

Copper–Zinc Alloy Nanopowder: A Robust Precious-Metal-Free Catalyst for the Conversion of 5-Hydroxymethylfurfural

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Noble-metal-free copper–zinc nanoalloy (< 150 nm) is found to be uniquely suited for the highly selective catalytic conversion of 5-hydroxymethylfurfural (HMF) to potential biofuels or chemical building blocks. Clean mixtures of 2,5-dimethylfuran (DMF) and 2,5-dimethyltetrahydrofuran (DMTHF) with combined product yields up to 97% were obtained at 200–220°C using 20–30 bar H₂. It is also possible to convert 10 wt% HMF solutions in CPME, with an excellent DMF yield of 90%. Milder temperatures favor selective (95%) formation of 2,5-furandimethanol (FDM). The one-pot conversion of fructose to valuable furan-ethers was also explored. Recycling experiments for DMF production show remarkable catalyst stability. Transmission electron microscopy (TEM) characterization provides more insight into morphological changes of this intriguing class of materials during catalysis.

The development of new, robust, and efficient catalysts, primarily ones that consist of earth-abundant metals, is of crucial importance and will enable the sustainable chemical conversion of nonedible lignocellulosic biomass resources^[1] or platform molecules derived from such resources.^[2] One of the most versatile platform chemicals is 5-hydroxymethylfurfural (HMF),^[2,3] which can be readily obtained from sugars.^[3b] Various conversion routes have been investigated^[4] and among these, reductive methods are of special importance.^[4a] A variety of new methodologies have been developed for selective carbonyl reduction to give 2,5-furan dimethanol (FDM) at milder temperatures.^[5] More extensive deoxygenation of HMF to potential biofuels or the fuel additive 2,5-dimethylfuran (DMF) has been first proposed by Dumesic.^[6a] A number of very efficient catalysts, mainly based on ruthenium^[6] or other noble metals, have

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been developed since,^[2,7] including very efficient examples that use milder temperatures.^[8] In contrast, only a few non-precious-metal-based catalysts have been reported. Recently Fu and co-workers described a Ni–W carbide catalyst that gave up to 96% DMF yield.^[9] Zhu and co-workers reported on Raney nickel catalysts with good DMF yields (88.5%) at 180 °C.^[10] Despite these promising results, the development of inexpensive, precious metal-free, and highly effective catalysts for this transformation is still highly desired.

Herein, we report on the use of a robust, sustainable, and commercially available new catalyst class that allows for modular and highly selective conversion of HMF to either FDM (up to 95%) or DMF (up to 90%). Under optimized conditions remarkably clean mixtures of the two biofuels DMF and DMTHF (97% yield) can be obtained.

Previously we reported on the use of copper-doped porous metal oxides^[11] in the conversion of HMF and other biomass resources.^[12] Although a promising combined DMF and DMTHF^[11b] yield of about 80% was obtained, ring-opening processes could not be completely prevented owing to the strong interaction of the relatively basic support with HMF and derived intermediates FDM and MFM (shown in Scheme 1). Thus,



Scheme 1. Hydrogenation/hydrogenolysis of HMF to DMF and DMTHF mixture (dashed arrows show the simplified pathway involving intermediate FDM and MFM).

we set out to investigate other suitable classes of copper-containing catalysts, preferably ones that do not readily undergo deactivation (e.g., by sintering) at elevated temperatures,^[13] and possess a relatively large surface area. We turned our attention to commercially available copper nanopowders, which are relatively unexplored in catalysis.

We first screened commercial copper-containing nanopowders of different composition (characterized by elemental anal-





Figure 1. Comparison of the product distribution (GC selectivities) obtained in the HMF hydrodeoxygenation over different copper nanopowders. Conditions: 0.500 g HMF, 0.100 g copper nanopowder, EtOH (20 mL), 220 °C, 30 bar H₂, 6 h (n.i: not identified; r.o.: ring-opening products). The corresponding numerical values are displayed in table S2.

ysis and XRD, see Supporting Information, Table S1 and Figure S1) in the conversion of HMF to DMF (Scheme 1). All reactions were carried out in ethanol at 220 °C using 30 bar H₂ pressure for 6 h (Figure 1; Supporting Information, Table S2). Complete or nearly complete (95% with CuZnFe₂O₄) conversion of HMF was achieved with all tested nanopowders, but variations in the composition of the obtained product mixtures were significant. Copper nanopowder showed a good (55%) DMF + DMTHF yield, with a DMF/DMTHF ratio of 20:1. Ether 2- (ethoxymethyl)-5-methylfuran (EMMF) was found as a main reaction product, and a small amount of ring-opening and hydrogenation products were also seen.

In this run many smaller peaks were also detected, which accounted for about 20% of unidentified products, likely caused by the relatively high loading of copper (20 wt %). As a comparison, with CuO a low DMF yield was found, and the biggest fraction of the product mixture (50%) consisted of FDM and MFM, indicating an overall slower reaction. Similarly, mixed copper-iron oxide nanopowder led to only 45% product. CuZnFe₂O₄ of similar composition performed better (73% product yield), however 12% of the products still remained unidentified. Best among the tested catalyst was the CuZn nanoalloy, which afforded 75% DMF+DMTHF yield with a DMF/ DMTHF ratio of 14:1, while the two main "precursors" to DMF (FDM and MFM) still represented 13% of the product mixture after 6 h reaction time. Overall, the cleanest product mixtures were obtained with this catalyst since only 3% of the products were unidentified.

Thus CuZn nanopowder was selected for further studies (Supporting Information, Table S3). First, the reaction time was prolonged to 18 h to ensure a full conversion of intermediates (FDM and MFM). Indeed, the product yield improved from 75% to 83%. Adjusting the H₂ pressure allowed for a further small increase to a very good, 88% product yield. The solvent engaged to a small extent in side reactions, as evidenced by the formation of 5% EMMF (Table S3 and Supporting Information, Scheme S1). To minimize these side processes and improve product yields even further, bulkier alcohol solvents were screened, as was earlier reported with copper porous

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Figure 2. Effect of different solvents for DMF + DMTHF production (0.500 g HMF, 0.100 g CuZn, 220 °C, 18 h, 20 bar H₂). On the right, the 10 wt% HMF experiment was conducted in CPME (1.72 g HMF, 0.2 g CuZn, 200 °C, 6 h, 20 bar H₂).

metal oxides.^[11b] Indeed, with *i*PrOH and methyl isobutyl carbinol (MIBC) excellent product yields were obtained (91% and 93% respectively). No corresponding etherification products were observed with bulkier alcohols. The quantity of unidentified compounds was below 3%. Interestingly, the DMF/DMTHF ratio reduced from 14:1 in EtOH to 4:1 in MIBC (Figure 2).

Ethereal solvents such as 2-MeTHF (2-methyltetrahydrofuran) and CPME (cyclopentyl methyl ether) were also tested. 2-MeTHF, which is directly accessible from renewable resources,^[14] performed comparably high to MIBC and *i*PrOH. To our delight CPME, a favorable solvent with low toxicity and negligible peroxide formation^[15] afforded the highest DMF + DMTHF yield (97%; see Supporting Information, Figure S8 for the corresponding GC trace). This practically means that upon HMF conversion under these conditions, analytically pure fuel mixtures were obtained.

In both these solvents, the DMF/DMTHF ratio was lower than in ethanol. Figure 2 shows an overview of the increase of the overall DMF + DMTHF yield from ethanol to CPME; however, at the expense of the DMF/DMTHF ratio.

The reaction conditions were further optimized in CPME. The reaction time could be reduced to 3 h at 200 °C with no apparent change in product yield, but increase in DMF content (Table 1, entries 1–3). To our delight, even concentrated HMF

Table 1. DMF + DMTHF production in CPME solvent.									
Entry ^[a]	$\mathbf{y}^{(a)}$ t T DMF + DMTH [h] [°C] yield [%] ^(b)		IF	DMF/DMTHF ratio ^(b)					
1	6	220	97			3:1			
2	6	200	97			5:1			
3	3	200	96			5:1			
4 ^[c]	6	200	94			18:1			
5 ^[d]	18	220	89			35:1			
[a] Reaction conditions: 0.500 g HMF, 0.100 g CuZn, 20 mL CPME, 0.250 mL decane, 20 bar H ₂ . Full HMF conversion. [b] Determined by GC-FID. [c] 10 wt% HMF concentration (1.72 g HMF in 20 mL CPME) and 0.2 g catalyst were used (7% Cu/HMF ratio). [d] 2.00 g HMF in 30 mL CPME, 40 bar H ₂ and 0.1 g catalyst were used (3% Cu/HMF ratio).									



solutions (10 wt%) were cleanly converted into a mixture of DMF and DTMHF (94% yield; entry 4 and Figure 2) in CPME, while DMF yield was 90%. Similarly a 10 wt% HMF solution was converted in MIBC at 220°C and longer reaction time, albeit with slightly lower DMF + DMTHF yield (88%). Interestingly, a 5 w% catalyst loading (3 w% Cu), typical for noble metal catalysts was adopted in CPME solvent with full substrate conversion, 89% combined fuel yield, and excellent DMF/DMTHF ratio of 35:1. This holds much promise for future upscaling, and continuous operation of this system.

In addition, 5-(ethoxymethyl)furfural (EMF) was used as starting material instead of HMF in CPME (220 °C, 18 h, 20 bar H₂). This ether also underwent hydrogenolysis, resulting in good DMF + DMTHF yield (78%). The corresponding EMMF, a potential fuel additive was detected as second major product (10%). This is promising regarding possible DMF production directly from hexoses, through HMF ethers.^[16]

The catalyst residues from the 10 wt% runs in CPME and MIBC were recovered and analyzed by transmission electron microscopy (TEM), and compared with the fresh catalyst (Supporting Information, Figure S4). The spent catalyst recovered from the run in CPME (Table 1, entry 4) mainly showed agglomerated particles with a core-shell structure. However, after reaction in MIBC (Table S3, entry 7), spike-shaped objects were visible on the catalyst surface in addition to coagulated rounded particles, also present in the fresh catalyst. For further direct morphological comparison, the reaction was also carried out in CPME using the same experimental conditions as in MIBC (10 wt% HMF, 220 °C, 18 h). No spiked objects were detected and cleaner product mixtures and higher DMF+DMTHF yields were observed in CPME. This shows that changes in catalyst morphology are dependent on the nature of the solvent and might influence catalytic activity.

The local composition of the spiked nanostructures was determined by energy dispersive X-ray (EDX) analysis, which revealed that these mostly comprise zinc (>90%) as highlighted by elemental analysis and lattice constant value (Figure 3 and Supporting Information, Figure S5).



Figure 3. TEM image of spent catalyst after the run at 10wt % HMF concentration in MIBC (Table S3, entry 7). In the insert, a magnification of a spiked-like object and the corresponding elemental mapping by EDX are provided.

In the bulk, core–shell structures in which the zinc is covering highly copper-dense particles were observed. These morphological changes in the alloy structure are probably due to copper migration, which becomes relevant above 200 °C.^[17] Despite these variances, only a slight difference between the bulk composition of the spent catalyst (MIBC) and the fresh catalyst could be determined by ICP analysis (Supporting Information, Table S7), showing practically no metal loss into the solution. In addition, combustion analysis detected an elevated carbon content (0.6%; Supporting Information, Table S7) in the spent catalyst (MIBC), and accordingly thermogravimetric analysis (Supporting Information, Figure S2) showed a slight (<2%) decrease in weight between 100 °C and 400 °C, which can be attributed to adsorbed organics.

Recycling experiments were successfully performed in both these solvents, with better performance in CPME. Experiments in MIBC were carried out with 0.5 g HMF and 0.2 g CuZn at 220 °C for 15 h (Supporting Information, Figure S7 and Table S9). Interestingly, with decreasing activity, the DMF/ DMTHF ratio increased up to 30:1, the 2nd cycle representing an almost perfect DMF selectivity. After the 2nd cycle, the product yield gradually decreased from ca. 90% (1-2nd cycle) to 17% (4th cycle). Notably, calcination of the spent catalyst after the 4th run at 500 °C for 6 h recovered the catalytic activity and even the DMF/DMTHF ratio in the 5th run was precisely identical to the initial value. Accordingly, TEM analysis of the catalyst recovered after the 4th run showed core-shell structures (Supporting Information, Figure S6), not present in the original solid; this morphological change together with the presence of organics adsorbed on the catalyst surface might be the cause of deactivation. After calcination, the morphology of the catalyst (Figure S6) displays a substantial regeneration of the original alloy structure. The transition from a core-shell structure into an homogeneous alloy has already been reported.^[18]

The catalyst has proven even more stable in CPME (Supporting Information, Figure S7 and Table S10). Recycling tests in CPME were performed at 220 °C using 0.5 g HMF and 0.2 g CuZn nanoalloy. No relevant loss in catalytic activity was observed in the first 5 cycles (ca. 90%), then the DMF + DMTHF yield decreased to 66% after the 6th cycle, and 3% product yield was observed in the 7th cycle, corresponding to a total of 3.5 g HMF converted. At this point, calcination was performed and the initial activity regained. From the above experiments it can be concluded that CuZn is a robust and highly active catalyst for the conversion of HMF to DMF, suitable for continuous-flow setup.

The specific roles of the copper and zinc metals in catalysis, or their oxides, which might also be present in smaller amounts, has yet to be elucidated. Recent photoelectron spectroscopy studies reported the formation of zinc oxide islands on particle surface in CuZn nanoalloys.^[19] The presence of the ZnO phase was confirmed during XRD analysis of the CuZn nanopowder (Figure S1). The beneficial effect on DMF production of acidic Zn²⁺ sites contained in Pd/Zn/C catalysts was recently proposed by Abu Omar et al.^[20] It seems plausible that active Cu⁰ species are responsible for hydrogenation/hydrogenolysis with the assistance of Lewis-acidic ZnO sites. Similar



synergistic effects were observed in a recent catalytic application.^[21] Cooperative effect in bimetallic noble metal catalysts designed for HMF to DMF conversion has been recently reported.^[22]

Particle size is a crucial parameter, and determining ideal size ranges is essential for catalytic application of "brasses".^[5d, 23, 27] We have briefly addressed this point by comparing the catalytic activity of commercially available CuZn alloys of various sizes. Indeed, CuZn alloys with 25–250 µm and < 25 µm particle size showed low activity at 220 °C for 6 h in EtOH, thus it appears that the <150 nm size is crucial. For future studies, several procedures for the synthesis of different nanosized CuZn structures with a bottom-up approach are available.^[23]

Another important aspect, using the commercially obtained CuZn nanopowder, is the reproducibility of results regarding batch to batch variations. No significant variation (within 6%) in DMF selectivities was observed when using four different batches from two different suppliers (Supporting Information, Table S8).

Next, the copper zinc nanopowder was tested in the hydrogenation of HMF at mild temperature to provide useful diol building blocks (Scheme 2). It is known that α,ω -diols, for ex-



Scheme 2. Selective formation of useful diol building blocks from HMF.

ample, 1,6-hexanediol are important polymer precursors.^[24] A screening of various commercial catalysts was carried out in ethanol at 120 °C for 3 h (for details see Supporting Information, page 5 and Tables S5–S6). All catalysts preferentially afforded either THFDM (2,5-tetrahydrofurandimethanol) or FDM (2,5-furandimethanol), depending on compositions. The best FDM selectivity (95%; Supporting Information, Figure S9 for GC trace) was achieved with the CuZn nanoalloy while >99% THFDM, was obtained over Pd/Al_2O_3 as a mixture of *cis* and *trans* isomer in 9:1 ratio (Supporting Information, Table S5, entry 7; Figures S10–S12).

Given the excellent performance of the CuZn nanoalloy in FDM formation, we next attempted the more challenging onepot dehydration/hydrogenation reaction starting directly from fructose. An elegant approach for obtaining HMF and its ethers from fructose in isopropanol solvent has recently been reported.^[25] First, fructose dehydration was conducted at 120 °C in *i*PrOH using different acid resins. HMF (**4**) and the corresponding isopropyl ether (**5**) were the main products, their ratio being dependent on the type of acidic catalyst used (Scheme 3; Supporting Information, Table S11). Amberlyst 15 and Nafion SAC-13 preferentially afforded HMF while with Dowex 50WX8 resin ether, **5** was found as main product.

Attempts to hydrogenate the crude mixtures with CuZn nanopowder after removal of the acidic resin by simple filtra-



Scheme 3. One-pot and two-step strategies for the valorization of fructose in *i*PrOH.

tion were moderately successful. **1**, **2**, and **3** were obtained in modest yields (20% in both cases, Table S12) when a mixture of **4** and **5** obtained by dehydration with Nafion SAC-13 and Amberlyst 15 were hydrogenated using 120° C and 30 bar H₂. Interestingly, the corresponding one-pot process starting directly from fructose with CuZn catalyst and Nafion SAC-13 or Amberlyst 15 (Supporting Information, Table S13) was more successful. In this case, fructose conversion was 96% using Nafion SAC-13 and **1** and **2** were found as only products in 1% and 33% yields, respectively. With Amberlyst 15, a good combined 50% yield of **1** and **2** was observed at full fructose conversion, in addition 7% FDM was detected. These results compare well with the yields found in the literature using noble metal catalysts.^[26]

In conclusion, a noble-metal-free copper-zinc nanoalloy is applied for the first time in the highly selective hydrodeoxygenation of HMF to biofuels (up to 97% DMF + DMTHF yield) and diol building blocks (up to 95% FDM). Alloys play a crucial role in heterogeneous catalysis, however, 'nanobrasses' are not yet explored in catalysis.^[5d,27] Recent reports identify CuZn alloys as promising systems for methanol^[23a] and dimethylether synthesis.^[21] Based on these studies and the results reported in this paper, we foresee a more general use of "nanobrasses" in the conversion of renewable resources in the future.

Experimental Section

General procedure for hydrogenation reactions: In a typical experiment, a glass insert containing 5-(hydroxymethyl)furfural (0.500 g), the catalyst (0.100 g) and toluene or decane (0.250 mL, internal standard) in the appropriate solvent (20 mL) was placed in a 100 mL stainless-steel Parr reactor. After purging 3 times with H₂, the reactor was pressurized at the desired pressure, heated, and stirred with a mechanical stirrer (600 rpm). After reaction, the reactor was cooled down to room temperature and the mixture was filtered and injected into a GC-MS-FID to determine conversion, product selectivity, and yield (by internal standard method). For characterization of the spent catalyst, the reaction mixture was centrifuged and the solid was washed two additional times with acetone and dried at 110 °C for 6 h. Recycling experiments are described in detail in the Supporting Information.

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Copper-Zinc Alloy Nanopowder: A Robust Precious-Metal-Free Catalyst for the Conversion of 5-Hydroxymethylfurfural **Revival of the 'brass-age':** Commercially available copper-zinc nanopowder proves very robust and highly effective in the reduction of HMF to either fuel additives or useful chemical building

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blocks. Fuel yields of up to 97% and FDM yield up to 95% were obtained. The one-pot conversion of fructose to furanic diethers is also achieved, in isopropanol solvent.

