Electronic supplementary information (ESI)

Pd-catalyzed *in-situ* domino process for mild and quantitative production of 2,5-dimethylfuran directly from carbohydrates

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1. Experimental Section

Materials: $Pd(NO_3)_2$ (≥99.9%), H_2PtCl_4 (≥99.9%), $RuCl_3$ (99%), $Ni(NO_3)_2$ (98%), $Co(NO_3)_2$ (99%), activated charcoal (≥99.9%), zirconium dioxide (ZrO_2, ≥99.99%), aluminum oxide (Al_2O_3; 99.9%), poly(methylhydrosiloxane) (PMHS), fructose (99%), glucose (≥99.5%), 5-methylfurfural (MFF, 98%), 5-hydroxymethylfurfural (HMF, >99%), sucrose (≥99.0%), cellobiose (98%), inulin (≥99.0%), 2-butanol (≥99.0%), dimethyl sulfoxide (>99.8%), dimethyl formamide (99.8%), and 2-propanol (99.5%) were purchased from Aladdin Industrial Inc. (Shanghai). Trimethyl chlorosilane (TMS, ≥98%) and 5-methyfurfuryl alcohol (MFA, 99.9%) were bought from Acros Organics Inc. (USA). 2,5-Dihydroxymethylfuran (DHMF, 98%) was purchased from Adamas Reagent, Ltd. (Shanghai). 5 wt% Pd/C (Type 87L, dry), methanol-d_1 (CH_3OD, 99.8 atom%D), DMSO-d_6 (99.8 atom%D), methanol-d_4 (CD_3OD, 99.8 atom% D) and chloroform-d_3 (99.6 atom% D) were purchased from Alfa Aesar Inc. Chlorosulfonic acid (97%), 2,5-dimethyltetrahydrofuran (DTHF, >98.0%) and butyl levulinate (BL, >98.0%) were bought from TCI Inc. (Shanghai). Diphenyl (silane-d_2) (97 atom % D) was purchased from Sigma-Aldrich Co. LLC. TiO_2 (99%) and 2,5-hexanedione (HD, >97%) were bought from Innochem Inc. (Beijing). 2,5-Dimethylfuran (DMF, >98%), *n*-butanol (AR), ethanol (AR), methanol (AR), *n*-propanol (AR), cyclohexanol (AR), dichloromethane (AR), cyclohexane (AR) and *n*-hexane (AR) were bought from J&K Scientific Ltd. (Beijing).

Preparation of catalysts

(1) Hydrophobic Pd/C-TMS

Pd/C-TMS was prepared by referring to a reported method with slight modifications.[S1] To a 50 mL round-bottom flask, 0.5 g of commercial Pd/C and 15 mL cyclohexane were added. Then, 3 mL trimethyl chlorosilane (TMS) was dropwise added into the above mixture, and stirred at 60 °C for 12 h. Upon completion, the suspension was filtered, washed with *n*-hexane for three times, and dried at 90 °C under N_2 overnight to give the desired catalyst.

(2) Acidic Pd/C-SO_3H

To a 50 mL round-bottom flask containing 0.5 g commercial Pd/C and 15 mL dichloromethane, 0.05-0.35 mL chlorosulfonic acid dissolved in 5 mL dichloromethane was dropwise added. After stirring for 12 h at ambient temperature, the solid was filtered, washed with dichloromethane and water for 4-7 times until neutral filtrate, and dried at 90 °C under N_2 for 6 h. ICP-OES and elemental analyses were conducted to examine the exact Pd/S molar ratios the obtained acidic Pd/C-SO_3H catalysts.

(3) Hydrophobic/acidic Pd/C-SO_3H-TMS

0.25 g Pd/C-SO_3H was pre-dispersed into 7.5 mL cyclohexane in a 50 mL round-bottom flask. Afterwards, 1.5 mL trimethyl chlorosilane (TMS) was dropwise added into the above solution, and kept stirring at 60 °C for 12 h. The black solid was filtered out, washed with *n*-hexane for three times, and dried at 90 °C under N_2 for 6 h.

(4) Other metal catalysts

5 wt% Pd/N (N = Al_2O_3, ZrO_2 and TiO_2), 5 wt% M/C (M = Pt and Ru), 5 wt% Pd-Ni(4:1)/C and 5 wt% Pd-Co(4:1)/C were prepared by incipient wetness impregnation.[S2,S3] In a typical procedure, 32 mg $Pd(NO_3)_2$ was firstly dissolved in 1.2 mL water. To the resulting mixture, 0.25 g of solid support was added, and kept stirring at ambient temperature for 24 h. Upon completion, the obtained suspension was dried at 80 °C overnight, calcined at 450 °C (heating ramp: 10 °C/min) in air for 4 h, and reduced in hydrogen with a flowing rate of 20 cm^3/min at 400 °C (heating ramp: 10 °C/min) for 2 h.

For comparison, Ru-Sn/ZnO was prepared via a previously reported procedure.[S4]

Catalysts Characterization

Scanning transmission electron microscope and high-angle annular dark-field (STEM-HAADF) imaging was acquired with an aberration corrected FEI TECNAI G2 F30 S-TWIN (S)TEM (Hillsboro, OR) operating at 300 kV, along with the capability of taking energy dispersive X-ray (EDX) spectra.The contents of metals were determined by ICP-OES (inductively coupled plasma-optical emission spectrometer) on an Optima 5300 DV instrument (PerkinElmer Inc., Waltham, MA), while sulfur and silicon contents were measured by Elemental analyses (Vario EL III, Elementar). FT-IR spectra were recorded on a Perkin-Elmer 1710 spectrometer at ambient conditions in KBr disks. XRD (X-ray diffraction) patterns were recorded with D/max-TTR III X-ray powder diffractometer (Rigaku International Corp., Tokyo) using Cu Kα radiation source. BET (Brunauer−Emmett−Teller) surface areas of the porous materials were determined from nitrogen physisorption measurements at liquid nitrogen temperature on a Micromeritics ASAP 2010 instrument (Tristar II 3020, Norcross, GA). XPS (X-ray photoelectron spectroscopy) measurements were recorded using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe (Physical Electronics Inc., PHI, MN) equipped with a monochromatic AlKa anode. The contact angle of a water droplet was measured using a SORPTION ANALYZER of MB-300G at 25 °C.

Reaction procedures

The reactions with different substrates were carried out in a 15 mL Ace tube. In a typical procedure, 5 wt% fructose (0.3 mmol), 2 mol% metal in the catalyst (with 10 mol% H^+), 1.5 mL *n*-butanol and 2.5 mmol PMHS (9 equiv. H^-) were added into the tube, which was magnetically stirred at 500 rpm for a specific reaction time. The time zero was defined as the tube was placed into an oil bath that was preheated to 60, 80,100 and 120 ºC. After the reaction, liquid products were quantitatively analyzed by HPLC, ^1H NMR and GC. The water content was measured by a KarlFischer titrator (Mettler Toledo V20).

To separate and purify the target product DMF from the reaction mixture, an attempt was made by adopting a simple distillation process under reduced pressure with a water pump at 55-75 ºC. The collected distillate was found to be DMF in purity of 87-95%, and >90% of DMF was distilled from the mixture.

Analysis of products

Liquid products and major by-products were identified with GC-MS (Agilent 6890N GC/5973 MS, Santa Clara, CA). The concentrations of sugars, furanic compounds and organic acid esters were determined by HPLC (LC-20A, Shimadzu, Kyoto) fitted with an Aminex HPX-87H column (Bio-Rad, Richmond, CA) and a refractive index (RI) detector as well as an ultraviolet (UV) detector at 280 nm. The reaction mixtures were also quantitatively analyzed with ^{1}H NMR (JEOL-ECX 500 NMR), and cross-checked on GC (Agilent 7890B) with a HP-5 column (30 m × 0.320 mm × 0.25 μm) and a flame ionization detector using naphthalene as internal standard and referring to the standard curves (with $R^2 \geq 0.995$) made from commercial samples.

Catalyst recycling

After each cycle of reactions, the remaining catalyst in the mixture was recovered by centrifugation, and successively washed with ethanol and *n*-hexane for 4 times, dried at 90 ºC in N_2 for 6 h, and directly used for the next run.

Isotopic labeling experiments

For isotopic kinetic study, ^{1}H NMR spectra of the reaction mixture were performed in the deuterium solvent methanol-d_1, methanol-d_4, or chloroform-d_3 on a JEOL-ECX 500 NMR spectrometer at room temperature spectrometer operating at 500 MHz.

2. Results and Discussion

Table S1. Direct conversion of fructose to DMF with different Pd-containing catalysts [a]

Entry	Catalyst	Fructose conv. (%)	Product yield (%)					
			HMF	MFF	MFA	HD	DTHF	DMF
1	Pd-Co/C	73	1	<1	4	3	8	51
2	Pd-Ni/C	75	1	<1	5	2	9	53
3	Pd/Al_2O_3	82	2	<1	2	<1	4	60
4	Pd/ZrO_2	68	3	3	1	<1	3	46
5	Pd/TiO_2	71	4	4	3	<1	4	48

[a] Reaction conditions: 5 wt% fructose, 2 mol% metal, 2.5 mmol PMHS (9 equiv. H^-), 1.5 mL *n*-butanol, 3 μL PhCl (10 mol%), 120 ºC and 1.5 h.

HMF: 5-hydroxymethylfurfural; MFF: 5-methylfurfural; MFA: 5-methylfurfuryl alcohol; HD: 2,5-hexanedione; DTHF: 2,5-dimethyltetrahydrofuran; DMF: 2,5-dimethylfuran.

Table S2. Direct conversion of fructose to DMF by varying reaction temperature

Entry	Temp. (ºC)	Time (h)	Fructose conv. (%)	Product yield (%)					
				HMF	MFF	MFA	HD	DTHF	DMF
1	120	1.5	97	2	<1	<1	<1	1	91
2	100	2	95	1	<1	<1	1	2	85
4	80	3	74	2	1	1	1	1	62
5	80	8	96	<1	<1	<1	2	3	84

[a] Reaction conditions: 5 wt% fructose, 2 mol% Pd/C-TMS, 2.5 mmol PMHS (9 equiv. H^-), 1.5 mL *n*-butanol, and 3 μL PhCl (10 mol%).

HMF: 5-hydroxymethylfurfural; MFF: 5-methylfurfural; MFA: 5-methylfurfuryl alcohol; HD: 2,5-hexanedione; DTHF: 2,5-dimethyltetrahydrofuran; DMF: 2,5-dimethylfuran.

Table S3. Direct conversion of fructose to DMF in different solvents over Pd/C-TMS [a]

Entry	Solvent	Fructose conv. (%)	Product yield (%)					
			HMF	MFF	MFA	HD	DTHF	DMF
1	Methanol	83	<1	1	0	2	3	64
2	Ethanol	89	<1	2	3	3	2	72
3	*n*-Propanol	92	1	<1	2	<1	1	78
4	2-Propanol	87	1	2	3	1	2	73
5	*n*-Butanol	97	2	<1	<1	<1	1	91
6	2-Butanol	85	1	1	3	<1	1	70
7	*n*-Hexanol	94	<1	1	<1	<1	<1	82
8	Dichloromethane	35	9	0	<1	0	0	10
9	Dimethylsulfoxide	52	35	0	0	0	0	0
10	Dimethylformamide	46	27	0	0	0	0	0

[a] Reaction conditions: 5 wt% fructose, 2 mol% metal, 2.5 mmol PMHS (9 equiv. H^-), 1.5 mL solvent, 3 μL PhCl (10 mol%), 120 ºC and 1.5 h.

HMF: 5-hydroxymethylfurfural; MFF: 5-methylfurfural; MFA: 5-methylfurfuryl alcohol; HD: 2,5-hexanedione; DTHF: 2,5-dimethyltetrahydrofuran; DMF: 2,5-dimethylfuran.

Table S4. Kinetic study for producing DMF from HMF in normal and deuterium methanol

Substrate	Solvent	Temp. (ºC)	Reaction constant (*k*; s^{-1})
HMF	Normal methanol (CH_3OH)	60	0.025
HMF	Deuterium methanol (CH_3OD & CD_3OD)	60	0.009

Reaction conditions: 5 wt% substrate, 2 mol% Pd/C-TMS, 2.5 mmol PMHS (9 equiv. H^-), 3 μL PhCl (10 mol%) and 1.5 mL solvent.

Table S5. Kinetic study for producing DMF from fructose and HMF

Substrate	Temp. (ºC)	Reaction constant (*k*; s^{-1})	Activation Energy (Ea; kJ mol^{-1})
Fructose	60	0.008	33.4
	80	0.025	
	100	0.039	
	120	0.052	
HMF	60	0.028	27.3
	80	0.065	
	100	0.099	
	120	0.127	

Reaction conditions: 5 wt% substrate, 2 mol% Pd/C-TMS, 2.5 mmol PMHS (9 equiv. H^-), 1.5 mL *n*-butanol, and 3 μL PhCl (10 mol%).

Table S6. Direct conversion of fructose to DMF with different acids over Pd/C-TMS [a]

Entry	Acidic additive	Fructose conv. (%)	Product yield (%)					
			HMF	MFF	MFA	HD	DTHF	DMF
1	H-beta(19)	84	2	1	2	<1	3	59
2	Amberlyst-15	98	1	1	0	2	4	79
3	Dowex 50WX8-100	96	2	0	1	2	4	77
4	Nafion NR50	>99	<1	<1	2	2	6	77

[a] Reaction conditions: 5 wt% fructose, 2 mol% Pd/C-TMS, 2.5 mmol PMHS (9 equiv. H^-), 1.5 mL *n*-butanol, 10 mol% acidic additive, 120 ºC and 2 h.

HMF: 5-hydroxymethylfurfural; MFF: 5-methylfurfural; MFA: 5-methylfurfuryl alcohol; HD: 2,5-hexanedione; DTHF: 2,5-dimethyltetrahydrofuran; DMF: 2,5-dimethylfuran.

Table S7. Surface area, volume and porosity of different catalysts

Sample	S_{BET} (m^2/g)[a]	S_{micro} (m^2/g)[b]	S_{meso} (m^2/g)[c]	V_{pore} (cm^3/g)[d]	$D_{average}$ (nm)[e]
Pd/C	807	130	677	0.94	4.7
Pd/C-TMS	510	168	342	0.64	5.0
Pd/C-SO_3H	571	135	437	0.71	4.9
Pd/C-SO_3H-TMS	452	159	293	0.61	5.4

[a] BET surface area was obtained from N_2 adsorption isotherm. [b] Surface area of micropore was gained from the t-plot method. [c] Surface area of mesopore = (S_{BET} − S_{micro}). [d] Volume of pores was estimated from BJH adsorption cumulative volume of pores. [e] Average pore size was estimated from the adsorption average pore diameter by BET.

N_2 adsorption-desorption shows that the modified Pd/C catalysts possess an enhanced average pore diameter (4.9-5.4 nm) with a decrease in surface area and pore volume, as compared with pristine Pd/C (Table S1, Figures S4 & S5). Wide bands in XRD patterns of Pd-containing catalysts demonstrate their amorphous structure (Figure S6), while the absence of characteristic peaks of Pd species in both XRD patterns (Figure S6) and FT-IR spectra (Figure S7) indicates the good dispersion of Pd on the catalyst surface,[S5] which is consistent with elemental mappings (Figure S1).

Table S8. Direct conversion of fructose to DMF by varying reaction time

Entry	Acidic additive	Catalyst	Time (min)	Fructose conv. (%)	Product yield (%)					
					HMF	MFF	MFA	HD	DTHF	DMF
1	PhCl	Pd/C-TMS	10	56	2	2	3	0	0	44
2	PhCl	Pd/C-TMS	25	82	4	5	4	0	<1	61
3	PhCl	Pd/C-TMS	45	91	3	3	1	<1	<1	76
4	PhCl	Pd/C-TMS	90	97	2	<1	<1	<1	1	91
5	PhCl	Pd/C-TMS	120	>99	<1	<1	<1	1	4	86
6	--	Pd/C-SO_3H-TMS	15	48	4	2	2	<1	0	29
7	--	Pd/C-SO_3H-TMS	30	63	5	1	3	1	0	43
8	--	Pd/C-SO_3H-TMS	60	80	2	1	<1	1	1	62
9	--	Pd/C-SO_3H-TMS	120	96	<1	1	<1	2	2	88
10	--	Pd/C-SO_3H-TMS	150	>99	<1	<1	<1	3	6	83

[a] Reaction conditions: 5 wt% fructose, 2 mol% catalyst, 2.5 mmol PMHS (9 equiv. H^-), 1.5 mL *n*-butanol, 10 mol% acidic additive, and 120 ºC.

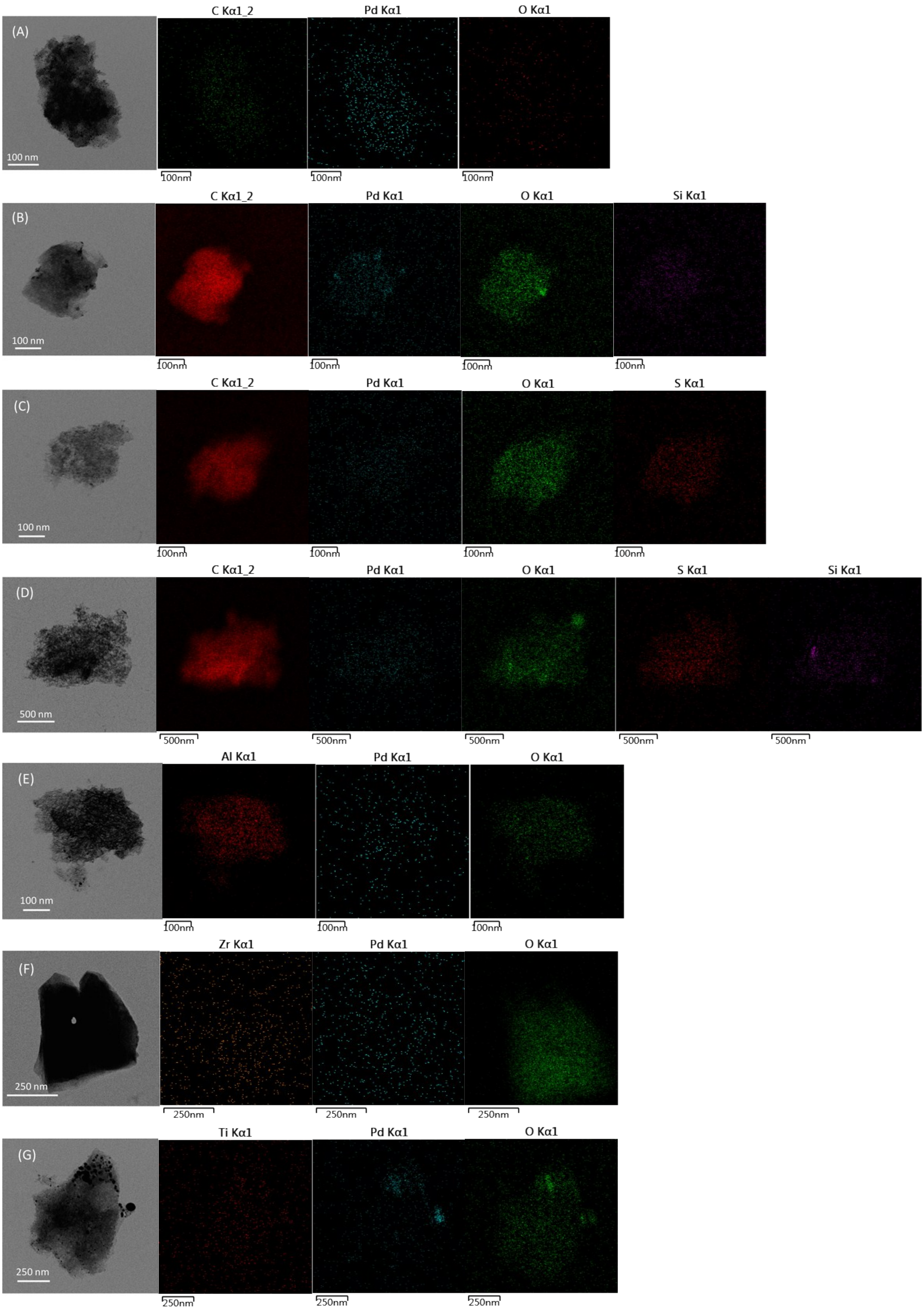
HMF: 5-hydroxymethylfurfural; MFF: 5-methylfurfural; MFA: 5-methylfurfuryl alcohol; HD: 2,5-hexanedione; DTHF: 2,5-dimethyltetrahydrofuran; DMF: 2,5-dimethylfuran.

Assumed that fructose-to-DMF conversion is a 1st order process, the reaction rate could be expressed as follows: $d[\mathrm{DMF}]/dt = k[\mathrm{fructose}] = d[\mathrm{fructose}]/dt$; after the subsequent integral calculation, the original equation would further become: $-\ln(1 - X) = kt + C$. Values of $-\ln(1 - X)$ (where X is conversion of fructose) were plotted against reaction time (t) at different temperatures in order to obtain rate constants (k): k(Pd/C-TMS) = 0.052 s^{-1} > k(Pd/C-SO_3H-TMS) = 0.021 s^{-1}.

Table S9. Effect of PMHS amount and Pd/C-SO_3H-TMS dosage on fructose-to-DMF conversion [a]

Entry	Catalyst dosage (mol %)	PMHS amount (mmol)	Time (h)	Fructose conv. (%)	DMF yield (%)	DMF selec. (%)
1	4	2.5 (9 equiv.)	2	98	83	85
2	2	2.5 (9 equiv.)	2	96	88	92
3	1.2	2.5 (9 equiv.)	3	97	90	93
4	0.8	2.5 (9 equiv.)	3.5	95	93	98
5	0.4	2.5 (9 equiv.)	5.5	99	91	92
6	2	1.5 (5 equiv.)	2.5	94	72	77
7	2	3.5 (12 equiv.)	1.5	98	89	91
8	2	6.0 (21 equiv.)	1.5	100	86	86

[a] Reaction conditions: 5 wt% fructose, 1.5 mL *n*-butanol, and 120 ºC.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Pd Kα1
O Kα1
100nm
(B)
100 nm
C Kα1_2
Pd Kα1
O Kα1
Si Kα1
100nm
(C)
100 nm
C Kα1_2
Pd Kα1
O Kα1
S Kα1
100nm
(D)
500 nm
C Kα1_2
Pd Kα1
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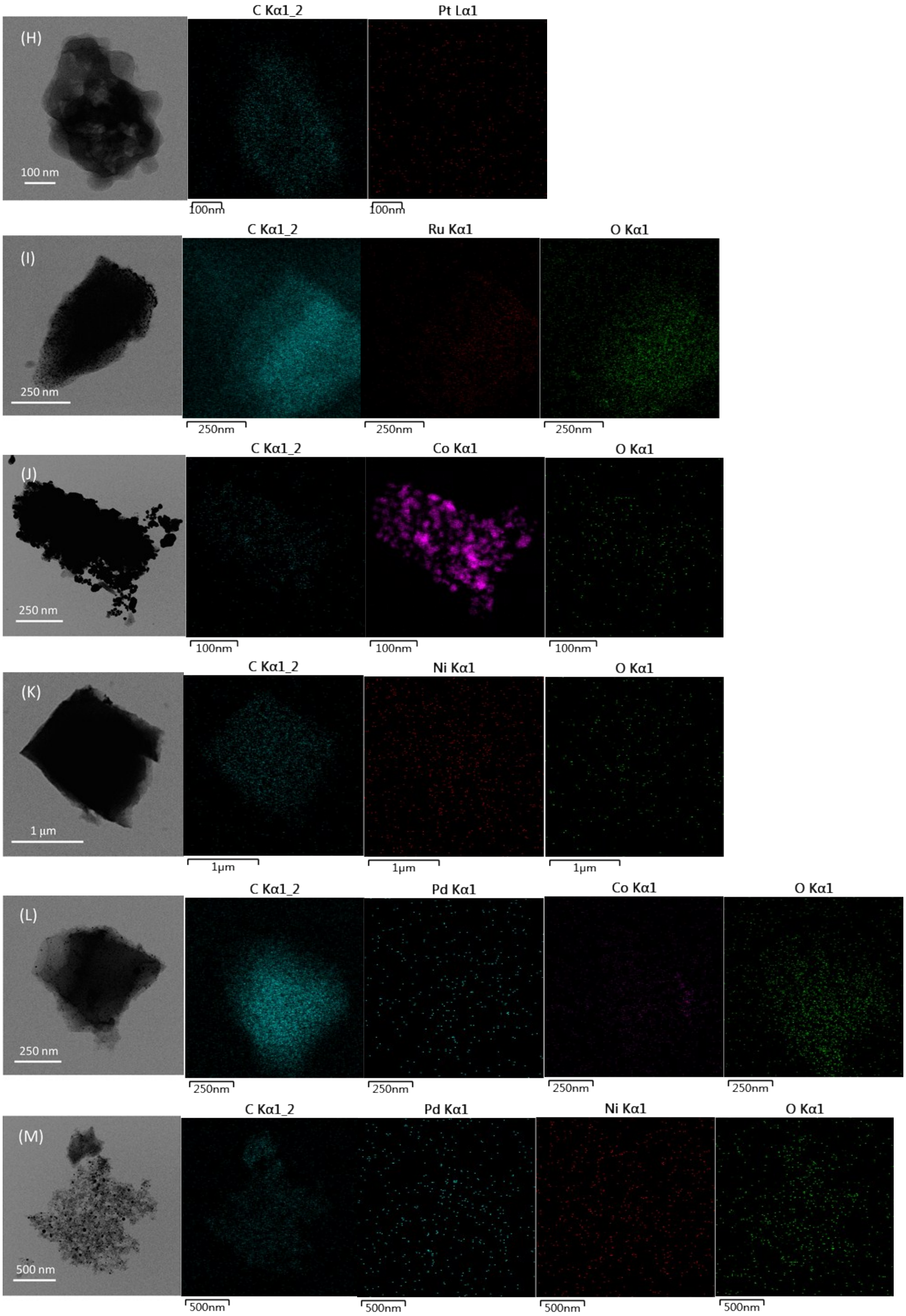
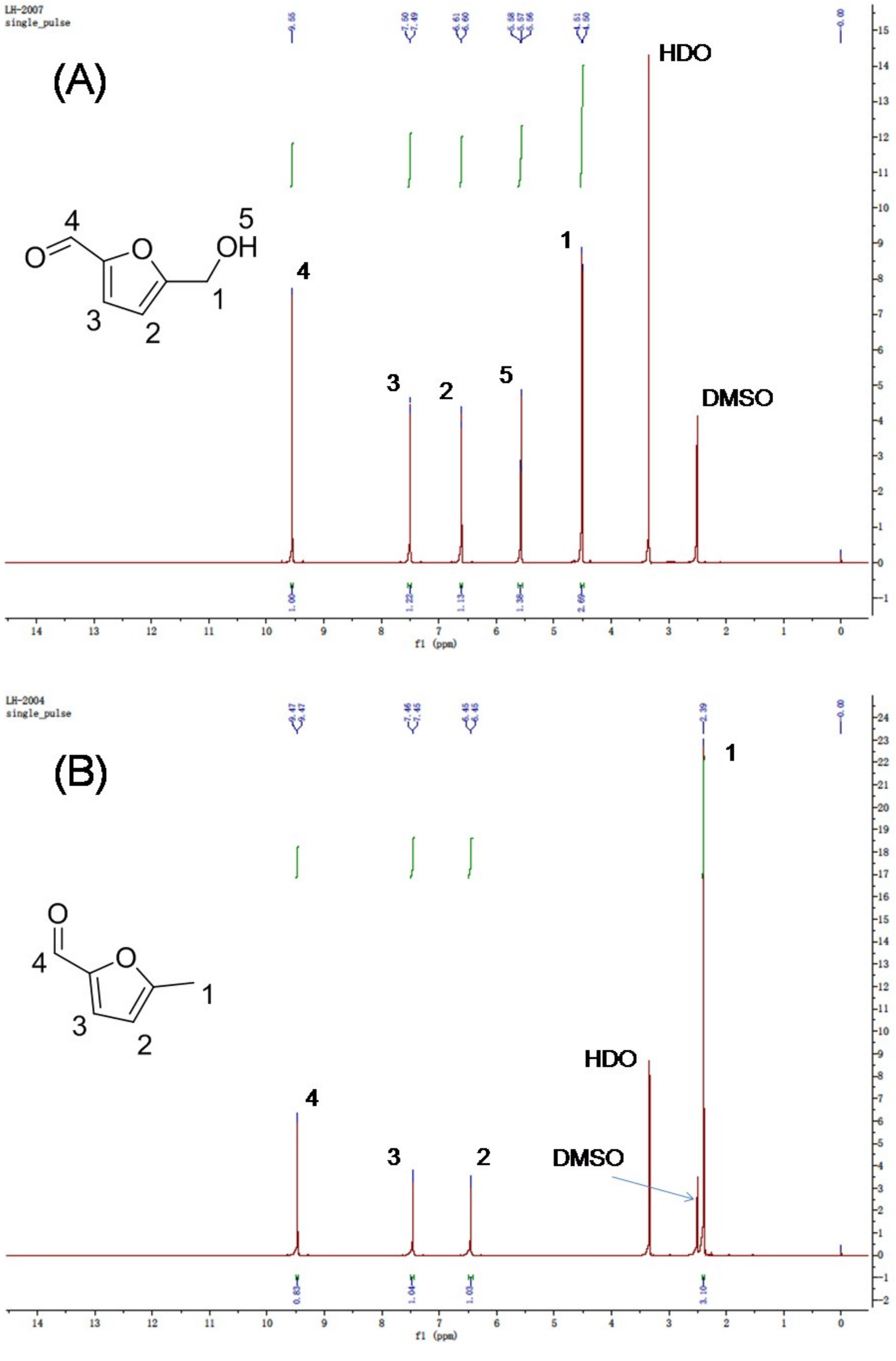


Figure S1. STEM-HAABF images and elemental mappings for Pd/C (A), Pd/C-TMS (B), Pd/C-SO_3H (C), Pd/C-SO_3H-TMS (D), Pd/Al_2O_3 (E), Pd/ZrO_2 (F), Pd/TiO_2 (G), Pt/C (H), Ru/C (I), Co/C (J), Ni/C (K), Pd-Co/C (L), and Pd-Ni/C (M)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7.49
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3
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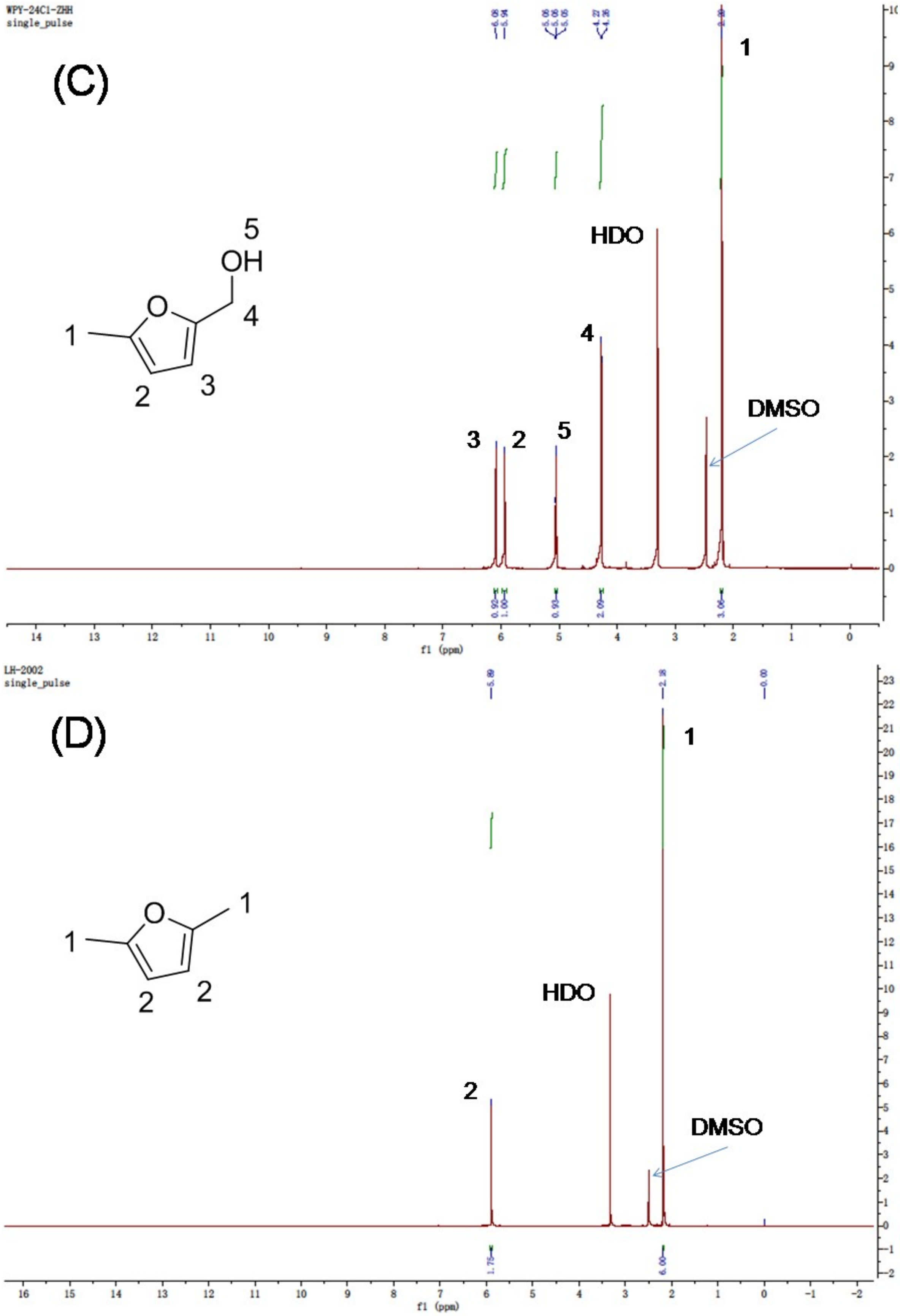


Figure S2. ^{1}H NMR spectra of isolated products in DMSO-d_6: 5-hydroxymethylfurfural (A), 5-methylfurfural (B), 5-methylfurfuryl alcohol (C), and 2,5-dimethylfuran (D)

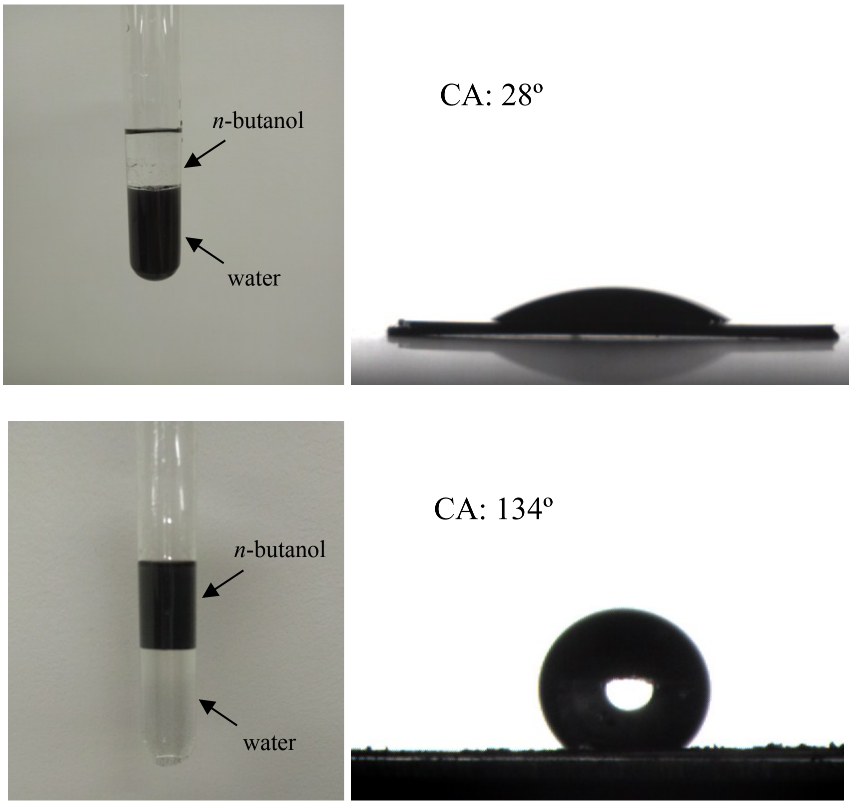


Figure S3. Dispersion of Pd/C (up) and Pd/C-TMS (down) in water and *n*-butanol and their water contact angle (CA)

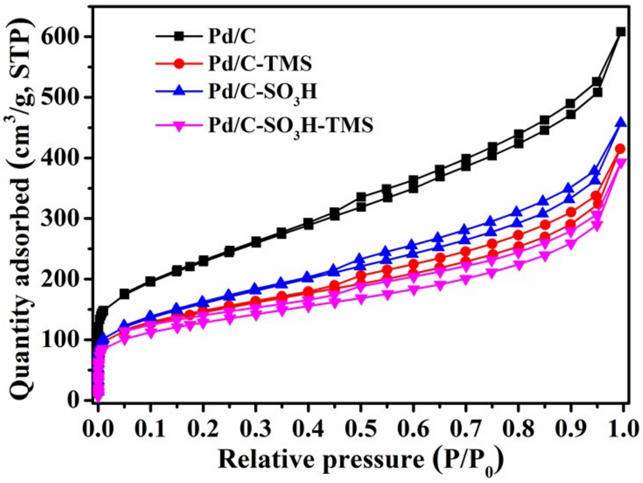


Figure S4. N_2 adsorption-desorption isotherms of Pd-containing catalysts

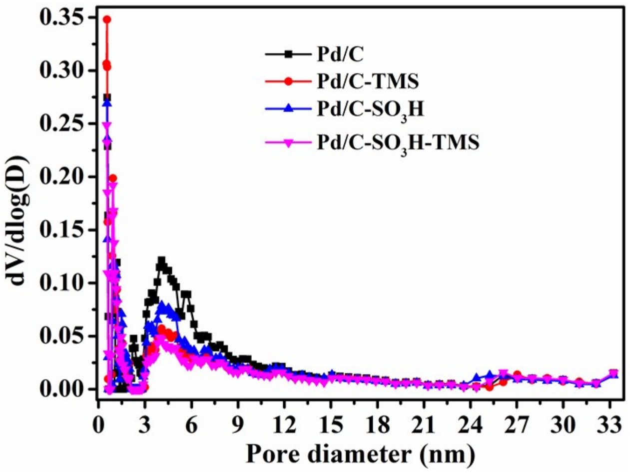


Figure S5. Pore size distribution of different Pd-containing catalysts

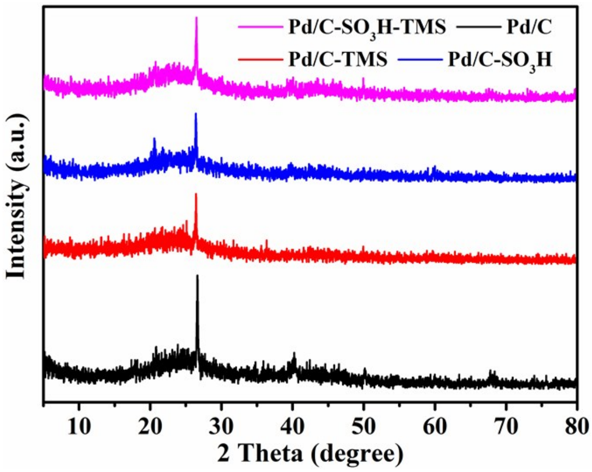


Figure S6. XRD patterns of different Pd-containing catalysts

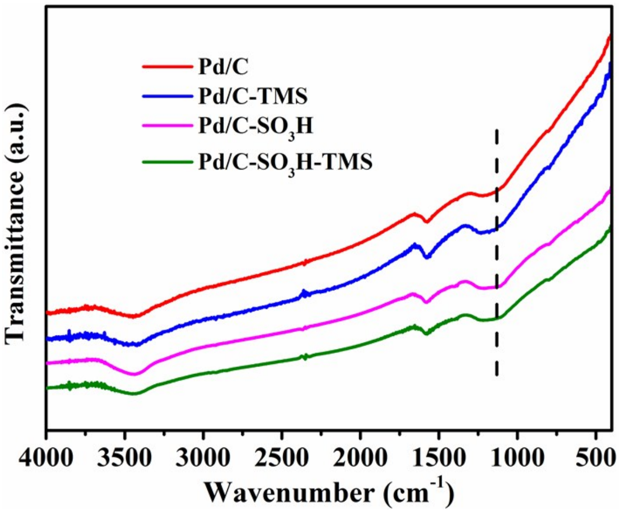


Figure S7. FT-IR spectra of different Pd-containing catalysts

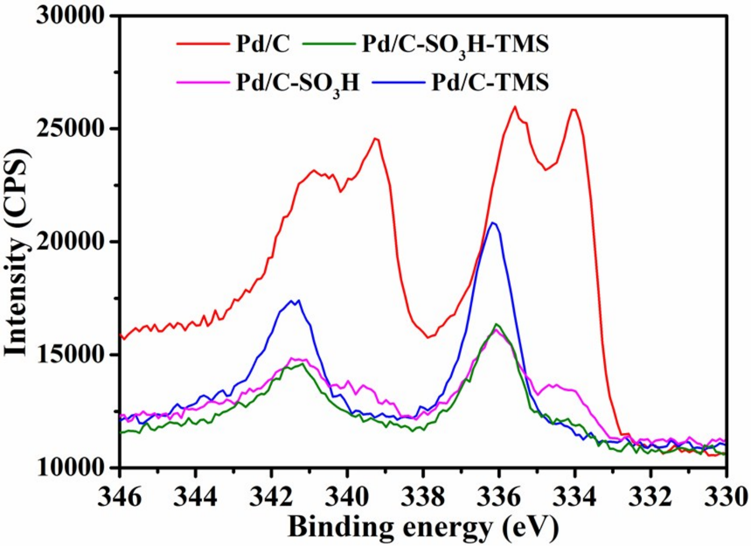


Figure S8. XPS spectra of different Pd-containing catalysts

A clear decrease of the relative intensity for the peaks belonging to Pd(0) at around 334.5 eV and Pd(II) at 336.1 eV was observed after post-grafting the $-SO_3H$ and/or –TMS components,[S6] wherein hydrophobic Pd/C-TMS still had a relatively higher content of surface Pd species that are possibly more available to substrates (Figure S8).

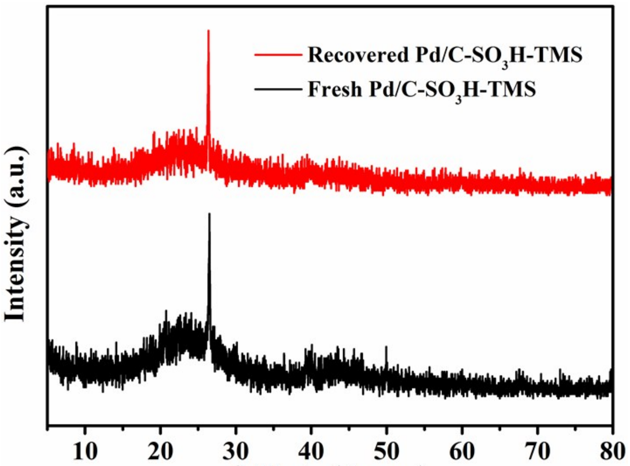


Figure S9. XRD patterns of fresh and recovered Pd/C-SO_3H-TMS after the sixth cycle

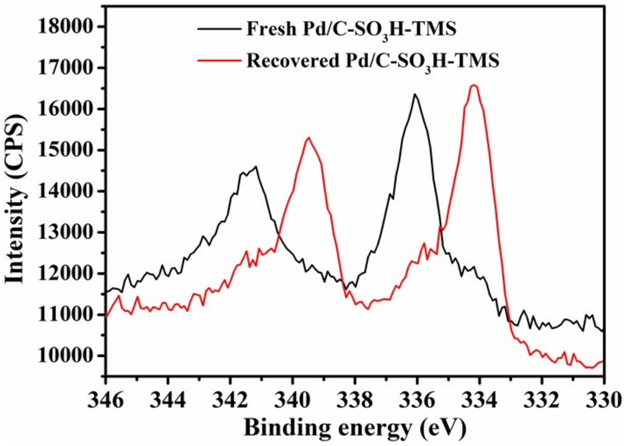


Figure S10. XPS spectra of fresh and recovered Pd/C-SO_3H-TMS after six cycles

The fresh Pd/C-SO_3H-TMS catalyst with surface Pd(II) at ~336.1 eV, wherein most of Pd(0) was covered by post-grafted components (Figure S8), was mostly reduced to Pd(0) at 334.5 eV after six consecutive cycles (Figure S10).

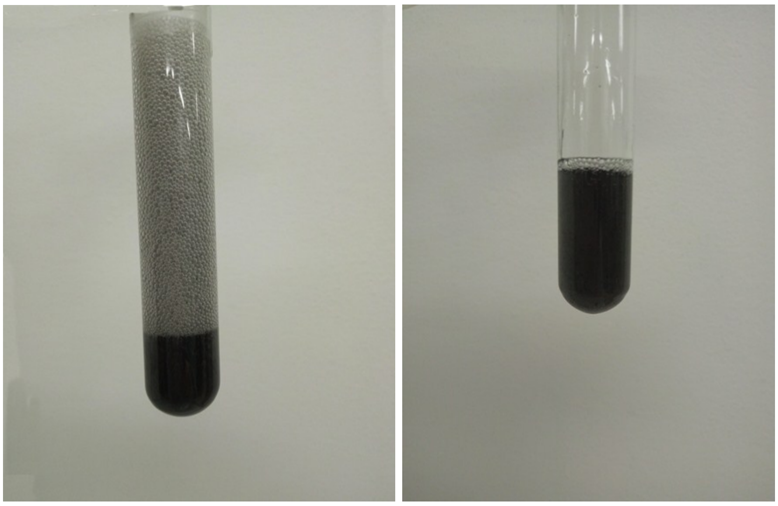


Figure S11. Images for immediately adding fresh (Left) and recovered (Right; after the second cycle) Pd/C-SO_3H-TMS into the reaction mixtures at room temperature

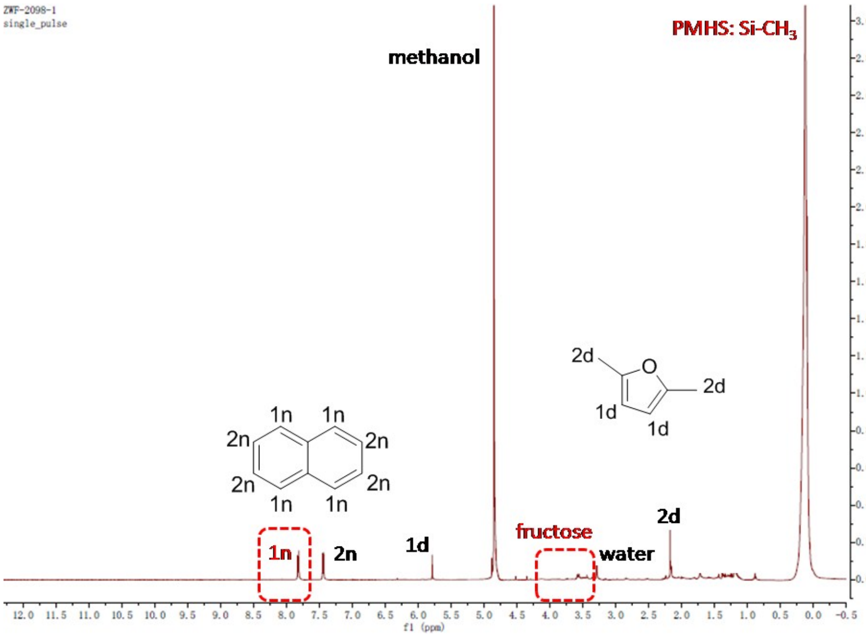


Figure S12. ^{1}H NMR spectrum of fructose-to-DMF conversion in methanol-d_4 (Reaction conditions: 5 wt% fructose, 2 mol% Pd/C-SO_3H-TMS, 2.5 mmol PMHS (9 equiv. H^-), 1.5 mL methanol-d_4, 120 ºC and 3 h)

After reaction, naphthalene (0.08 mmol) with chemical shifts at ~7.4 and 7.7 ppm was added and used as internal standard (**1n** at 7.7 ppm) for quantative analysis of DMF and other identifiable products (GC and GC-MS were also used for cross-check). The dominant product was DMF (**1d** & **2d**) at the almost complete conversion of fructose. It’s worth noting that the integral area of **2d** is 1.8 times higher than that of **1d** (it should be normally 3 times), indicating that the deuterium (D) incorporation from CD_3OD takes place via a facile H/D exchange with the surface-generated Pd-H species. This speculation can be well supported by the varying m/z values of DMF (i.e., m/z = 96, 97, and 98), as demonstrated by GC-MS (Figure S13 A).

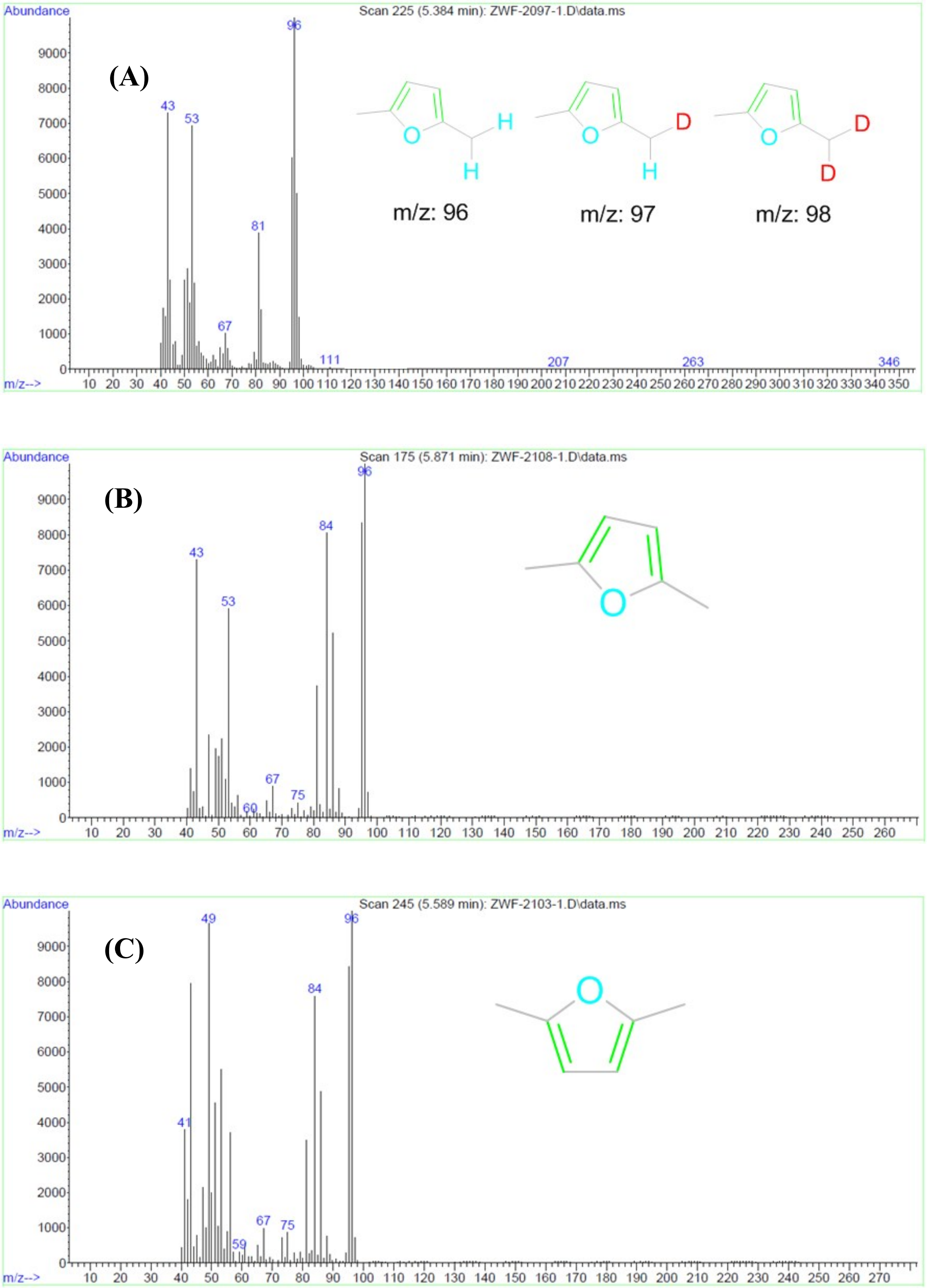


Figure S13. GC-MS spectra for producing 2,5-dimethylfuran (DMF) from fructose in different reaction solvents: methanol-d_4 (A), chloroform-d_3 (B), and normal *n*-butanol (C).

For directly producing 2,5-dimethylfuran (DMF) from fructose with PMHS and Pd/C-SO_3H-TMS, the H/D exchange takes place in methanol-d_4 while it's not applicable in chloroform-d_3, as illustrated by GC-MS spectra (Figure S13).

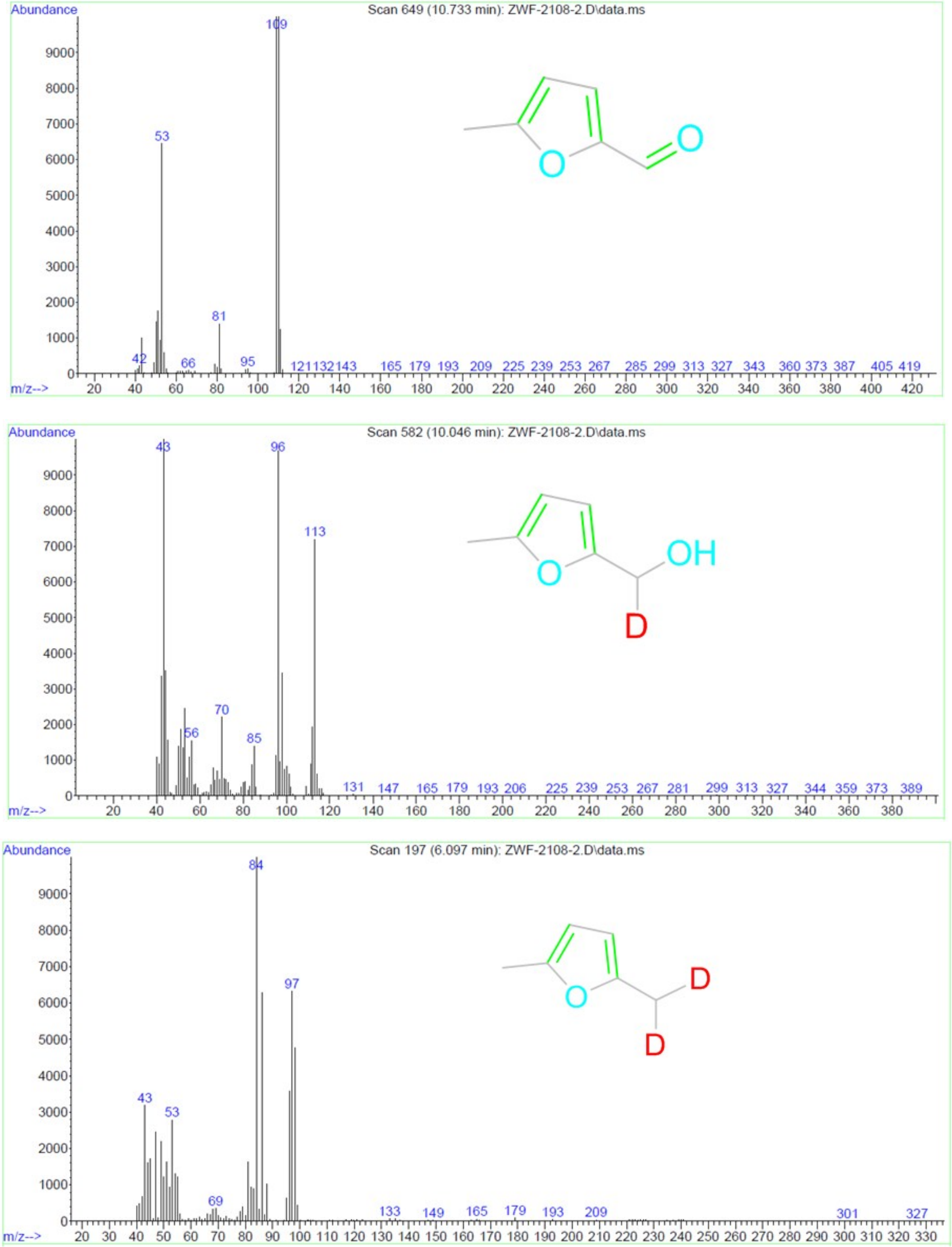


Figure S14. GC-MS spectra for deoxygenation of 5-methylfurfural (MFF) to 2,5-dimethylfuran (DMF) via 5-methylfurfuryl alcohol (MFA) in chloroform-d_3 (Reaction conditions: 5 wt% MFF, 2 mol% Pd/C-SO_3H-TMS, 1.25 mmol diphenylsilane-d_2 (4.5 equiv.), 1.5 mL chloroform-d_3, 60 ºC and 0.5 h).

Using MFF as substrate and diphenylsilane-d_2 as H-donor, the hydrogenation/deoxygenation of MFF in chloroform-d_3 can exclusively give MFA and DMF with 1 and 2 more m/z (Figure S14), respectively, demonstrating that both hydrogenation and deoxygenation processes are achieved via hydrosilyation by separately offering hydrides to furyl aldehydes and alcohols.

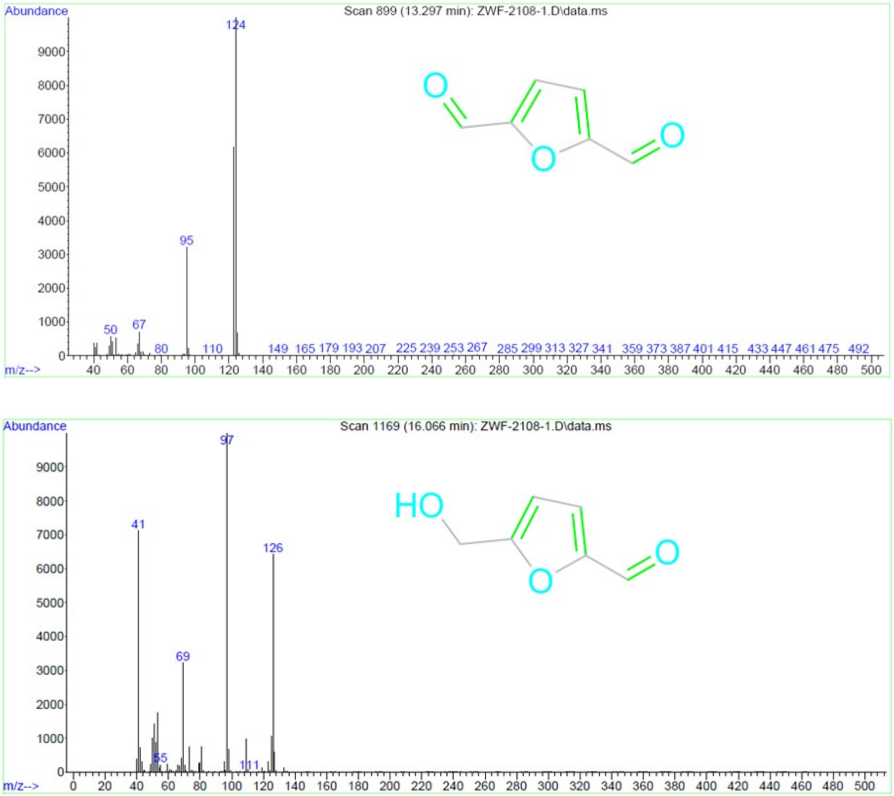


Figure S15. GC-MS spectra for the oxidized product (2,5-diformylfuran) derived from HMF during hydrogenation in chloroform-d_3

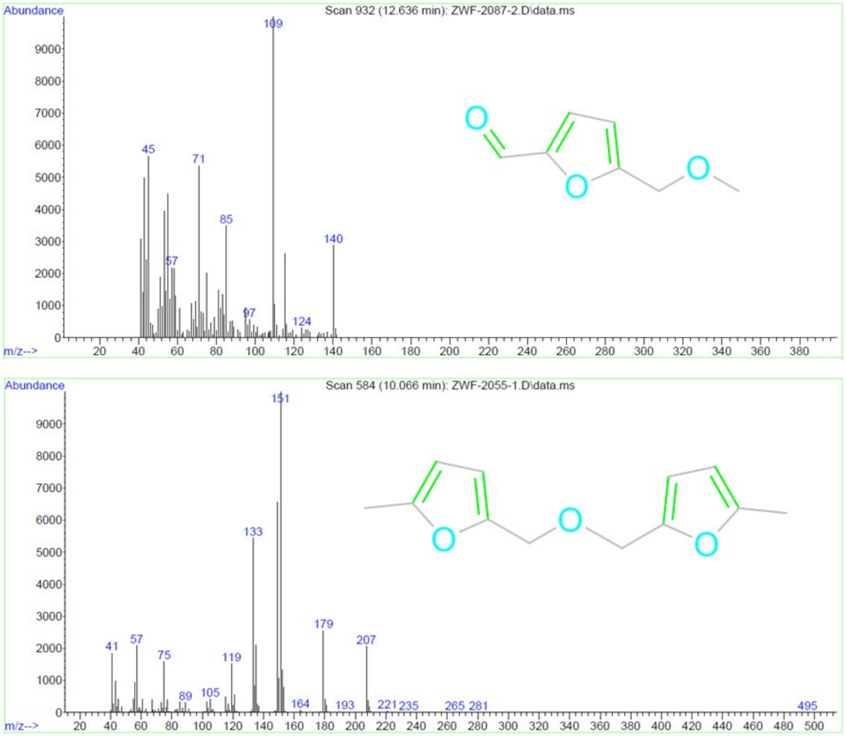
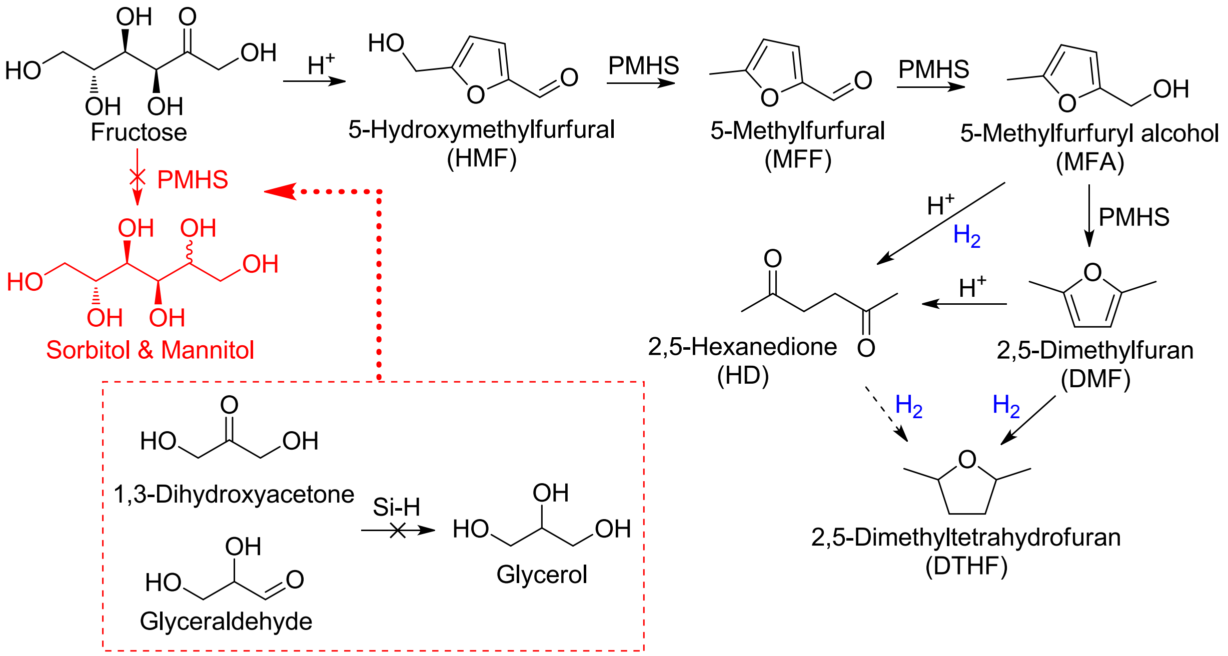
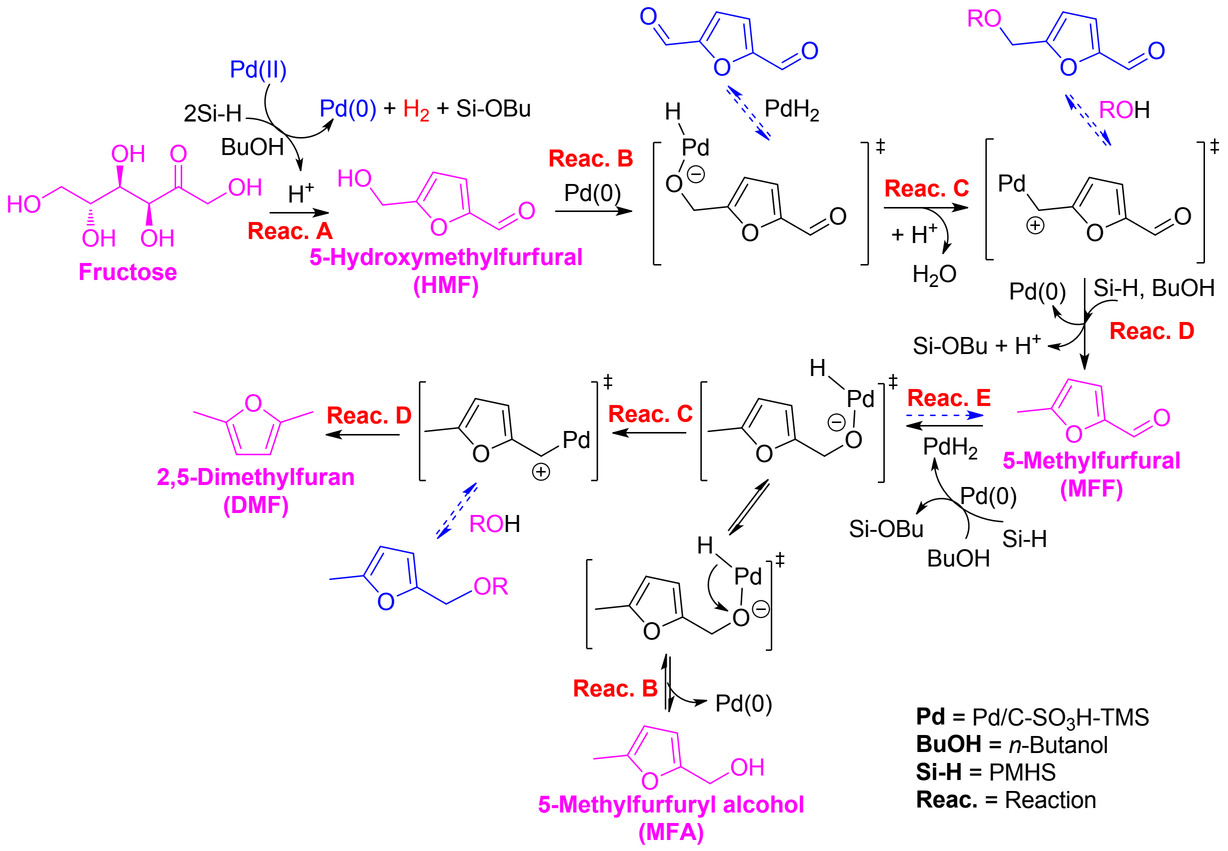


Figure S16. GC-MS spectra for etherified products during fructose-to-DMF conversion in methanol



Scheme S1. Possible pathways involved in the production of 2,5-dimethylfuran (DMF) from fructose



Scheme S2. Proposed reaction pathways for producing DMF from sugars (e.g., fructose) using PMHS as H-donor catalyzed by Pd/C-SO$_3$H-TMS in *n*-butanol

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