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PAPER

One-pot reduction of 5-hydroxymethylfurfural *via* hydrogen transfer from supercritical methanol†

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Catalytic conversion of HMF to valuable chemicals was achieved over a Cu-doped porous metal oxide in supercritical methanol. The hydrotalcite catalyst precursor is prepared following simple synthetic procedures, using inexpensive and earth-abundant starting materials in aqueous solutions. The hydrogen equivalents needed for the reductive deoxygenation of HMF originate from the solvent itself upon its reforming. Dimethylfuran, dimethyltetrahydrofuran and 2-hexanol were obtained in good yields. At milder reaction temperatures, a combined yield (DMF + DMTHF) of 58% was achieved. Notably, the formation of higher boiling side products and undesired char from HMF is not detected under these reaction conditions.

Introduction

Obtaining transportation fuels and chemicals from renewable feedstocks is highly desired, since the availability of fossil fuels is limited and they release large quantities of CO₂ when combusted.^{1–3} One key platform compound identified for the renewable chemicals and fuel industry⁴ is 5-hydroxymethylfurfural (HMF) which can be readily obtained from hexose sugars.^{5–7} Among several options, HMF can be oxidized to monomeric building blocks that serve as precursors for polymer synthesis.^{8,9} It can also undergo reductive deoxygenation to 2,5-dimethylfuran (DMF)¹⁰ or more extensive reduction to 2,5-dimethyltetrahydrofuran (DMTHF). Both of these products have high energy density and low volatility which makes them suitable fuel replacements or additives.^{10,11} DMTHF could further serve as a potential solvent substitute for tetrahydrofuran (THF).⁷ Although this approach is attractive, selective transformation of HMF to its reduced counterparts remains a challenge as it requires a series of particular chemical transformations, involving C–O bond cleavage. Moreover formation of undesired side products from the reactive HMF molecule should be prevented. Recent efforts towards selective conversion of HMF involve both heterogeneous and homogeneous catalysts. Dumesic and coworkers presented an efficient strategy for the conversion of fructose derived HMF to DMF by hydrogenolysis over a

copper–ruthenium catalyst.¹⁰ Leitner and coworkers have developed highly selective iridium catalyzed decarbonylation of HMF to furfuryl alcohol in compressed carbon dioxide.¹²

Porous metal oxides (PMOs) derived from hydrotalcite-like precursors have been successfully used in a variety of chemical transformations, such as reductions, and can be conveniently doped with suitable metal-ions, for example Cu²⁺, Ni²⁺, Fe³⁺, Ga³⁺ *etc.*^{13–17} Previously, Cu-doped PMOs have proven promising in the one step–one pot depolymerization of organosolv lignin¹⁸ by extensive deoxygenation/hydrogenation in supercritical MeOH (Sc-MeOH).^{19,20} It was also demonstrated that raw biomass can be efficiently converted to a mixture of combustible liquids and gases without the formation of undesired biochar.²¹ In this work we apply the same approach for the reductive deoxygenation of HMF to DMF and DMTHF by *in situ* generated hydrogen over a multifunctional Cu-PMO catalyst. We demonstrate that the formation of higher boiling side products will be similarly suppressed when using HMF as a substrate. At 300 °C rapid conversion of HMF to volatile products is achieved, affording a combined yield of 61% to DMF, DMTHF and 2-hexanol. At milder reaction temperatures 50% DMF yield was achieved.

Experimental

Materials

5-Hydroxymethylfurfural (99%), Mg(CH₃COO)₂·4H₂O (≥99.0%), Cu(NO₃)₂·2.5H₂O (98%) were purchased from Sigma Aldrich, MeOH (99.8%, anhydrous) used as a reaction medium was from Acros, MeOH (99.9%) used for washing the catalyst was from Merck, Al(NO₃)₃·9H₂O (98.7%), Na₂CO₃·H₂O (p.a.) were from J. T. Baker and NaOH (98.6%) was purchased from Mallinckrodt Chemicals. All chemicals were used as received without further purification.

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Cu-PMO synthesis

The copper-containing porous metal oxide (Cu-PMO) was synthesized by slowly adding aliquots (10 mL) of an aqueous solution containing $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (18.8 g, 0.05 mol), $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (25.7 g, 0.12 mol) and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (7.0 g, 0.03 mol) in demineralized water (300 mL) along with aliquots of 1 M NaOH (10 mL) over a period of 4 h to an aqueous solution of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (6.2 g, 0.05 mol) in demineralized water (375 mL) preheated to 65 °C and under vigorous stirring. The addition was conducted so the pH after the NaOH addition was kept relatively constant at pH \sim 10. Subsequently, the mixture was left stirring for 3 days. The resulting light blue slurry was collected by vacuum filtration and the solids were washed with water (\sim 1.5 L). The filter cake was then re-suspended in 2 M warm aqueous $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (62 g, 250 mL) and left overnight before harvesting the Cu-doped hydrotalcite-like compound by vacuum filtration followed by washing with demineralized water (\sim 2.5 L). The resulting blue compound was dried overnight in an oven at 100 °C and then calcined at 460 °C for 24 h in air to yield the final Cu-PMO.

Catalytic reduction of HMF

In a typical experiment, HMF (100 mg, 0.8 mmol), Cu-PMO (100 mg) and MeOH (3 mL) along with an internal standard (decane, 5 μL , 25 μmol) were placed in a stainless steel bomb (SwagelokTM, 10 mL, see picture in ESI†) and heated to 300 °C for a specified time. After the reaction, the stainless steel bomb was rapidly cooled in an ice bath. The bomb was then carefully opened and the contents were filtered through a glass filter funnel and the filter washed with MeOH (10 mL). Finally, the liquid was analyzed by GC-FID and GC-MS.

Catalyst recycling

A typical catalytic run was conducted with 100 mg Cu-PMO, and 100 mg HMF using 3 mL methanol. After the first run, the reaction was stopped, and the content of the reactor was transferred to a centrifuge tube using 10 mL methanol in total. The liquid phase was decanted, analyzed by GC-FID, and the catalyst was additionally washed 2 times with 5 mL methanol. After centrifugation, the methanol washings were discarded and the solid was dried in a desiccator *in vacuo*. The dry, purple solid was used in the next experiment. This procedure was repeated four more times.

Analysis

GC-FID measurements were performed on a Shimadzu GC 2010 plus instrument equipped with a Shimadzu SHRIX-5MS column (30 m, 0.25 mm ID, 0.25 μm) and a Shimadzu AOC-20i auto injector. The carrier gas was helium with a total flow of 30.9 mL min^{-1} . The temperature program for analysis was: 30 °C kept for 6.5 min, 15 °C min^{-1} to 50 °C kept for 0.5 min, 20 °C min^{-1} to 100 °C and 35 °C min^{-1} to 300 °C kept for 5 min.

GC-MS measurements were made on a Shimadzu GCMS-QP2010S equipped with a Shimadzu DB-5ms column

(30 m, 0.25 mm ID, 0.25 μm). The carrier gas was helium with a total flow of 14 mL min^{-1} , column pressure was 49.7 kPa. Linear velocity was 36.1 cm s^{-1} and split ratio was kept at 10. The temperature program for analysis was: 40 °C kept for 6 min, 15 °C min^{-1} to 60 °C kept for 2 min, 20 °C min^{-1} to 150 °C and kept for 2 min and finally heated at 25 °C min^{-1} to 260 °C and kept for 5 min.

X-ray powder diffraction (XRPD) experiments were performed on a Bruker D8-focus X-ray diffractometer equipped with a Cu line-focus sealed tube, a divergent beam geometry and a NaI scintillation detector. Measurements were made with a 40 kV, 40 mA beam in the range 2θ from 3° to 80° locked couple scan type, a step size of 0.05° and a scan speed of 10 s. The Cu-PMO compound was measured with a scan speed of 5 s.

Fourier transformed infrared spectroscopy (FT-IR) measurements were conducted on a Thermo Scientific Nicolet 6700 FT-IR instrument with a Thermo Scientific Smart Orbit, diamond 30 000 to 200 cm^{-1} accessory.

NMR experiments were conducted on a Bruker Avance 500 MHz spectrometer running Topspin 1.3 with a broadband observe probe.

Results and discussion

A 20 mol% copper-doped hydrotalcite (HTC) was synthesized by co-precipitation of a mixture of $\text{Al}(\text{NO}_3)_3$, $\text{Mg}(\text{CH}_3\text{COO})_2$ and $\text{Cu}(\text{NO}_3)_2$ with Na_2CO_3 and NaOH using a 3 : 1 molar ratio of M^{2+} with respect to M^{3+} . The blue colored HTC turned green during calcination (460 °C, 24 h, see picture in ESI†) resulting in the active porous Cu-PMO catalyst (BET surface area: 142 $\text{m}^2 \text{g}^{-1}$).

The HTC catalyst precursor was analyzed by XRPD (Fig. 1) and FT-IR (ESI, Fig. S4 and S5†). XRPD revealed a highly ordered crystalline structure with distinct hydrotalcite features consistent with the literature.²² After calcination, a porous near-amorphous material was identified by the lack of any characteristic HTC reflections and the appearance of weak MgO and CuO reflections (Fig. 1).²²

Catalytic runs were carried out in a 10 mL stainless steel bomb (see ESI† for details) containing Cu-PMO (100 mg) and HMF (100 mg) in methanol (3 mL) at 300 °C. Three main products were observed: DMF, DMTHF and 2-hexanol (Scheme 1).

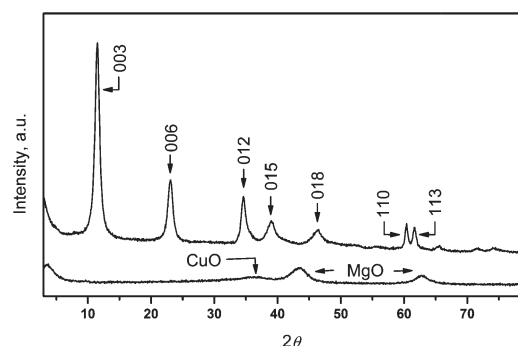
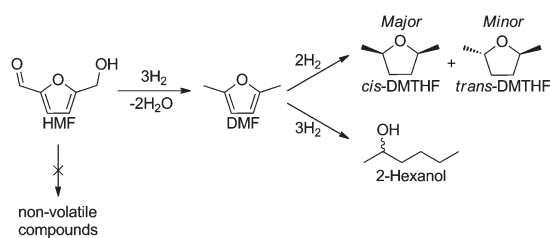


Fig. 1 XRPD of 20 mol% Cu-HTC (top) and the corresponding calcined Cu-PMO (bottom).



Scheme 1 Proposed reaction pathway from HMF to the three main products DMF, DMTHF and 2-hexanol.

These compounds were quantified by GC-FID[‡] using calibration curves of the pure compounds and an internal standard.

Several intermediates were identified by GC-MS especially in the earlier stages of the reaction (ESI, Scheme S1[†]). These intermediates were converted to the main products over time. Considerable deoxygenation starting from HMF takes place, finally resulting in the main products that are monooxygenates. Based on these intermediates we hypothesize that the reaction proceeds by rapid reduction of the aldehyde group in HMF followed by hydrogenolysis of the hydroxyl functionalities. Subsequent reduction of the furan ring of DMF results in the formation of *cis*- and *trans*-DMTHF while ring-opening of furan under hydrogenolysis and hydrogenation leads to 2-hexanol. Experiments elucidating the product distribution as a function of time revealed that the DMF yield peaked after only 30 min. All HMF was consumed in 45 min resulting in a product mixture consisting of 34% DMF, 8% DMTHF and 2% 2-hexanol. Prolonged reaction times gave full conversion of DMF to DMTHF and 2-hexanol where yield of the latter reached its maximum after 300 min. After 720 min, the DMF yield was <1% and DMTHF was observed as the major product in 38% yield and 2-hexanol in 15% yield (Fig. 2). Surprisingly, 2-hexanol did not seem to arise from the ring-opening of DMTHF but rather from DMF. Experiments using DMF and DMTHF as substrates supported this observation (ESI, Table S3[†]).

The three quantified products did not fully account for the consumed starting material in terms of mass balance. A series of volatile side-products were also found during GC analysis, although present in low quantities. Additional GC-MS analysis revealed that the nature of these intermediates is similar to the main products, comprising mainly isomers of aliphatic alcohols and tetrahydrofuran or furan derivatives. Thus, HMF was fully converted without the formation of non-volatile side products (ESI, Table S1[†]). Likely sources of these compounds are reactions of main products or by-products which engage in chain prolongation *via* alkylation through the *in situ* formed reactive intermediates. Similar chain prolongation/alkylation reactions of the formed primary products were observed using cellulose²¹ and organosolv lignin²⁰ as substrates. To confirm that there were no higher boiling side-products originating from the inherent reactivity of HMF, a reaction mixture obtained after 2 h[‡] was evaporated at reduced pressure. Indeed, >98% of the products

[‡] DMTHF was calibrated using a 1 : 1 mixture of the *cis*- and *trans*-isomer, which were separable by GC-FID. After 2 h of reaction with HMF most of the reaction intermediates identified by GC-MS capable of converting into the major products were consumed.

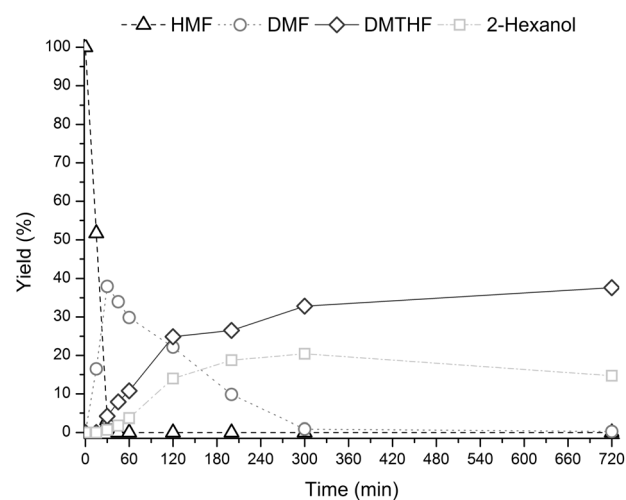
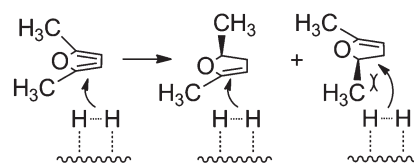


Fig. 2 The conversion of HMF to DMF, DMTHF and 2-hexanol over the Cu-PMO as a function of time. Conditions: HMF (100 mg, 0.8 mmol), Cu-PMO (100 mg), MeOH (3 mL), 300 °C. Each point on the graph corresponds to a separate experiment.



Scheme 2 Proposed mechanism for the preferential formation of the *cis*-DMTHF isomer over the *trans*-DMTHF isomer.

were volatile. In contrast, a control experiment conducted with a Mg/Al PMO (Mg : Al = 3 : 1) not containing any Cu resulted in <1% DMF while neither DMTHF nor 2-hexanol were detected. However, a significant amount of high-boiling compounds was found (ESI, Table S4[†]) in the form of a brownish tar-like residue. A blank reaction with HMF in supercritical methanol in the absence of a catalyst resulted in a similar product mixture. Most likely, rapid deoxygenation of HMF was the main reason why undesired side-reactions such as polymerizations and condensations were suppressed in the presence of Cu-doped PMO.

The *cis*- and *trans*-DMTHF isomers have distinct physical properties, *e.g.* boiling points.²³ Consequently, the isomers could be distinguished by NMR experiments (ESI, Fig. S6–S8[†]) and quantified separately by GC-FID. The *cis*-DMTHF isomer was favored in all experiments over the *trans*-DMTHF isomer, which can be explained by steric reasons. During the reduction, addition of the second H₂ molecule occurring to the same face as the first would result in less steric hindrance, whereas the methyl group restricts the formation of the *trans*-DMTHF (Scheme 2). A molar ratio of ~7 : 1 (*cis* : *trans*) was observed after 45 min at 300 °C which slowly changed to ~3 : 1 after 720 min. We speculate that this might be due to isomerization caused by the basic catalyst through a non-ring-opened intermediate. However, a more thorough study will be required to understand this aspect in more detail.

Although HMF was rapidly converted to a mixture of DMF, DMTHF and 2-hexanol at 300 °C with 60% total yield, the

Table 1 Reduction of HMF at varying temperatures^a

Entry	<i>T</i> (°C)	DMF yield (%)	DMTHF yield (%)	<i>cis</i> : <i>trans</i> ratio	2-Hexanol yield (%)
1	320	32	11	6.5	6
2	310	36	8	6.2	2
3	300	34	8	6.8	2
4	290	40	5	6.8	1
5	280	35	3	6.6	1
6	270	31	2	6.4	<1
7	260	26	<1	n.a	0
8	240	20	<1	n.a	0

^a Reaction conditions: HMF (100 mg, 0.8 mol), Cu-PMO (100 mg), MeOH (3 mL), 45 min.

Table 2 Reduction of HMF at milder reaction temperatures and varying reaction times^a

Entry	<i>T</i> (°C)	Time (h)	DMF yield (%)	DMTHF yield (%)	Total ^b (%)	Yield DMF + DMTHF (%)
1	240	0.75	21	0	58	21
2	240	1.5	26	0	73	26
3	240	3	41	0	79	41
4	240	4	39	2	77	41
5	260	3	48	10	84	58
6	270	3	40	15	79	55
7	270	2	46	11	81	57

^a Reaction conditions: HMF (100 mg, 0.8 mmol), Cu-PMO (100 mg), MeOH (3 mL). ^b Selectivity of total identified components based on GC-FID. Products are depicted in ESI, Scheme S6.†

individual DMF yield was rather moderate at this reaction temperature primarily due to over-reduction. Therefore, we were interested to determine whether HMF could be reduced at milder reaction temperatures. First we conducted experiments at temperatures ranging from 240 to 320 °C for 45 min. The results are summarized in Table 1. The highest DMF yield (40%) was achieved at 290 °C (Table 1, entry 4), but gratifyingly the reaction took place at all reaction temperatures utilized. Entries 7 and 8 (Table 1) show that at 240 and 260 °C HMF reduction to DMF was slower, resulting in 20 and 26% product yield, respectively, but no DMTHF or 2-hexanol was obtained.

These observations allowed for further optimization at milder reaction temperatures. The results are summarized in Table 2. At 240 °C, the DMF yield gradually improved from 20% at 45 min (Table 2, entry 1) to 25% at 1.5 h (Table 2, entry 2), and 41% at 3 h reaction time (Table 2, entry 3). After 4 h, slight over-reduction to DMTHF took place and the total fuel output was 41% (Table 2, entry 4), identical to the 3 h run. At 260 °C the DMF yield could be further improved to 48% and total fuel output to 58% after 3 h (Table 2, entry 5). At 270 °C, 46% DMF yield was achieved in 2 h, and a slightly lower, 40% yield in 3 h, due to formation of 2-hexanol. Total fuel output was 53 and 57% at this reaction temperature (Table 2, entries 7 and 8). While no 2-hexanol could be detected at 240 °C even after prolonged reaction times, it was present in lower quantities at 260 and 270 °C. In addition, the GC-FID traces of the product mixtures only displayed a few main signals allowing for

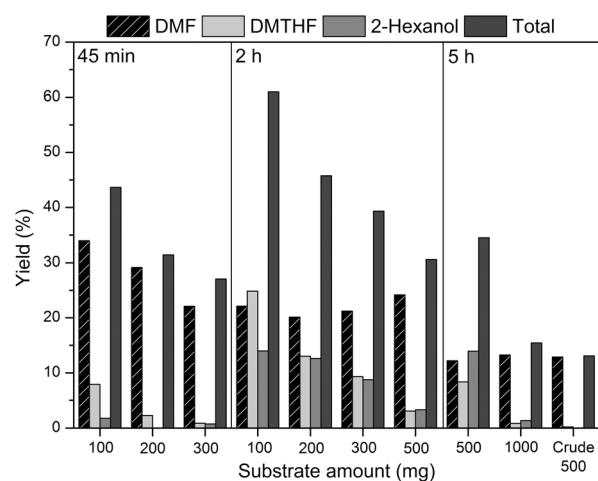


Fig. 3 Experiments with different HMF to catalyst ratios using different reaction times. General conditions: Cu-PMO (100 mg), MeOH (3 mL), 300 °C.

identification of the major intermediates by GC-MS measurements (ESI, Scheme S6†). The product of one step reduction and hydrogenolysis of HMF, 5-methyl-2-furanmethanol, and its methyl ether could be identified. Its reduced counterpart, isomers of 5-methyl-2-tetrahydrofuran methanol were also detected, suggesting that besides direct DMF reduction, alternative pathways may also be the source of DMTHF. No furfuryl alcohol was observed. The selectivity of total identified products was high in all cases, reaching 84% at 260 °C (Table 2, entry 5). Quantification and additional information regarding reaction intermediates are described in the ESI, Table S2 and Scheme S6.† In summary, milder reaction conditions afforded cleaner product mixtures, and a 48% DMF yield together with a total fuel output of almost 60%.

The substrate to catalyst ratio was additionally varied at 300 °C with the Cu-PMO catalyst (100 mg) and MeOH (3 mL) by changing the substrate amount and reaction time (Fig. 3). Here, experiments revealed that the HMF to catalyst ratio could be increased significantly compared to the initial experiments. Although the total yield of the three main products decreased with increasing HMF amount (when compared at 45 min), yields became comparable at longer reaction times. The total yield of the three products went from 44% with a 100 mg substrate loading to 27% at 300 mg after 45 min. A maximum total yield of 61% was obtained after 2 h using 100 mg substrate. This value decreased to 44% at 200 mg HMF loading and 31% at 500 mg HMF loading. Subjecting 500 mg HMF to a 5 h reaction time gave a slightly higher total yield of 34%. This demonstrates that the substrate loading can be significantly improved. The system proved capable of converting up to 1000 mg HMF in 5 h, though decomposition products of HMF here partially covering the bottom of the reactor and catalyst (Fig. 3).

Recycling experiments showed that it was possible to recycle the catalyst over five runs using HMF with only a moderate decrease in conversion (ESI, Table S5 and Fig. S11†). However, to maintain the initial combined product yields of DMF and

DMTHF longer reaction times might be needed for the latter runs. In addition, our recent catalyst stability studies using Cu-PMO in the conversion of lignocellulose and cellulose revealed that no leaching occurs and that the catalyst is sufficiently robust for a variety of biomass conversion reactions.²¹

Finally, we were interested in converting crude HMF synthesized by dehydration of fructose as previously developed in our laboratories.²⁴ The reaction mixture was extracted with MIBK (methyl-isobutyl ketone) as the only method of purification, resulting in a brown sticky material after removal of the solvent *in vacuo*. A slurry containing 0.5 g of this crude HMF material in 3 mL MeOH was reacted for 5 h at 300 °C with 100 mg Cu-PMO. Impressively, the reaction proceeded and resulted in DMF (12% yield) besides other volatile products even though the conversion from fructose to HMF was not optimized. Hence, with an optimized reaction process an even higher DMF yield might be obtainable.

Conclusions

In this work, we have shown that a Cu-doped PMO catalyst obtained by the calcination of a hydrotalcite-like precursor is capable of converting HMF into valuable and interesting chemicals in supercritical MeOH, thus paving a new direction toward a renewable chemical industry. Complete conversion of HMF to volatile compounds could be achieved in only 45 min, without the formation of higher boiling side products. Reduction of HMF at 300 °C for 2 h resulted in 61% total yield of three main products: DMF, DMTHF and 2-hexanol. The reaction conditions were tunable and offer a degree of flexibility to the process such that either DMF or DMTHF and 2-hexanol could be obtained as the major reaction product. At 240 °C DMF yield reached 41% after 3 h, and at 260 °C 48%. A total yield for DMF and DMTHF of 58% was achieved at 260 °C after 3 h. Further in-depth studies of the catalyst structure and optimization of reaction conditions are desired to improve activity, and selectivity toward DMF and DMTHF.

Notably, both the fructose dehydration²⁴ as well as the catalytic HMF conversion method described in this study could be performed utilizing inexpensive and environment-friendly materials (boric acid and earth abundant metals). The combination of these two novel routes would enable a simple two-step production of DMF or DMTHF and 2-hexanol directly from fructose. The Cu-PMO catalyst system was even able to convert a tar-like slurry containing HMF. This could ultimately eliminate one of the major challenges in the chemical infrastructure based on HMF, namely purification.

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