Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information

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

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1.1 Pictures of catalyst and reactor setup

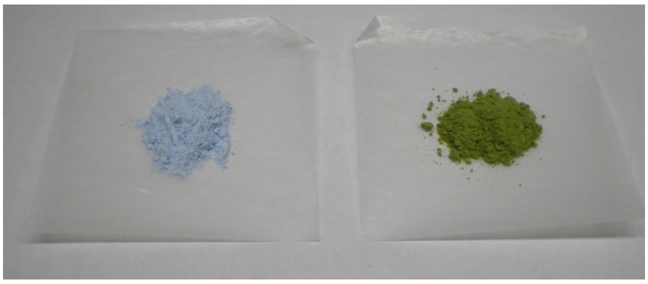


Figure S1. Picture of the blue Cu-doped HTC (left) and the corresponding green Cu-PMO (right).

The Swagelok^{TM} reactors were made of stainless steel and had an internal volume of about 10 mL (Figure S2). They were mounted in a preheated aluminum block for a specified time and subsequently removed and placed in an ice bath. When cooled they were mounted in a clamp before carefully opening with an adjustable wrench.

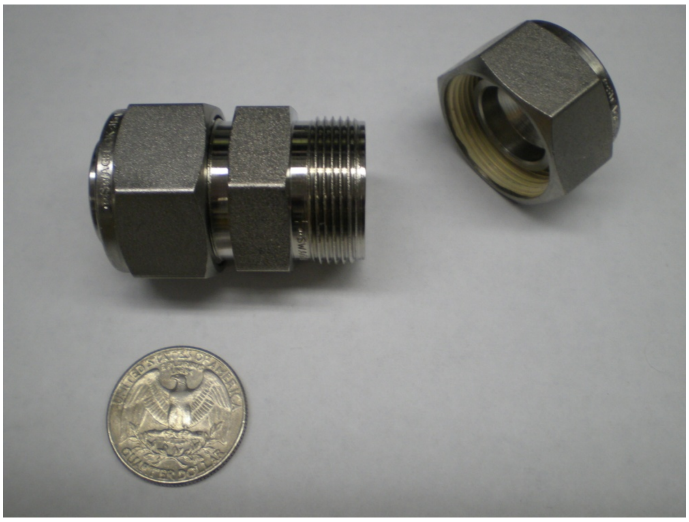


Figure S2. Picture of the Swagelok^{TM} stainless steel reactor. An American quarter is placed in the bottom of the picture to allow visual scale comparison.

1.2 Typical GC-FID elution profile

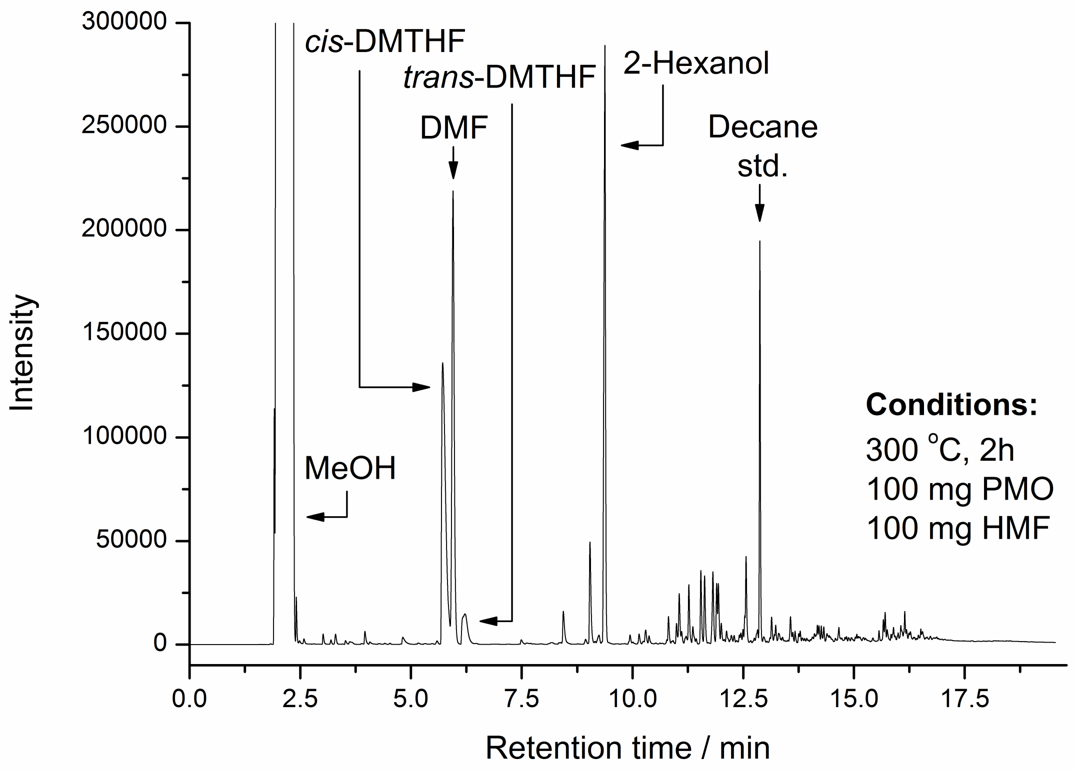


Figure S3. Typical GC-FID elution profile of a reaction mixture. Conditions of the shown experiment: 300 °C, 2 h, 100 mg Cu-PMO and 100 mg HMF in 3 mL MeOH.

1.3 IR spectroscopy measurements

The main absorptions of the Cu-doped HTC are; 3500 cm^{-1} which is attributed to the OH stretch in the lattice. The shoulder occurring around 3000 cm^{-1} is generally assigned to OH stretch in H_2O. The absorbance at 1360 cm^{-1} is assigned to CO_3^{2-} and the shoulder at 1600 cm^{-1} is corresponding to OH bent in H_2O (Figure S4).[i]

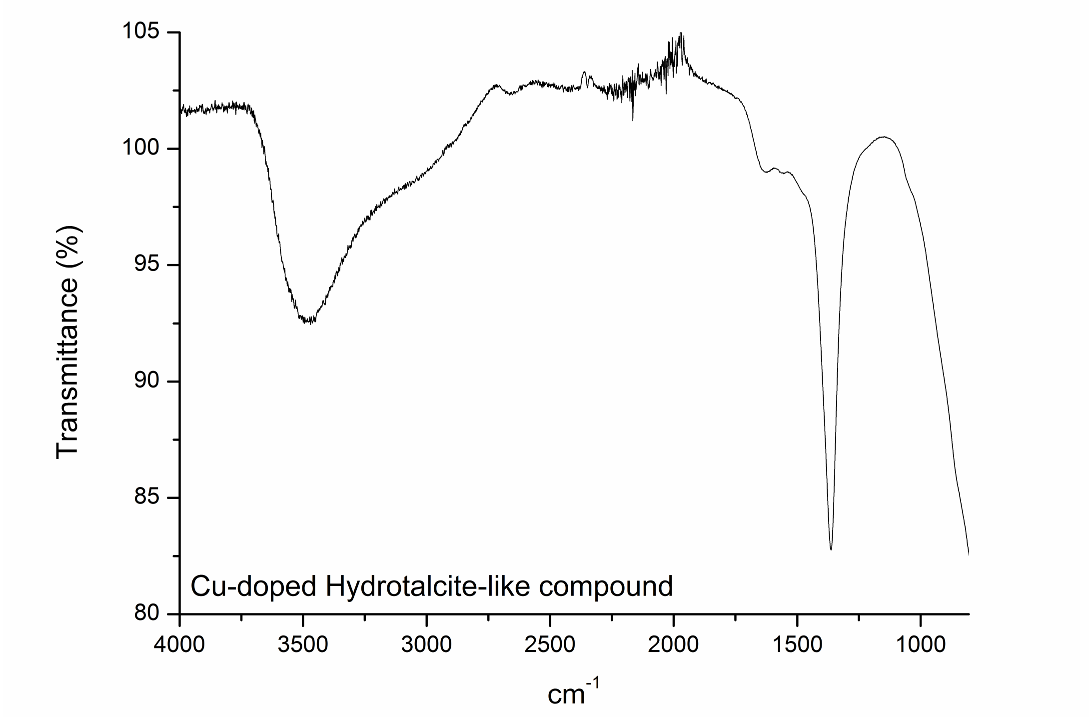


Figure S4. FT-IR spectrum of the Cu-doped HTC.

The corresponding Cu-PMO compound is characterized by the absence of the strong absorbance at 3500 and 1370 cm^{-1} caused by the collapse of the HTC structure and absence of CO_2. Instead relatively weak absorbances are observed (Figure S5).

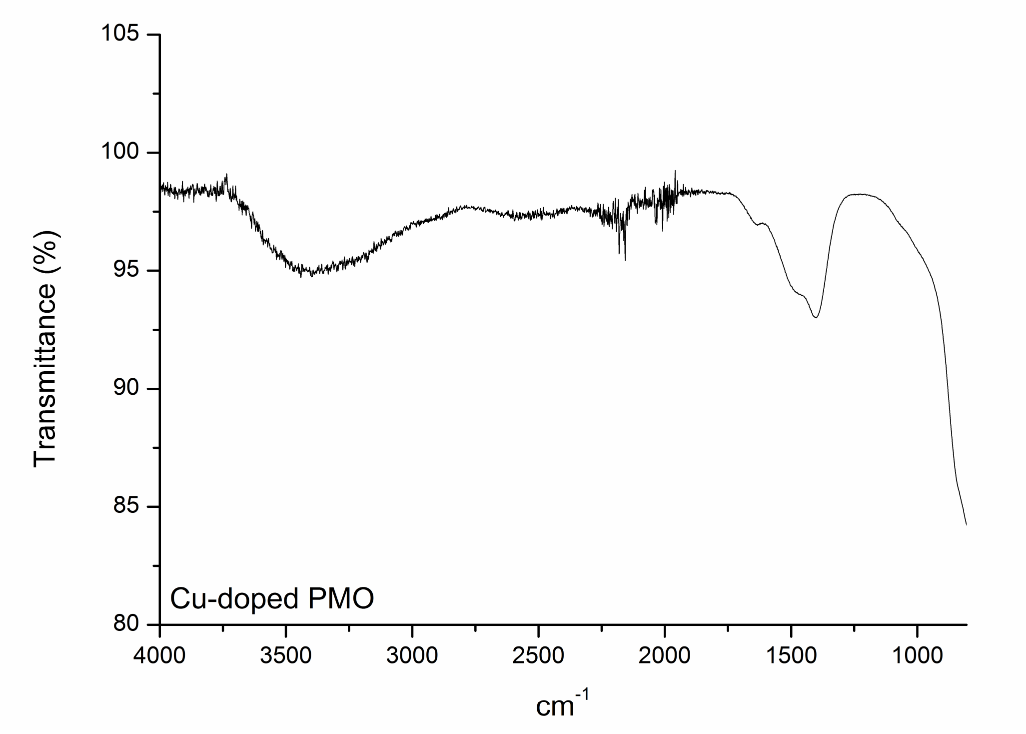
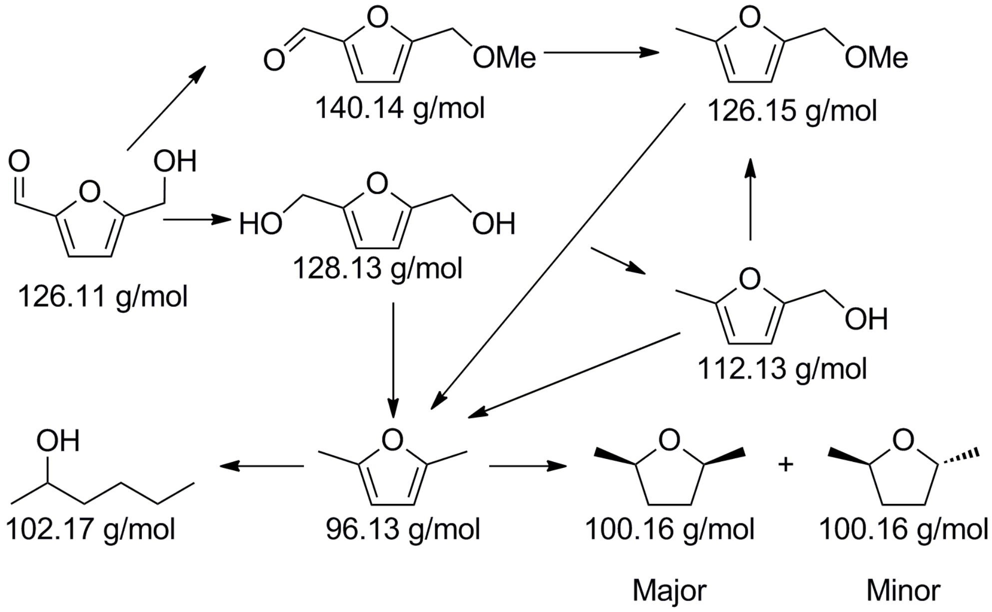


Figure S5. FT-IR spectrum of the Cu-PMO.

1.4 Intermediates identified by GC-MS and proposed reaction pathway

Besides the three main products of the reaction, several reaction intermediates were identified based on GS-MS which was correlated with possible intermediates from HMF to DMF and DMTHF. Three intermediates that were consistently observed had molar masses of 140 g/mol, 126 g/mol and 112 g/mol. These could correspond to; methylether of HMF, methylfurfuryl alcohol and the methylfurfuryl alcohol methylether, respectively. These products are plausible reduction products along the reaction pathway from HMF to DMF and DMTHF (Scheme S1).



Scheme S1. Proposed reaction pathway from HMF to DMF and DMTHF at 300 °C based on the identification of intermediates by GC-MS.

1.5. Identification of all components by GC-MS using standard libraries

Table S1. GC-MS data and identification of individual components

Sample: 100 mg HMF, 100 mg Cu-PMO, 300 °C, 45 minutes

Peak no.	retention time	base peak	mass peak	library match
1	5.49	45	n.v.	2-pentanol
2	6.64	42	n.v.	1-pentanol
3	7.07	43	100	2-hexanone
4	7.29	45	101	2-hexanol
5	7.4	43	115	5-Methyl-2-THFmethanol (cis or trans)
6	7.61	43	115	5-Methyl-2-THFmethanol (cis or trans)
7	8.03	57	100	methyl-cyclopentanol
8	8.7	56	n.v.	1-hexanol

9	9.5	71	n.v.	THF-methanol
10	9.63	45	n.v.	methyl-hexanol (or isomer)
11	9.73	71	n.v.	THF-methanol (or isomer)
12	10.06	85	112	5-methy-2-furanmethanol methyl ether
13	10.28	95	126	methyl-furoate (or regioisomer)
14	10.42	85	126	tetrahydropyrane methanol
15	10.8	95	126	methyl-furoate (or regioisomer)
16	10.88	85	n.v.	5-methyl-THF methanol
17	10.97	95	112	5-methyl-2-furanmethanol
18	11.53	95	112	furan derivative
19	11.77	59	n.v.	n.i.
20	11.83	59	110	3-methoxy-1 butanol
21	11.88	95	126	furan derivative
22	11.95	45	n.v.	2,5-hexanediol
23	12.14	85	126	n.i.
24	12.2	69	n.v.	2,3 dimethyl-pentanol
25	12.42	69	125	n.i.
26	12.53	69	n.v.	1,2-hexanediol
27	12.61	95	126	furan derivative
28	12.63	45	n.v.	1,5-hexanediol
29	12.69	85	n.v.	2,3-dimethyl-1-pentanol
30	12.77	109	140	(methyl)-methylfuranoate
31	12.94	109	140	(methyl)-methylfuranoate
32	13.03	109	140	furan derivative
33	13.66	111	142	1-methoxymethyl-furanemethanol
34	13.73	74	n.v.	valeric acid derivative
35	13.87	57	n.v.	long chain alcohol
36	14	83	n.v.	n.i.
37	14.24	57	170	dodecane
38	14.32	111	142	furan derivative
39	14.51	57	n.v.	THF derivative
40	14.7	43	141	long chain alcohol branched
41	15.33	43	n.v.	long chain alcohol branched
42	16.34	85	n.v.	THF derivative
43	16.62	109	n.v.	furan derivative
44	17.73	95	n.v.	furan derivative
45	19.59	95	n.v.	furan derivative

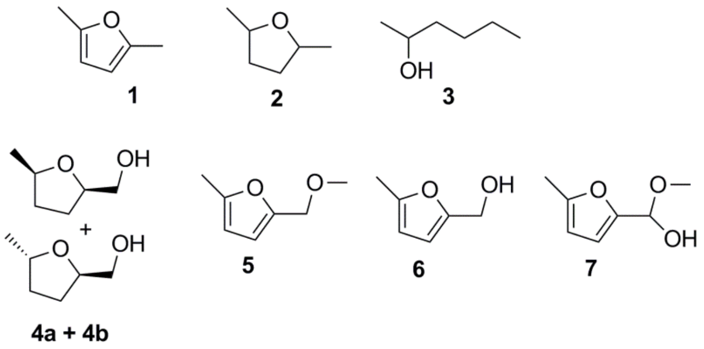
All components in the sample are listed, except main products DMF and DMTHF which eluted below 5 minutes on the available column. The results are not quantitative.

Library: the matches in the table are identified according to the NIST08 standard library taking into account best quality match.

1.6. Reactions at lower reaction temperature and intermediates

Table S2. GC-FID data on reactions at milder reaction temperatures

			1 (%)	**2** (%)	1+2 (%)	**3**	**4a** **(%)**	**4b** (%)	**5** (%)	**6** (%)	**7** (%)	**HMF** Conv (%)	Tot * (%)	Yield **1**	Yield **1+2**
	t (h)	*T* (°C)	2.99 min	2.903 +3.05 min		6.42 min	7.21 min	7.68 min	10.07 min	10.51 min	12.31 min				
1	0.75	240	24.9	0.00	24.9	0	2.8	2.0	3.9	22.9	1.8	97.4	58.2	20.8	20.8
2	1.5	240	33.2	0.00	33.2	0	4.1	2.7	7.6	20.8	4.3	97.1	72.7	26.4	26.4
3	3	240	43.7	0.00	43.7	0	5.9	4.0	13.1	6.4	6.1	99.7	79.2	41.4	41.4
4	4	240	42.4	1.93	44.4	0	5.4	3.8	13.9	3.4	5.7	99.9	76.7	38.7	40.5
5	3	260	50.6	10.05	60.6	1.3	1.9	1.4	13.5	1.2	4.0	>99.9	84.1	48.0	57.5
6	3	270	42.5	15.96	58.4	10.5	0.3	0.6	5.9	2.9	0	99.6	78.7	38.9	53.6
7	2	270	50.1	12.05	62.2	3.5	0.6	0.4	10.6	1.7	1.8	99.1	80.9	45.7	56.7



Scheme S6. Reaction intermediates identified by GC-MS.

GC-MS measurements were made on a Shimadzu GCMS-QP2010S equipped with a Shimadzu DB-5ms column (30 m, 0.25 mmID, 0.25 um). The carrier gas was helium with a total flow of 14 ml/min, column pressure was 49.7 kPa. Linear velocity was 36.1 cm/sec and split ratio kept at 10.

The temperature program for analysis was: 40 °C kept for 6 min, 15 °C/min to 60 °C kept for 2 min, 20 °C/min to 150 °C and for 2 minutes and finally heated at 25 °C/min to 260 °C and kept for 5 min.

Library: the matches in the table are identified according to the NIST08 standard library taking into account best quality match.

1.7. DMF and DMTHF as substrates

DMF and DMTHF were utilized as substrates in the reaction to investigate which one converted to 2-hexanol. DMF (85 µL, 0.8 mmol) was dissolved in MeOH (3 mL), the Cu-PMO (100 mg) catalyst was added and the reactor closed and heated for 5 h. Similarly, DMTHF (96 µL, 0.8 mmol) was dissolved in MeOH (3 mL), the Cu-PMO (100 mg) catalyst was added and the reactor closed and heated to 300 °C for 5 h (Table S3).

Table S3. Results of utilizing DMF and DMTHF as substrates.

Substrate	DMF yield (%)	DMTHF yield (%)	2-Hexanol yield (%)	Total yield (%)
DMF	39	23	8	70
DMTHF	0	80	<1	81

The experiments resulted in 61% DMF conversion which was mainly into DMTHF (23%) and 2-hexanol (8%) after 5 h at 300 °C. The corresponding experiment with DMTHF surprisingly only showed 20% DMTHF conversion of which <1% was converted into 2-hexanol. Based on these findings we propose that 2-hexanol mainly originated from DMF rather than DMTHF.

1.8. Volatility experiments

In order to confirm that no higher boiling side products were produced from the reduction of HMF, a reaction mixture after 2 h reduction at 300 °C with HMF (100 mg) and Cu-PMO (100 mg) was subjected to reduced pressure over a prolonged period of time at 80 °C. For comparison an experiment with a PMO that did not contain any Cu was conducted under otherwise similar reaction conditions (Table S4).

Table S4. Results of volatility experiments

Catalyst	Residual weight in the flask (mg)
Cu-PMO	1.6
Mg:Al PMO without Cu	55.5

Clearly, as Table S4 indicates, there was a correlation between the volatility of the products and the presence/absence of Cu. This was also observed visually as the reaction with the Cu-PMO resulted in a colorless solution whereas the reaction with Mg:Al PMO resulted in a yellow reaction solution which turned to a brownish tar-like compound upon removal of the solvent.

1.9. NMR measurements – elucidating the *cis*-DMTHF:*trans*-DMTHF ratio

According to the GC measurements there were a distinct difference in the formed amount of *cis*-DMTHF and *trans*-DMTHF products in most experiments. 1D and 2D ^{1}H NMR experiments were conducted on a sample containing a few drops of reaction mixture in $CDCl_3$. These data were compared with previous studies[ii] on the DMTHF isomers and showed that *cis*-DMTHF was favored over *trans*-DMTHF (Figures S6-S8).

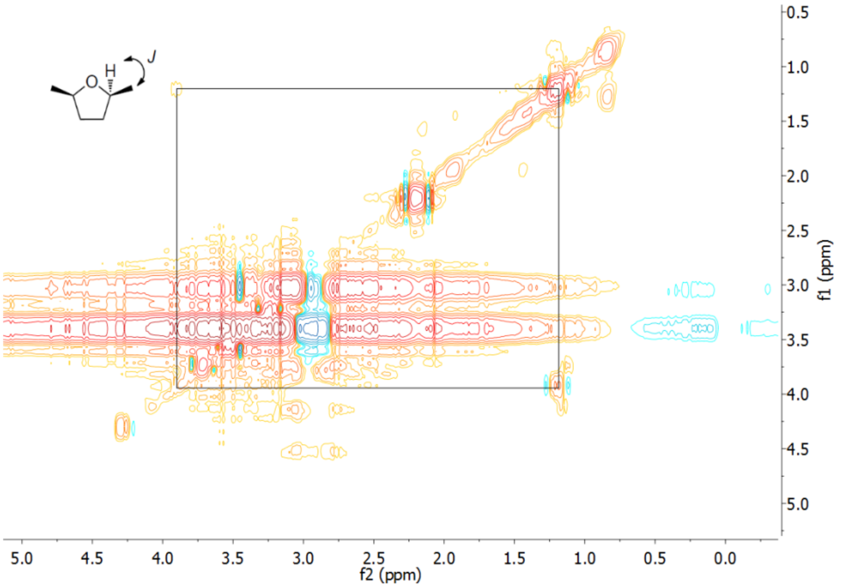


Figure S6. 2D COSY NMR of the product mixture.

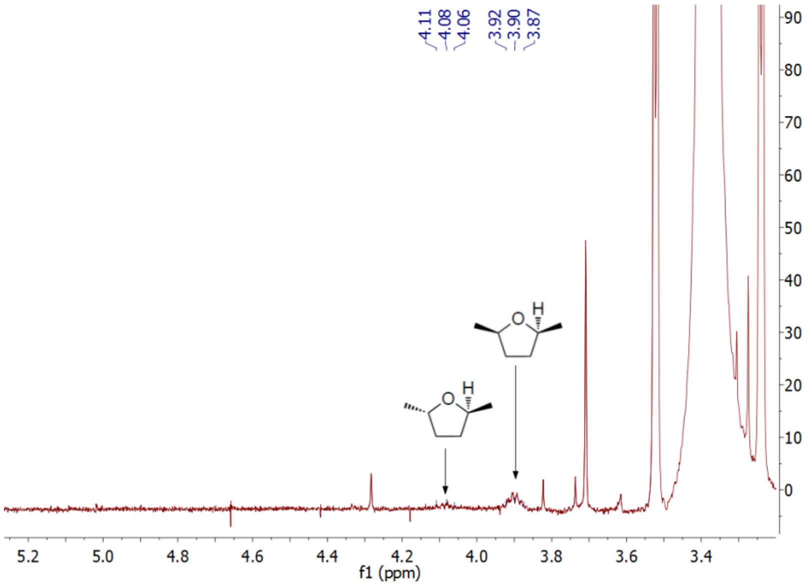


Figure S7. Down field ^{1}H NMR of the product mixture.

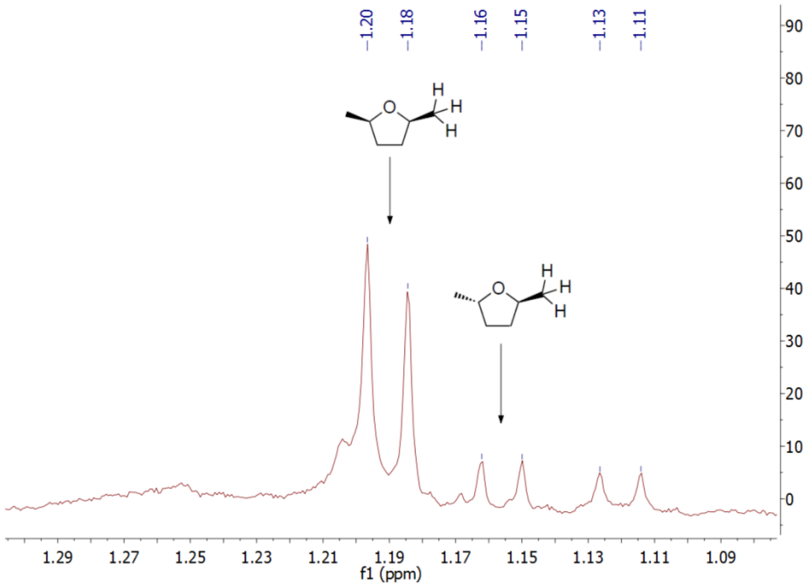


Figure S8. Up field ^{1}H NMR of the product mixture.

1.10. Pictures of reaction mixture

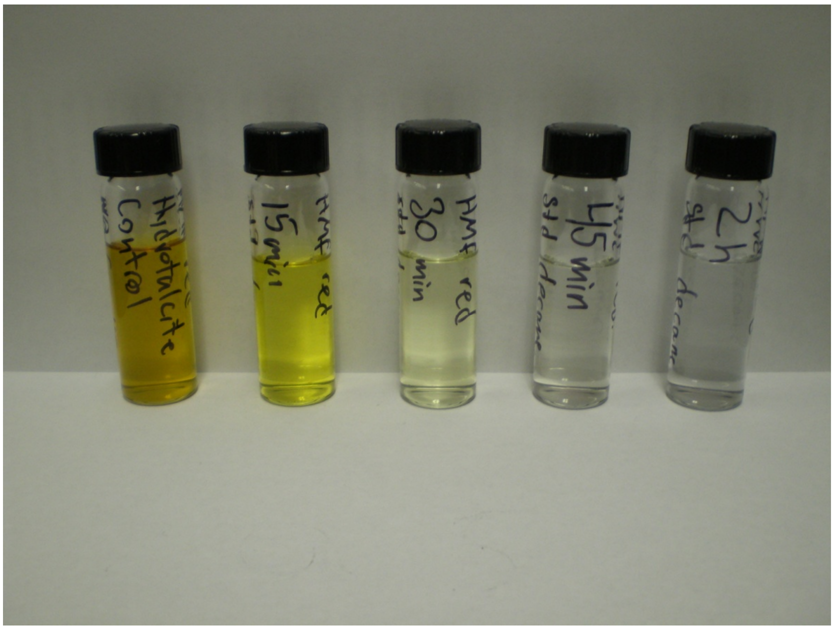


Figure S9. Picture of reaction mixtures: Control experiment with Mg:Al PMO (left). Reduction of HMF as function of time with the Cu-PMO at 300 °C after 15 min (2nd from left), 30 min (middle), 45 min (2nd from right) and 2 h (right).

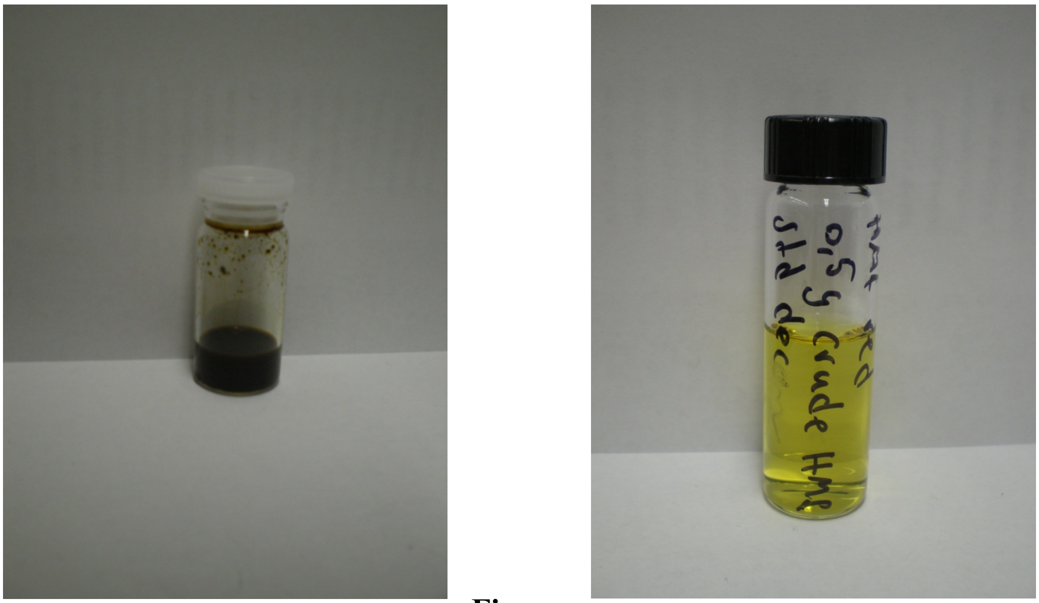


Figure S10. Pictures of crude HMF (0.5 g) in MeOH (3 mL) (left) and the reaction mixture after 5 h at 300 °C with the Cu-PMO (right).

1.11. 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 filtrate was 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 4 more times.

Table S5. Results of recycling experiments

	Total yield (DMF+DMTHF) (%)	**HMF conversion (%)**
cycle 1	51.5	100
cycle 2	36.8	100
cycle 3	32.8	100
cycle 4	31.7	91
cycle 5	25.5	85

*Note: total yield of DMF and DMTHF is given based on total area percentages of these peaks. GC conditions changed compared to the original experiments.

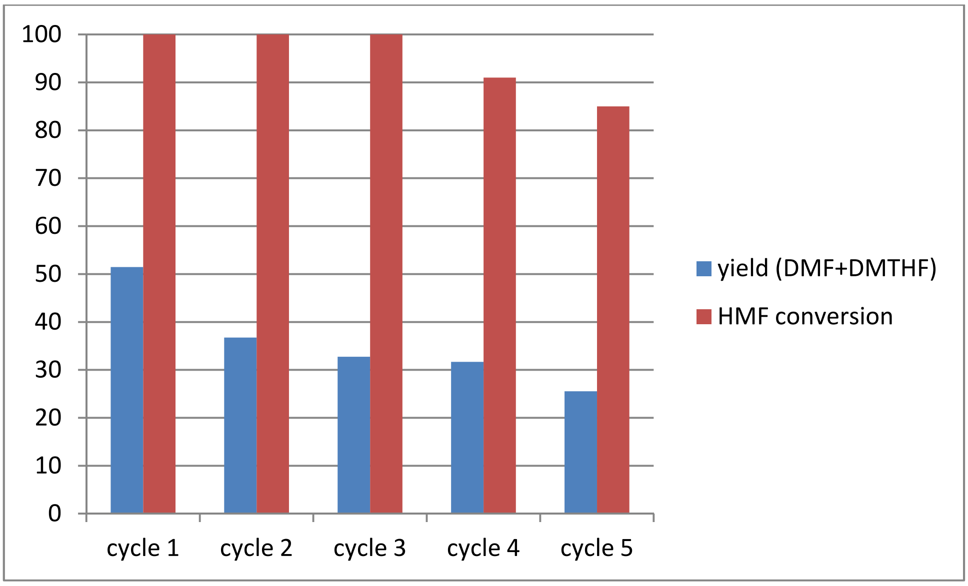


Figure S11: Recycling experiment at 300°C using 100 mg Cu-PMO and 100 mg HMF.

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[i] F. Cavani, F. Trifirò, A. Vaccari, *Cat. Today* **1991**, *11*, 173-301.

[ii] M. LJ. Mihailović, R. I. Mamuzić, LJ. Žigić-Mamuzić, J. Bošnjak, Ž. Čeković, *Tetrahedron* **1967**, *23*, 215-226