA is hydrogenated to THFA and then hydrogenolyzed to 2-MTHF; 3) FA is converted to IPMF by the etherification between FA and the alcohol and then hydrogenolyzed/hydrogenated to 2-MF and 2-MTHF.

To verify these three hypothesis, the related intermediates were subjected to the CTH reaction. The reaction with IPL (route 1) as the reactant provided a 78.5% yield of GVL with only a 4.6% yield of 2-MTHF (Table 2, entry 2). Accordingly, the Cu-Pd catalyst showed a limited HDO ability to convert GVL to 2-MTHF under the current reaction conditions. This was further confirmed by using GVL as the starting material in the CTH reaction (Table 2, entry 7). Accordingly, the pathway via IPL contributed very little to the production of 2-MTHF. To examine route 2, THFA was subjected to CTH and there was almost no conversion within the reaction time and no desired product was found (Table 2, entry 3). This result shows clearly that THFA was not able to be converted to 2-MTHF in our system but was just an undesired byproduct. In the case of IPMF in route 3, an analogous substrate 2-(ethoxymethyl)furan was used instead of IPMF for the CTH reaction as IPMF was not commercially available. A 66.1% conversion was obtained with 11.8 and 3.1% yields of 2-MF and 2-MTHF, respectively (Table 2, entry 4). A considerable amount of GVL was also produced. These results showed that the ether may also undergo the hydrogenolysis of the C–O bond to the desired product but with a relatively slow reaction rate. Although IPMF was only detected in a very low amount in our reaction optimization, it may contribute to the formation of the desired products. Similar conversions of the ether group to the methyl group have been reported previously for the CTH of furanics.[26] Finally, 2-MF was also tested in the CTH reaction (Table 2, entry 5) to give a 18.6% yield of 2-MTHF under the reaction conditions, which was similar to the result obtained from the CTH of furfural (20.4% yield of 2-MTHF). If Pd/ZrO_2 was used, the ring hydrogenation proceeded efficiently with an 84.0% yield of 2-MTHF, which confirmed the high reactivity of the Pd particles in the hydrogenation. These results agreed with and further supported our earlier discussion that 2-MTHF was produced mainly through the ring hydrogenation of 2-MF. The CTH of 2-MTHF did not provide any products, and the carbon balance was 92%, which further confirmed the thermal decomposition of the desired products under the reaction conditions (Table 2, entry 6). Based on the experimental results outlined above, we found that multiple reaction pathways existed in the CTH of furfural, among which the hydrogenation of furfural to FA and further hydrogenolysis/hydrogenation to 2-MF and 2-MTHF was the main route. In parallel to this route, the other two pathways via the intermediates IPL and IPMF also contributed partially to the formation of the desired products.

Catalyst recycling

Stability and recyclability are of great importance for a heterogeneous catalyst in practical applications. Therefore, the recycling of the catalyst was also investigated. After the reaction, the catalyst was separated simply from the reaction mixture by filtration, washed with 2-propanol, and used directly in the next run. Five catalytic runs were performed, and the results are presented in Figure 6. The desired products 2-MF+2-MTHF were obtained in a total yield of approximately 82% in each

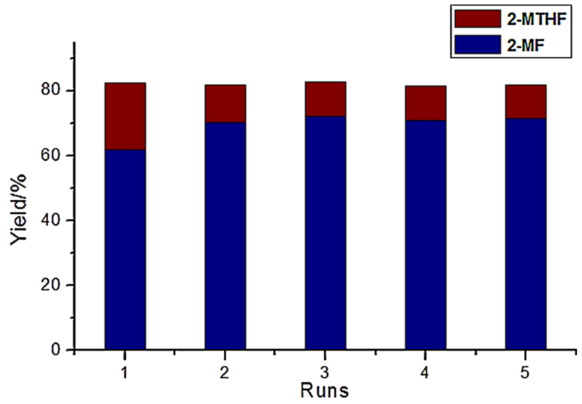


Figure 6. Recycling of the 10Cu-3Pd/ZrO_2 catalyst. Conditions: furfural 1 mmol, catalyst 120 mg, 2-PrOH 14 mL, 220 °C, 4 h.

run, and no clear decrease was observed in the fifth run. These results demonstrate that 10Cu-3Pd/ZrO_2 possesses a high reactivity and stability in recycling. Notably, the yields of 2-MF and 2-MTHF in the first run over the fresh catalyst were 61.9 and 20.4%, respectively. In the following four runs, the yield of 2-MF increased to ≈70%, whereas that of 2-MTHF decreased to ≈10%. This change in the product distribution may be caused by the different chemical states of the metal species in the catalyst. Thus, to investigate out this change, spent 10Cu-3Pd/ZrO_2 was analyzed by using XPS (Figure 7). In the XPS Cu 2p$_{3/2}$ spectrum, the peak that corresponds to Cu^0/Cu^+ species became stronger and the peak that corresponds to Cu^{2+} became weaker than that of fresh 10Cu-3Pd/ZrO_2. This change indicated that the Cu species underwent in situ reduction in the CTH reaction system, which might cause the catalyst to be more active toward the HDO of the aldehyde group. However, no significant change was observed for Pd species in the Pd 3d$_{5/2}$ spectrum because of the overlap with the stronger diffraction peak of Zr. In spite of that, we can still speculate from experimental data that the ring hydrogenation ability of Pd species was suppressed after the reaction as more furanics were retained in the final products. The active Pd sites may be poisoned slightly during the reaction. However, the catalyst still showed a high reactivity toward the formation of 2-MF+2-MTHF. The spent catalyst was also analyzed by using TEM and XRD, and the results are presented in Figures S2 and S3. No difference was observed in the XRD patterns of the fresh and spent catalysts. However, the used catalyst showed a slight increase in the metal particle size (from 10.8 to 13.9 nm). Overall, 10Cu-3Pd/ZrO_2 showed an excellent reactivity and recycling ability in the CTH of furfural to the desired products 2-MF and 2-MTHF.

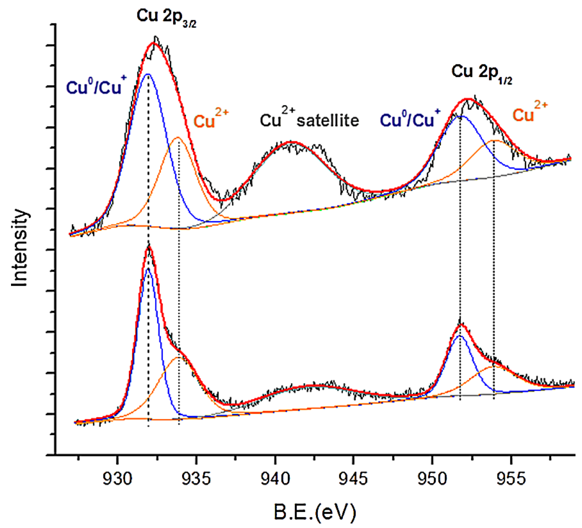


Figure 7. XPS spectra of the fresh and recycled 10Cu-3Pd/ZrO_2 catalysts.

Conclusions

We have demonstrated an efficient catalytic system based on bimetallic Cu-Pd catalysts for the transfer hydrogenation of furfural to 2-methylfuran (2-MF) and 2-methyltetrahydrofuran (2-MTHF) with high yields of up to 83.9% in the presence of the hydrogen donor 2-propanol. By changing the ratio of the two metals of the bimetallic catalyst, 2-MF and 2-MTHF could also be obtained selectively as the major products in high yields. Reaction studies on the catalysts revealed that the synergism between Cu and Pd enhanced the hydrodeoxygenation ability of the catalyst significantly and suppressed the side reactions. Mechanistic studies showed that the reaction proceeded mainly via the intermediate furfuryl alcohol, which was then hydrogenolyzed to 2-MF or hydrogenated to 2-MTHF. Finally, the catalyst showed an excellent reactivity and stability in the recycling experiment to provide approximately 82% yield of 2-MF+2-MTHF in each catalytic run. Characterization of the spent catalyst revealed that the in situ reduction of the metal particles helped to maintain its activity. The current reaction provides a new efficient system for the upgrade of furfural, which might also find important applications in the reductive upgrade of other biomass-derived molecules for the production of value-added products.

Experimental Section

Materials

Furfural (98%), furfuryl alcohol (98%), 2-methylfuran (99%), 2-methyltetrahydrofuran (98%), and tetrahydrofurfuryl alcohol (97%) were purchased from TCI Chemical Reagent Company (Shanghai, China). GVL (98%), $RuCl_3{\cdot}xH_2O$ (99%), and $Pd(OAc)_2$ (98%) were purchased from J&K Chemical company (Shanghai, China). $Ni(NO_3)_2{\cdot}6H_2O$ and solvents were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). The metal oxide supports were purchased from Saint-Gobain NorPro Company (USA). Other chemicals were purchased from local companies and used without further purification.

Catalyst preparation

All the catalysts were prepared by an incipient impregnation method. Typically, to prepare 10Cu-3Pd/ZrO_2, ZrO_2 (1.74 g) was first impregnated with a aqueous solution that contained $Cu(NO_3)_2{\cdot}3H_2O$ (0.753 g) and $Pd(OAc)_2$ (0.127 g). The mixture was stirred vigorously for 12 h and dried at 110 °C overnight. The resulting powder was ground and calcined at 500 °C for 4 h. The catalyst was reduced in a flow of 5% H_2/N_2 from RT to 500 °C at 10 °C min^{-1} then kept at 500 °C for another 2 h. After cooling to RT, the catalyst was collected and weighed. This catalyst was denoted as 10Cu-3Pd/ZrO_2 (10%Cu-3%Pd/ZrO_2). The other catalysts were prepared by the same procedure.

Characterization

XRD patterns of the catalysts were recorded by using a Rigaku D MAX III VC diffraction system. XPS spectra were recorded by using a Scientific Escalab 250-X-ray photoelectron spectrometer. The BET surface area, average pore size, and total pore volume of the catalyst were measured by using an Automatic Surface Area and Pore Analyzer (Tristar II 3020M, Micromeritics). TEM images were acquired by using a JEOL-2010 electron microscope.

The reaction mixture was analyzed by using GC–MS (Agilent 7890A, Agilent 5975C MS and GC Agilent 7890A) with a DB-5 capillary column (30 m×0.25 mm×0.25 µm, Agilent). The temperature of the column increased from 62 to 250 °C at a 15 °C min^{-1} rate. Naphthalene was used as the internal standard.

Catalytic reactions

The CTH of furfural was performed by using a Parr reactor. Typically, furfural (1.0 mmol), 10Cu-3Pd/ZrO_2 (120 mg), and 2-propanol (14 mL) were charged into the reactor with a magnetic stirrer. The reactor was then sealed and purged with N_2 three times to remove air. The reactor was heated to 220 °C and kept at this temperature for 4 h at a stirring speed of 600 rpm. At the end of the reaction, the reactor was cooled to RT, and the reaction mixture was sampled and subjected to product analysis.

For the recycling of the catalyst: the catalyst was centrifuged after the reaction and washed with 2-PrOH three times. All the liquid was collected, combined, and analyzed by using GC. The solid catalyst was added directly to the reaction tube for the next run.

Acknowledgements

The authors are grateful for the financial support by National Natural Science Foundation of China (NSFC 21502095), Natural Science Foundation of Jiangsu Province (BK20150872), Jiangsu student's platform for innovation training program (SPITP 201510298026Z, 201510298048Z) and Top-notch Academic Programs Project of Jiangsu Higher Education Institutions (TAPP).

Keywords: alloys · biomass · copper · palladium · supported catalysts

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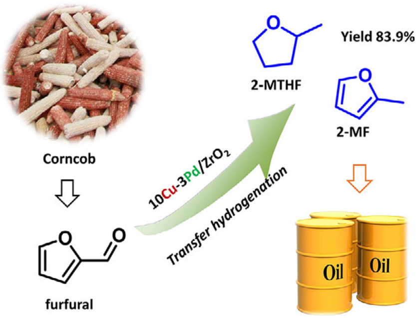
Received: August 15, 2016
Revised: September 20, 2016

Identifying the intermediates: The catalytic transfer hydrogenation of biomass-derived furfural to fuel additives 2-methylfuran and 2-methyltetrahydrofuran is performed over a bimetallic Cu-Pd catalyst in the presence of 2-propanol. The reaction proceeds via the intermediate furfuryl alcohol, which is then deoxygenated/hydrogenated to the desired products.



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Catalytic Transfer Hydrogenation of Furfural to 2-Methylfuran and 2-Methyltetrahydrofuran over Bimetallic Copper–Palladium Catalysts