Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

For

Pd/C-Catalyzed Reactions of HMF: Decarbonylation, Hydrogenation, and Hydrogenolysis

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I. List of Abbreviations

5-MF	5-Methylfurfural
AcMF	5-[(Acetoxy)methyl]furfural
BFMF	2,5-Bis[(formyloxy)methyl]furan
BHMF	2,5-Bis(hydroxymethyl)furan
BHMTHF	2,5-Bis(hydroxymethyl)tetrahydrofuran
DMF	2,5-Dimethylfuran
DMDHF	2,5-Dimethyldihydrofuran
DMTHF	2,5-Dimethyltetrahydrofuran
DMDC	Dimethyl dicarbonate
FA	Formic acid
FFA	Furfuryl alcohol
FMF	5-[(Formyloxy)methyl]furfural
HMF	5-(Hydroxymethyl)fufural
MMF	Mesitylmethyl furfural

II. Representative Procedures

Commercially available starting materials were used for all the experiments, unless otherwise mentioned. Acetic anhydride, acetic acid (glacial), formic acid (97%, Acros), pyridine, 5 wt% Pd on Activated Carbon (Sigma-Aldrich Cat. No. 75992), 5-(hydroxymethyl)furfural (Sigma-Aldrich), dimethyl dicarbonate (Sigma-Aldrich) were used without further purification. AcMF, BFMF[1] and BHMF[2] were synthesized according to the literature reported procedure. ^{1}H NMR spectra were acquired on Varian Unity 500 or Varian VXR 500. NMR spectra of the synthesized compounds were compared to those of authentic samples.

Decarbonylation of HMF to FFA

A flask was charged with HMF (1.0 mmol, 0.13 g), 5 wt % Pd/C (0.1 g), and dioxane (5 mL). The suspension was stirred under reflux in air for 15 h. After cooled to room temperature, a known amount of $MeNO_2$ was added as internal standard. An aliquot was taken and analyzed by ^{1}H NMR. FFA: ^{1}H NMR (acetone-d_6) δ 7.47 (s, 1H, furanic H), 6.34 (d, 1H, furanic H), 6.25 (d, $^3J_{HH}$ = 2.96, 1H, furanic H), 4.50 (d, $^3J_{HH}$ = 5.77, 2H, -CH_2-), 4.15 (t, $^3J_{HH}$ = 5.77, 1H, -OH).

Decarbonylation of mesitylmethylfurfural to mesitylmethylfuran.

Similar procedure was applied to the conversion of mesitylmethylfurfural to mesitylmethylfuran. MMF (0.23 g, 1.0 mmol), 5 wt% Pd/C (0.1 g), dioxane (5 mL).

Mesitylmethylfuran: ^{1}H NMR (acetone-d_6) δ 7.38 (d, 1H, furanic H), 6.84 (s, 2H, Ar-H), 6.26 (m, 1H, furanic H), 5.79 (d, 1H, furanic H), 3.94 (s, -CH_2-), 2.27 (s, 6H, -CH_3), 2.22 (s, 3H, -CH_3).

Hydrogenolysis of HMF with Formic acid to DMF. A pressure reactor was charged with HMF (63 mg, 0.5 mmol), 5 wt% Pd/C (0.1 g), dioxane (5 mL), and formic acid (0.19 mL, 10 equiv.). The mixture was stirred at 120 ºC (oil bath temperature) for 15 h and cooled to room temperature. ^{1}H NMR experiments indicated quantitative conversion to DMF. A known amount of $MeNO_2$ was added to the reaction mixture as internal standard. DMF: ^{1}H NMR (DMSO-d_6) δ 5.89 (s, 2H, furanic H), 2.19 (s, 6H, -CH_3).

Hydrogenolysis/Hydrogenation of HMF with hydrogen. In a typical experiment, a 150 mL Fisher-Porter reactor was charged with HMF (63 mg, 0.50 mmol), 5 wt% Pd/C (0.1 g), and dioxane (5 mL). The reactor was pressurized with 30 psi H_2 and the closed system was stirred at 120 ºC (oil bath temperature). After 15 h, the mixture was cooled to room temperature. A known amount of $MeNO_2$ was added as internal standard and the conversion and selectivity of the product mixture were analyzed by ^1H NMR. Each component in the product mixture was matched with the 1H NMR spectra of pure samples to establish their identity.

Hydrogenolysis/Hydrogenation of HMF with hydrogen in presence of CO_2/H_2O as additive. In a typical experiment, a 150 mL Fisher-Porter reactor was charged with 5 wt% Pd/C (0.1 g), HMF (63 mg, 0.50 mmol) dissolved in dioxane:H_2O mixture (9:1 v/v, total vol: 5 mL). The reactor was pressurized with 30 psi CO_2 and 30 psi H_2 simultaneously. The closed system was stirred at 120 ºC (oil bath temperature). After 15 h, the mixture was cooled to room temperature. A known amount of $MeNO_2$ was added as internal standard and the conversion and selectivity of the product mixture were analyzed by ^1H NMR. Each component in the product mixture was matched with the 1H NMR spectra of pure samples to establish their identity.

Monitoring Hydrogenolysis of HMF over time. In a typical experiment, a pressure reactor was charged with HMF (63 mg, 0.5 mmol), 5 wt% Pd/C (0.1 g), dioxane (5 mL), and formic acid (0.19 mL, 10 equiv). The mixture was stirred at 120 ºC (oil bath temperature). The course of the reaction was monitored by ^1H NMR experiments at different time intervals by removing aliquots from the reaction mixture.

Hydrogenolysis of FMF, BHMF and BFMF in presence of FA was similarly monitored.

Monitoring Hydrogenolysis/Hydrogenation of HMF with H_2 over time. In a typical experiment, a 150 mL Fisher-Porter reactor was charged with HMF (63 mg, 0.5 mmol), 5 wt% Pd/C (0.1 g), and dioxane (5 mL). The reactor was pressurized with 30 psi H_2 and the closed system was stirred at 120 ºC (oil bath temperature). The course of the reaction was monitored by ^1H NMR experiments at different time intervals by removing aliquots from the reaction mixture.

Monitoring Hydrogenolysis / Hydrogenation of HMF with H_2 over time in presence of Acetic acid. In a typical experiment, a 150 mL Fisher-Porter reactor was charged with 0.1 g of 5 wt % Pd/C (10 mol %), HMF (63 mg, 0.50 mmol) dissolved in dioxane (5 mL) and 0.28 mL acetic acid (10 equiv). The reactor was pressurized with 30 psi H_2 and the closed system was stirred at 120 ºC (oil bath temperature). The course of the reaction was monitored by ^1H NMR experiments at different time intervals by removing aliquots from the reaction mixture.

III. Effect of Additives on Hydrogenation / Hydrogenolysis of HMF

Table S1. Effect of HMF concentration on Hydrogenation / Hydrogenolysis under H_2 [a]

Entry	HMF Conc. (mmol)	Additive	Yield (%)[c]				
			BHMF	DMF	BHMTHF	DMDHF	DMTHF
1	2	none	0	26	7	23	43
2[b]	2	CH_3CO_2H (20 mmol)	9	85	0	0	0
3	2	30 psi CO_2, 0.5 mL H_2O	0	62	0	32	5
4	0.5	none	0	0	24	11	64
5	0.5	CH_3CO_2H (20 mmol)	0	42	0	10	42
6	0.5	30 psi CO_2, 0.5 mL H_2O	0	38	0	50	13

[a] Reaction conditions: HMF (2 mmol or 0.5 mmol), H_2 (30 psi), dioxane (5 mL), the mixture was heated in a 120 ºC, 15 h. [b] ~ 5 % unconverted HMF. [c] Yields determined by ^1H NMR.

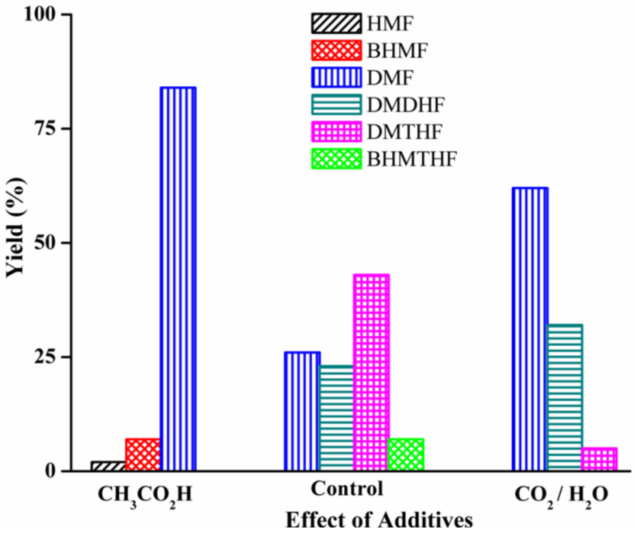

Figure S1. Effect of additives on hydrogenolysis / hydrogenation of HMF with H_2 (30 psi). Reaction conditions: HMF (2mmol) in 5 mL dioxane pressurized with 30 psi H_2 in presence of 10 mol % Pd/C in a Fischer-Porter reactor heated at 120 ºC on a oil bath. *Control:* Hydrogenation of HMF under H_2 (30 psi) pressure in absence of additives.

IV. Effect of catalyst loading

Table S2: Effect of Catalyst Loading on Hydrogenation / Hydrogenolysis of HMF under H_2 [a]

Entry	Catalyst Loading	Additive	Yield (%)[b]				
			BHMF	DMF	BHMTHF	DMDHF	DMTHF
1	10%	none	0	26	7	23	43
2	5%	none	0	39	0	25	35

[a] Reaction conditions: A mixture of 0.26 g HMF (2 mmol) dissolved in 5 mL dioxane and 0.4 g or 0.2 g of 5 wt % Pd/C (10 mol % and 5 mol % catalyst loading respectively), pressurized with 30 psi H_2, the mixture was heated in a 120 ºC, 15 h. [b] Yields determined by ^1H NMR.

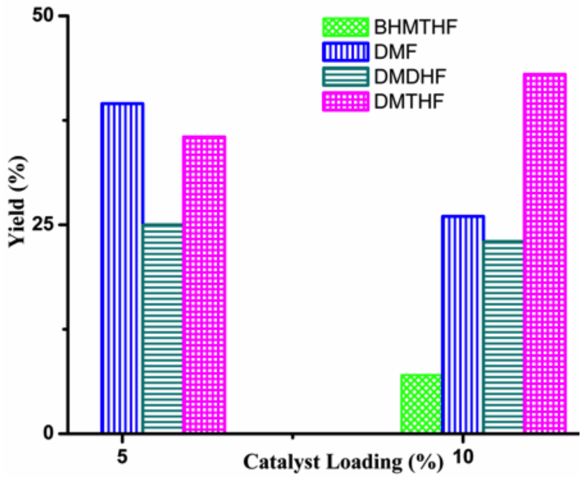

Figure S2. Effect of catalyst loading on hydrogenation and hydrogenolysis of HMF. Reaction conditions: 0.26g HMF (2 mmol) in 5 mL dioxane pressurized with 30 psi H_2 in presence of 0.4 g of 5 wt % Pd/C (10 mol %) in a 150 mL Fischer-Porter reactor heated at 120 ºC on a oil bath.

References:

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2 D. Scholz, C. Aellig, I. Hermans, *ChemSusChem*, 2014, **7**, 268-275.