Electronic Supplementary Information

One-Pot Tandem Conversion of Monosaccharide and Disaccharide to 2,5-Diformylfuran using Ru Nanoparticles Supported H-Beta Catalyst

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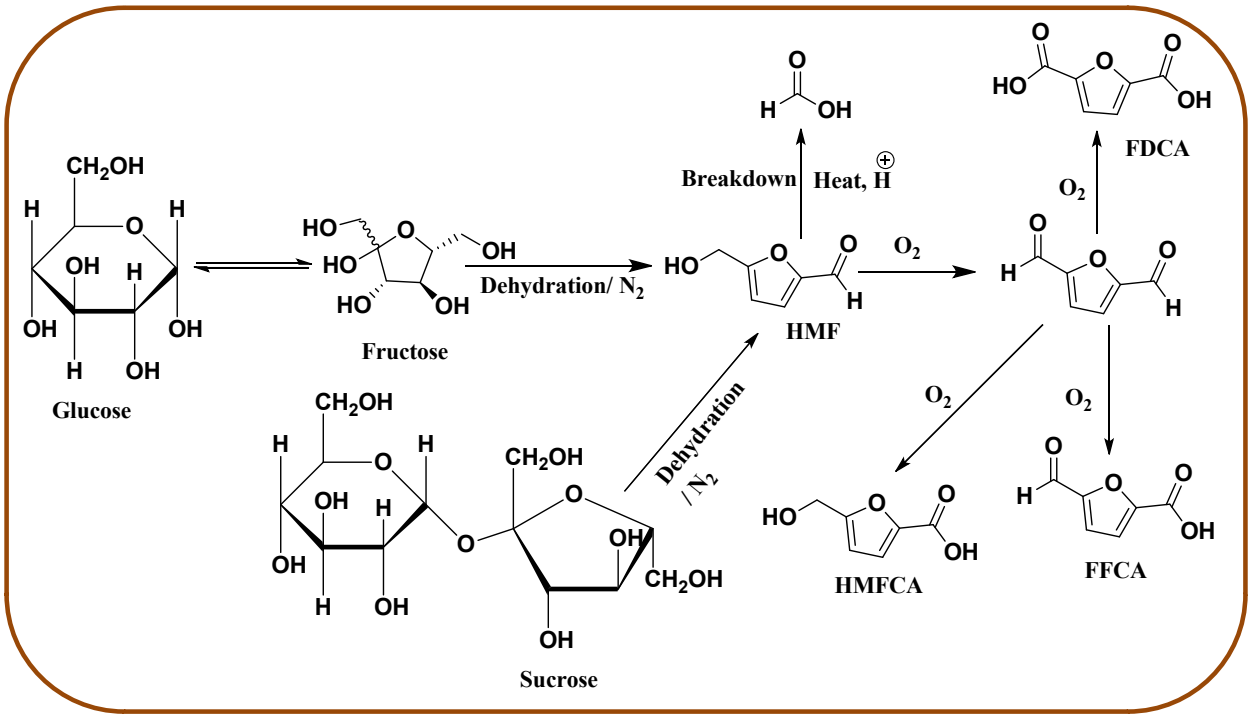
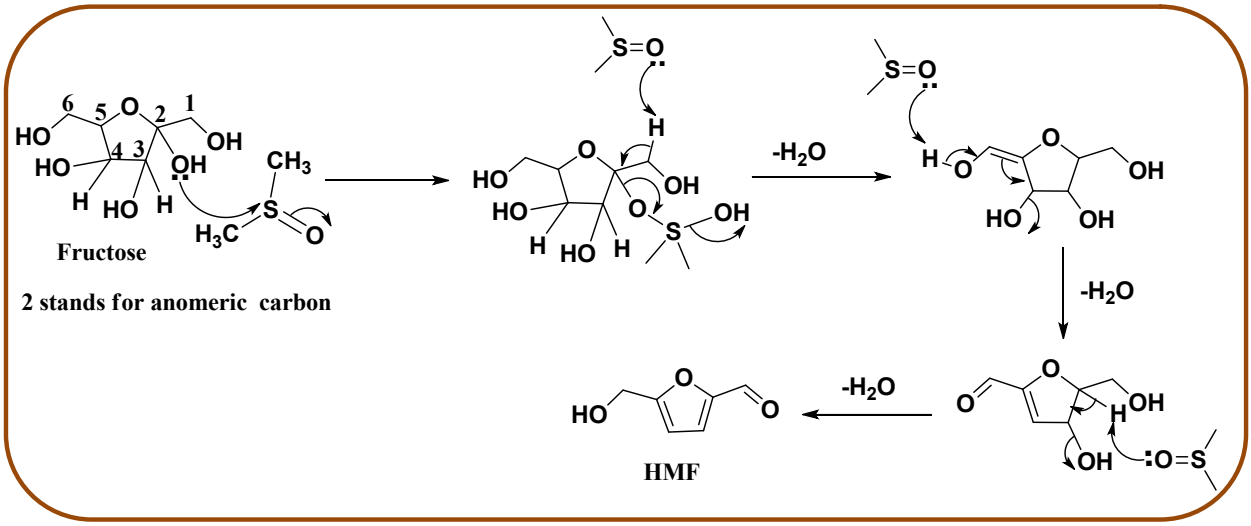
Catalyst characterization

X-ray diffraction (XRD) patterns were recorded in the 2θ range of 5–80° with a scan speed of 2°/min on a PANalytical X'PERT PRO diffractometer using Cu Kα radiation (λ=0.1542 nm, 40 kV, 40 mA). Nitrogen adsorption measurements were performed at 73 K by Quantachrome Instruments, Autosorb-IQ volumetric adsorption analyzer. Sample was degassed at 573 K for 3 h in the degas port of the adsorption apparatus. The specific surface area of the material was calculated from the adsorption data points obtained at P/P_0 between 0.05–0.3 using the Brunauer-Emmett-Teller (BET) equation. The pore diameter was estimated using the non local density function theory (NLDFT) and Barret–Joyner–Halenda (BJH) methods. Scanning electron microscopy (SEM) measurements were carried out on a JEOL JSM-6610LV to investigate the morphology of the materials. For deeper understanding structural analysis were carried out using a FEI, TF30-ST transmission electron microscope (TEM) operating at 300 kV equipped with a scanning unit and a high-angle annular dark field (HAADF) detector from Fischione (model 3000). The compositional analysis was performed using energy dispersive X-ray (EDX, EDAX) spectroscopy attachment on the TF30. Sample was dispersed in ethanol using ultrasonic bath, and dispersed sample was mounted on a carbon coated Cu grid, dried, and used for TEM measurement. Temperature-programmed desorption (TPD) experiments were conducted on a Quantachrome ChemBET^{TM} TPR/TPD instrument. In a typical TPD experiments, 100 mg of sample was placed in a U-shaped, flow through, quartz sample tube. The catalyst was pretreated in He (30 mL/min) at required temperature for 1 h. After cooling down to desired temperature, ammonia (partial pressure 100 Torr) was adsorbed on the samples for 1 h. The sample was subsequently flushed by He stream (30 mL/min) at desired temperature for 1 h to remove physisorbed ammonia. The TPD experiments were carried out in the different range at a heating rate of 10 K/min. The ammonia concentration in the effluent was monitored by using a gold-plated, filament thermal conductivity detector. X-ray photoelectron spectroscopy (XPS) measurements were carried out on PHI 5000 Versa Prob II, FEI Inc. at ACMS, IIT Kanpur.



Scheme S1 Possible routes for the formation of oxidized products from HMF.



Scheme S2 Proposed mechanism for the synthesis of HMF from fructose in DMSO

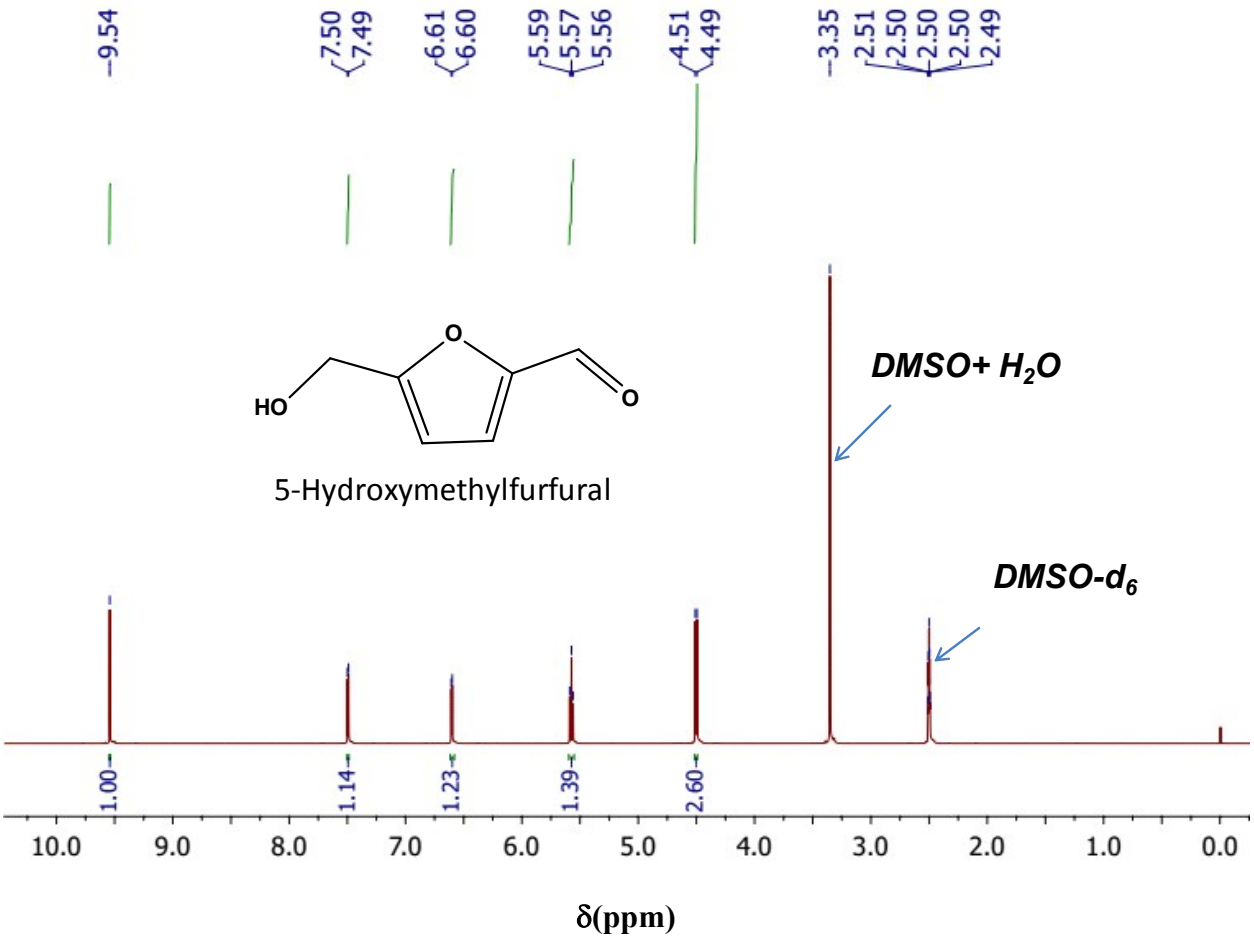


Fig. S1 ^{1}H-NMR of 5-hydroxymethylfurfural (HMF).

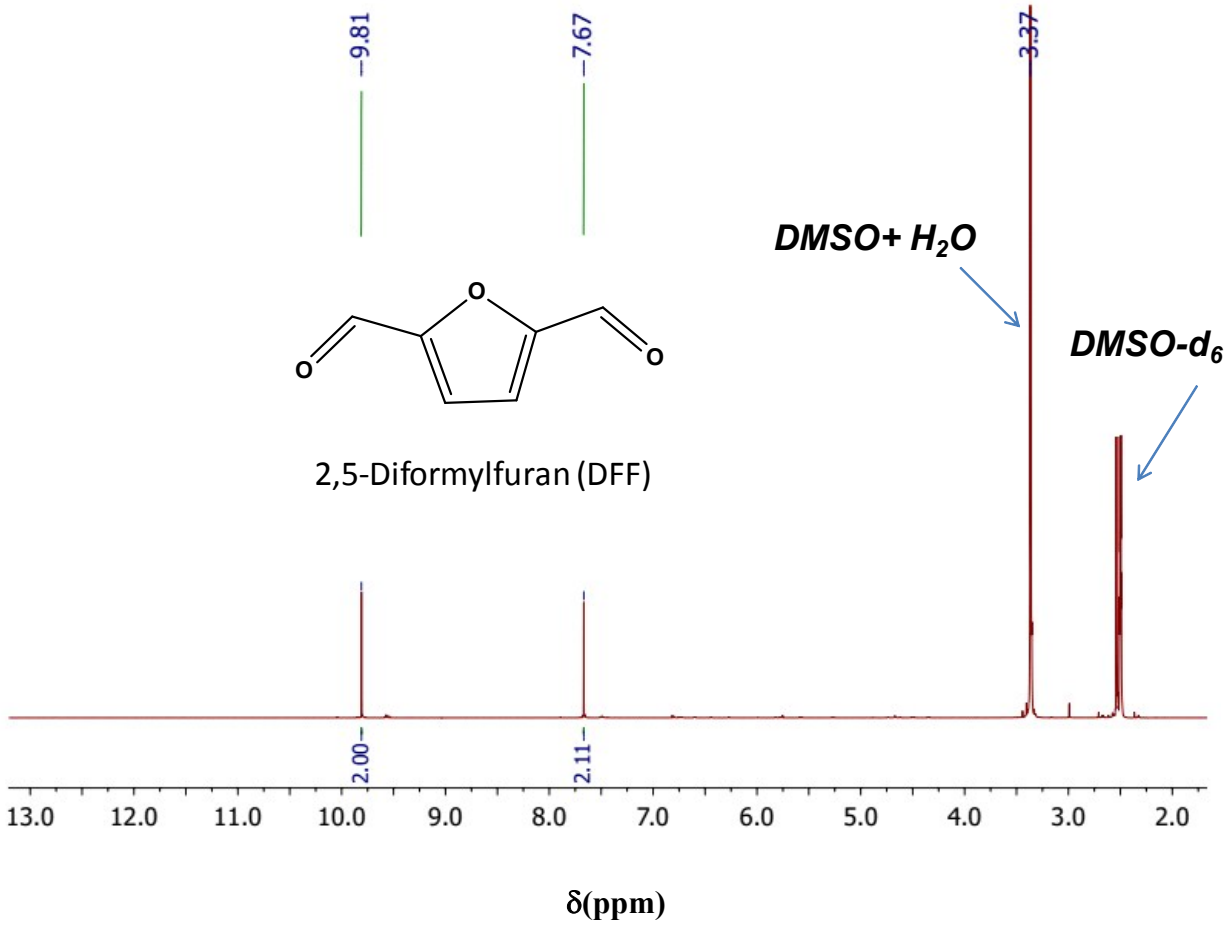


Fig. S2 ^{1}H-NMR of 2,5-Diformylfuran (DFF).

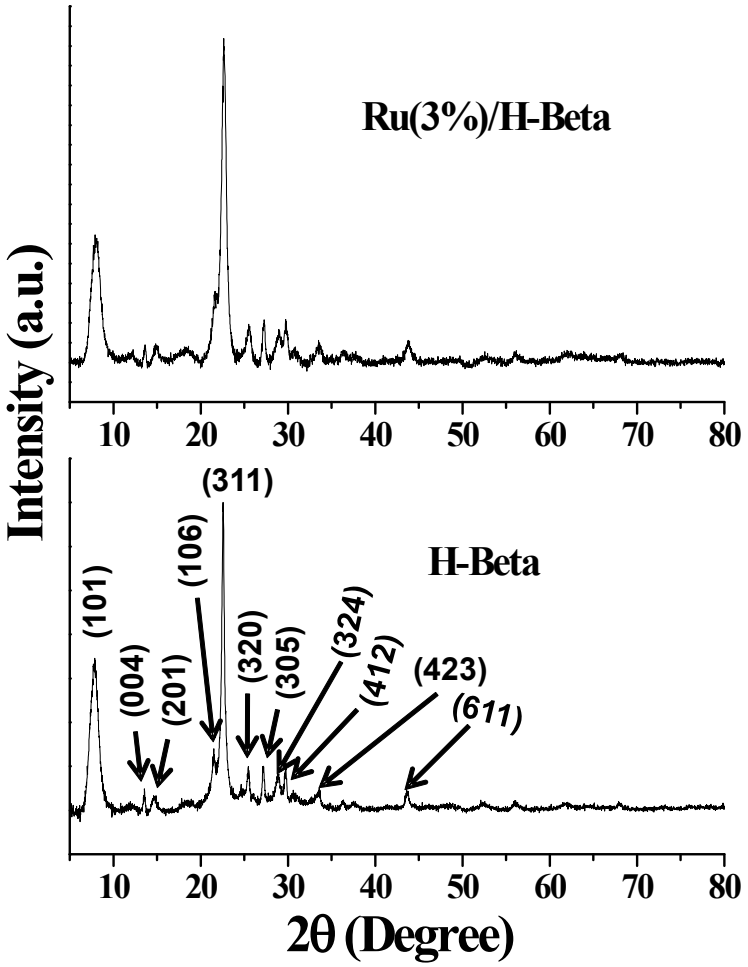


Fig. S3 XRD patterns of H-Beta and Ru(3%)/H-Beta prepared in this study.

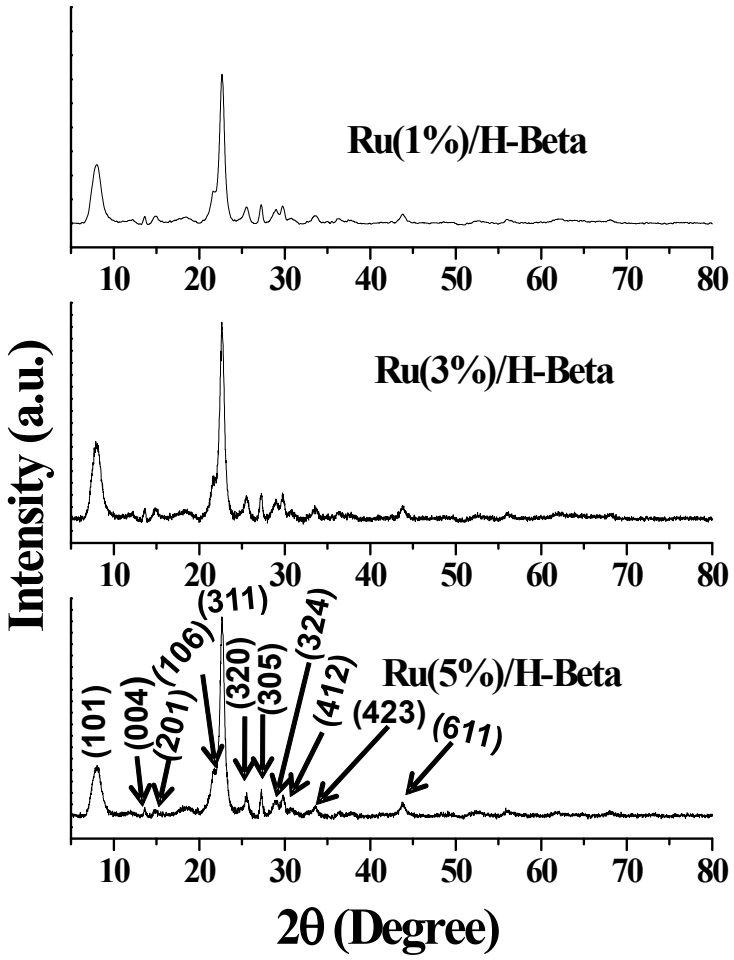


Fig. S4 XRD patterns of Ru nanoparticles supported H-Beta samples prepared in this study.

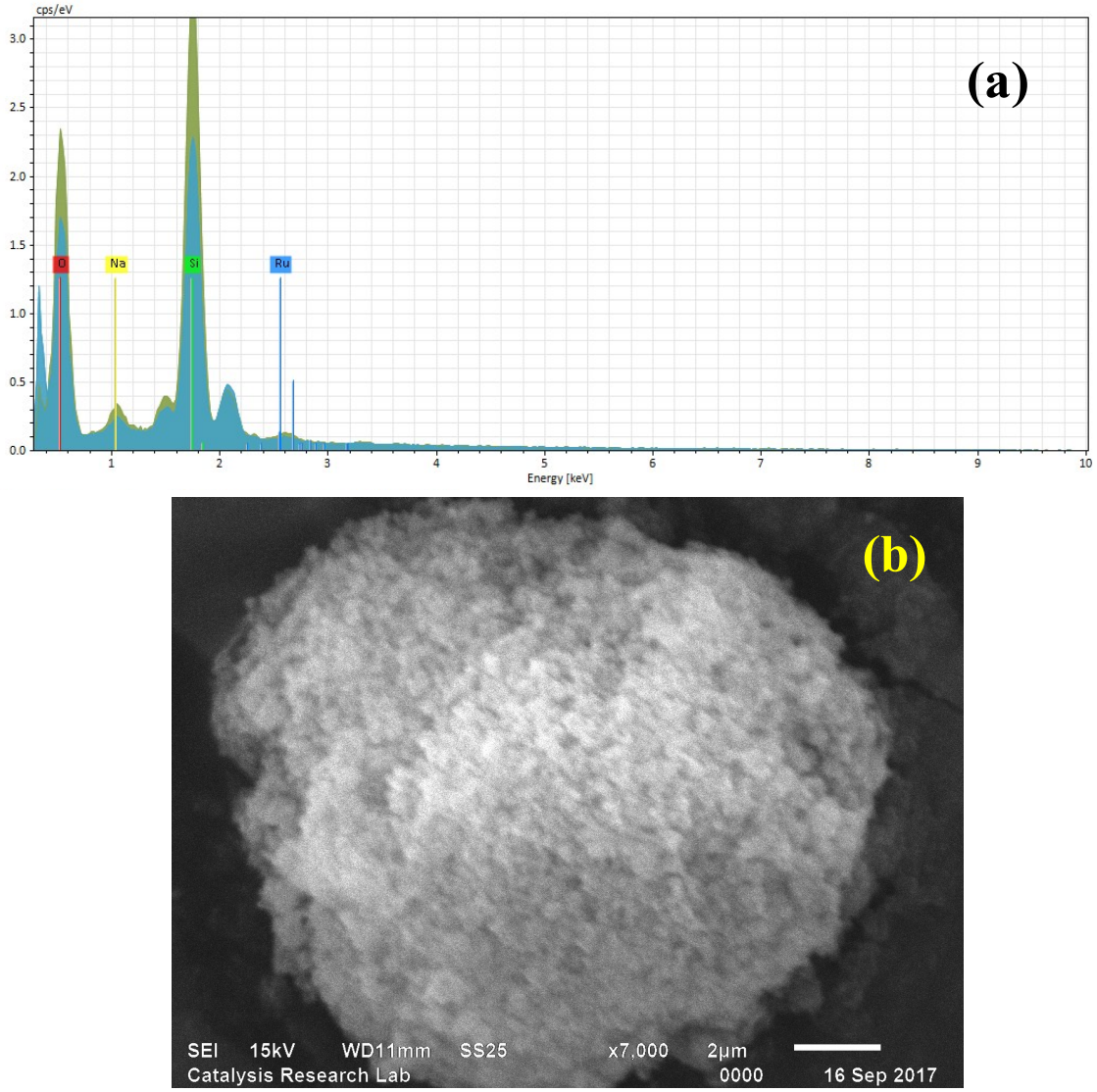


Fig. S5 (a) EDAX spectrum obtained during the SEM analysis of Ru(3%)/H-Beta; (b) SEM images of the recycled catalyst.

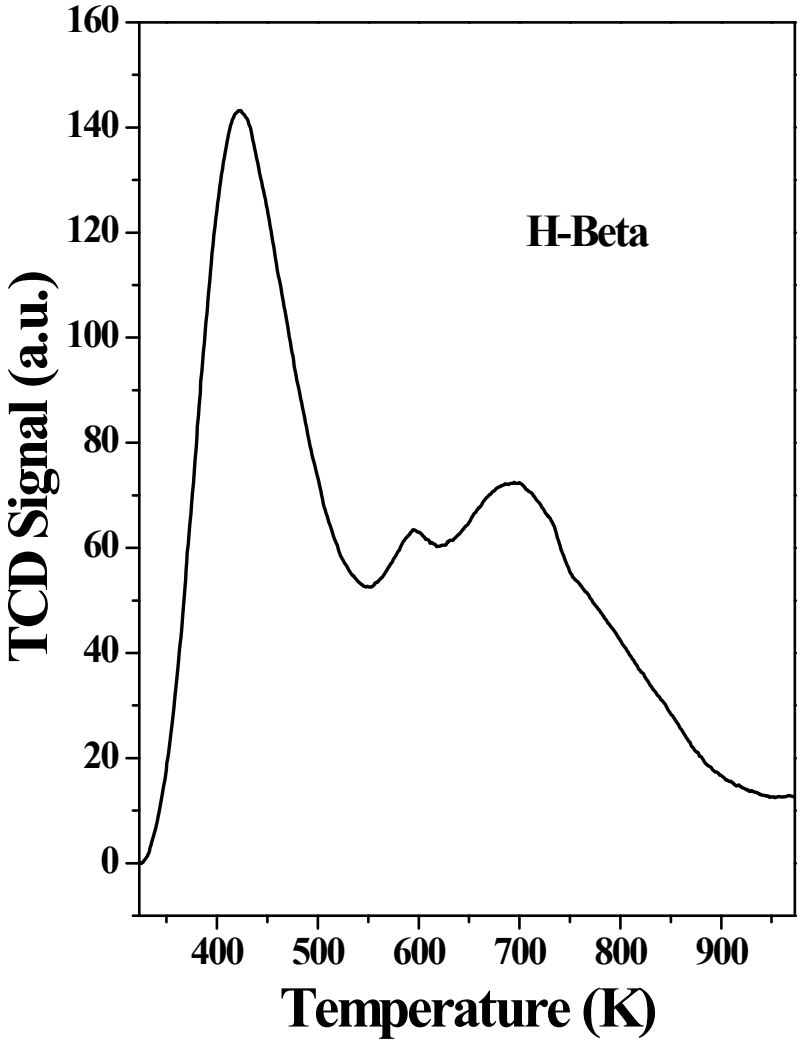


Fig. S6 NH_3-TPD profile of H-Beta investigated in this study.

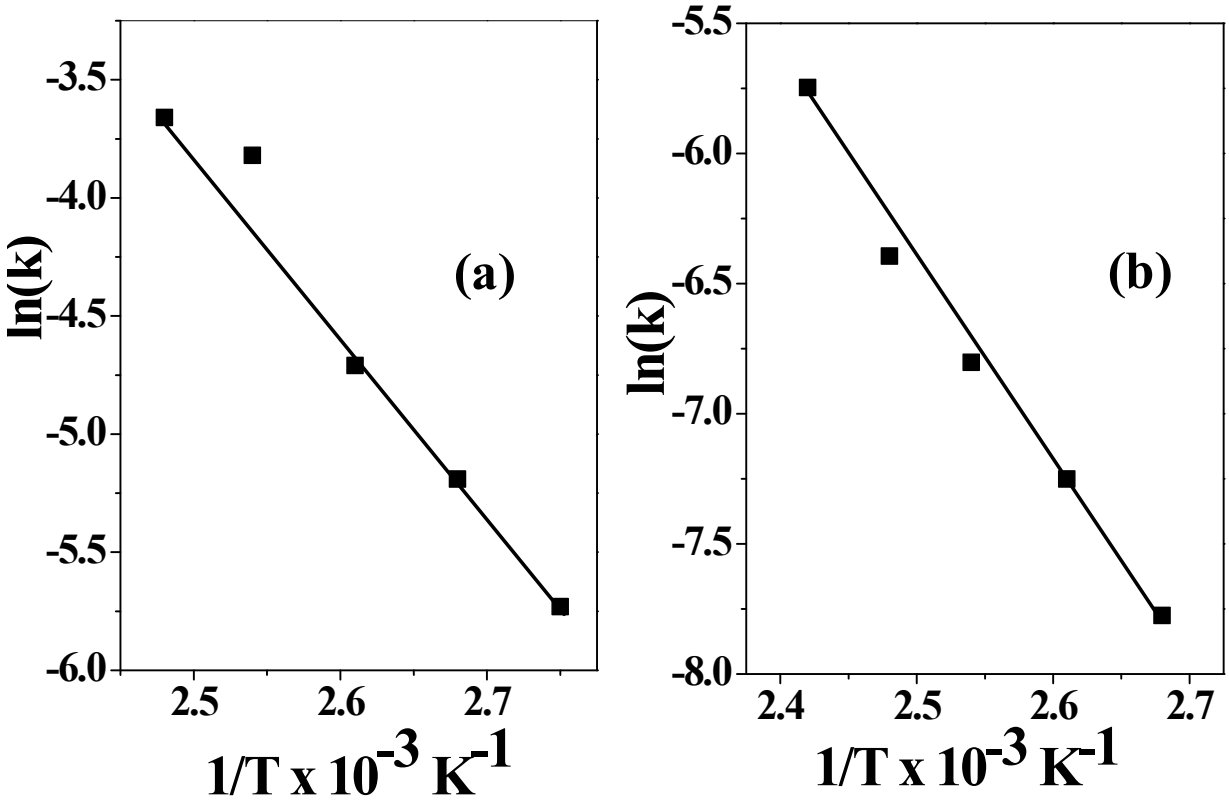


Fig. S7 Plot for ln k vs 1/T for the calculation of activation energy in the (a) dehydration of sucrose to HMF using H-Beta and (b) oxidation of HMF to DFF using Ru(3%)/H-Beta.

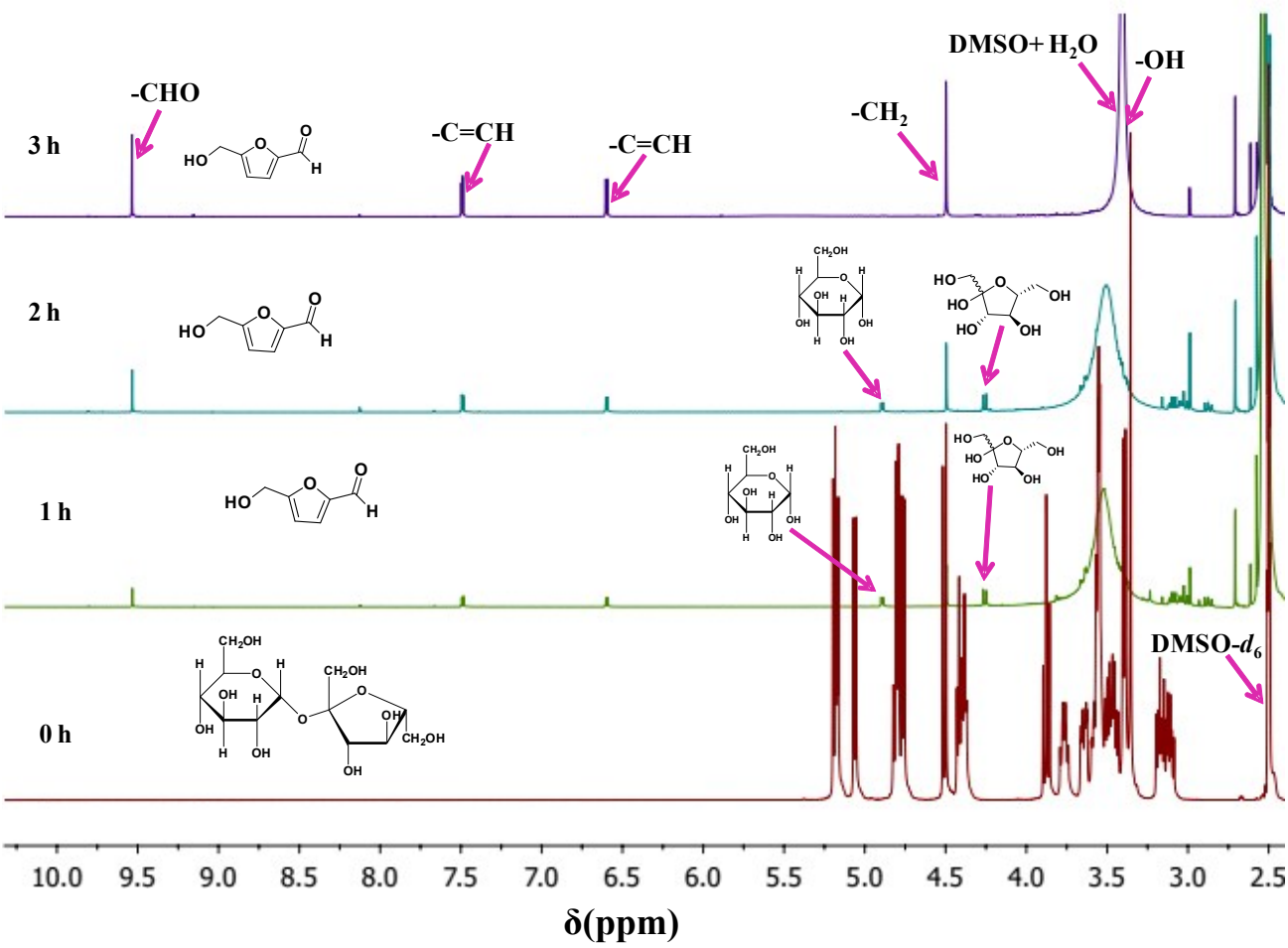


Fig. S8 ^{1}H NMR spectra recorded during one-pot conversion of sucrose to HMF.

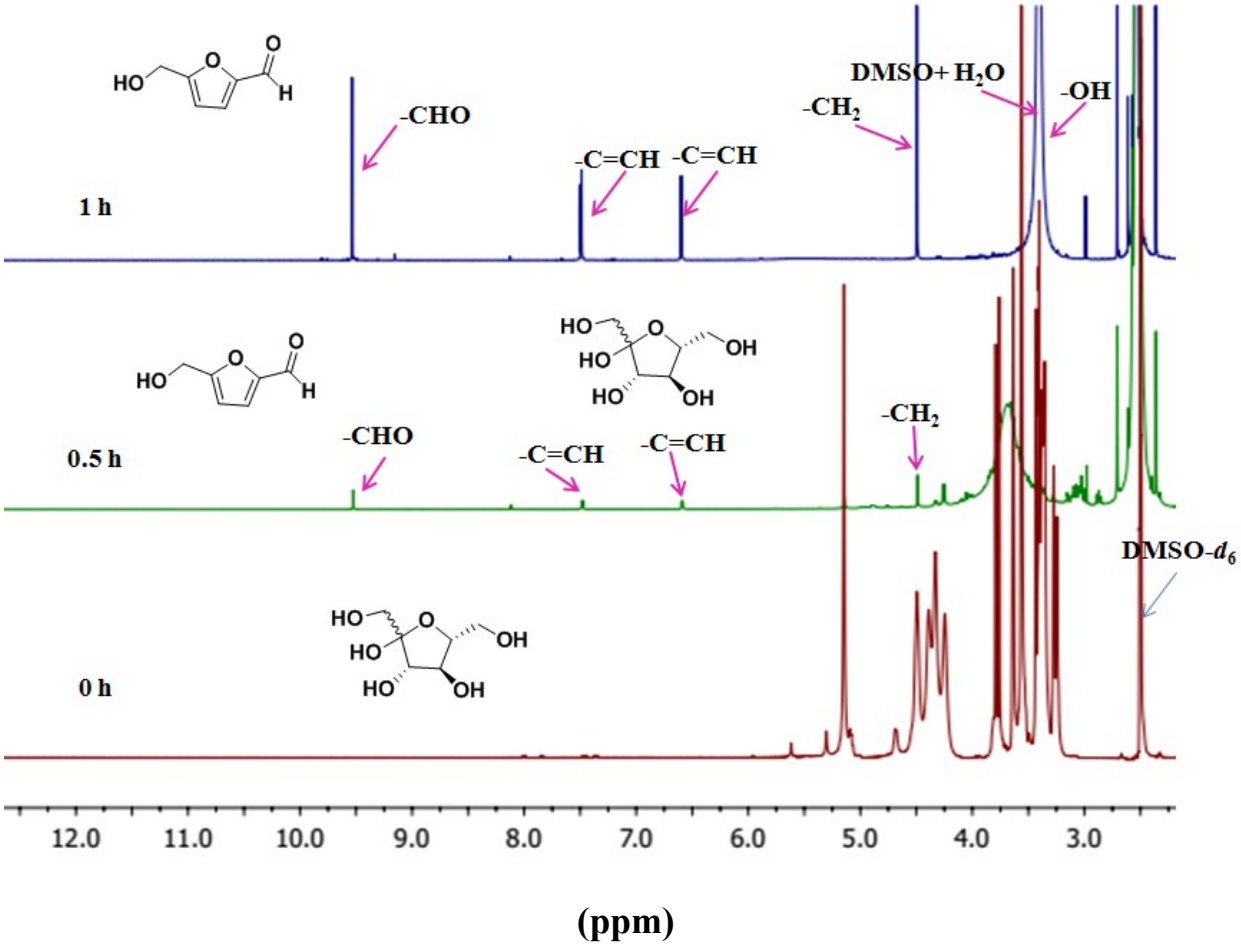


Fig. S9 ^{1}H NMR spectra recorded during one-pot conversion of fructose to HMF.

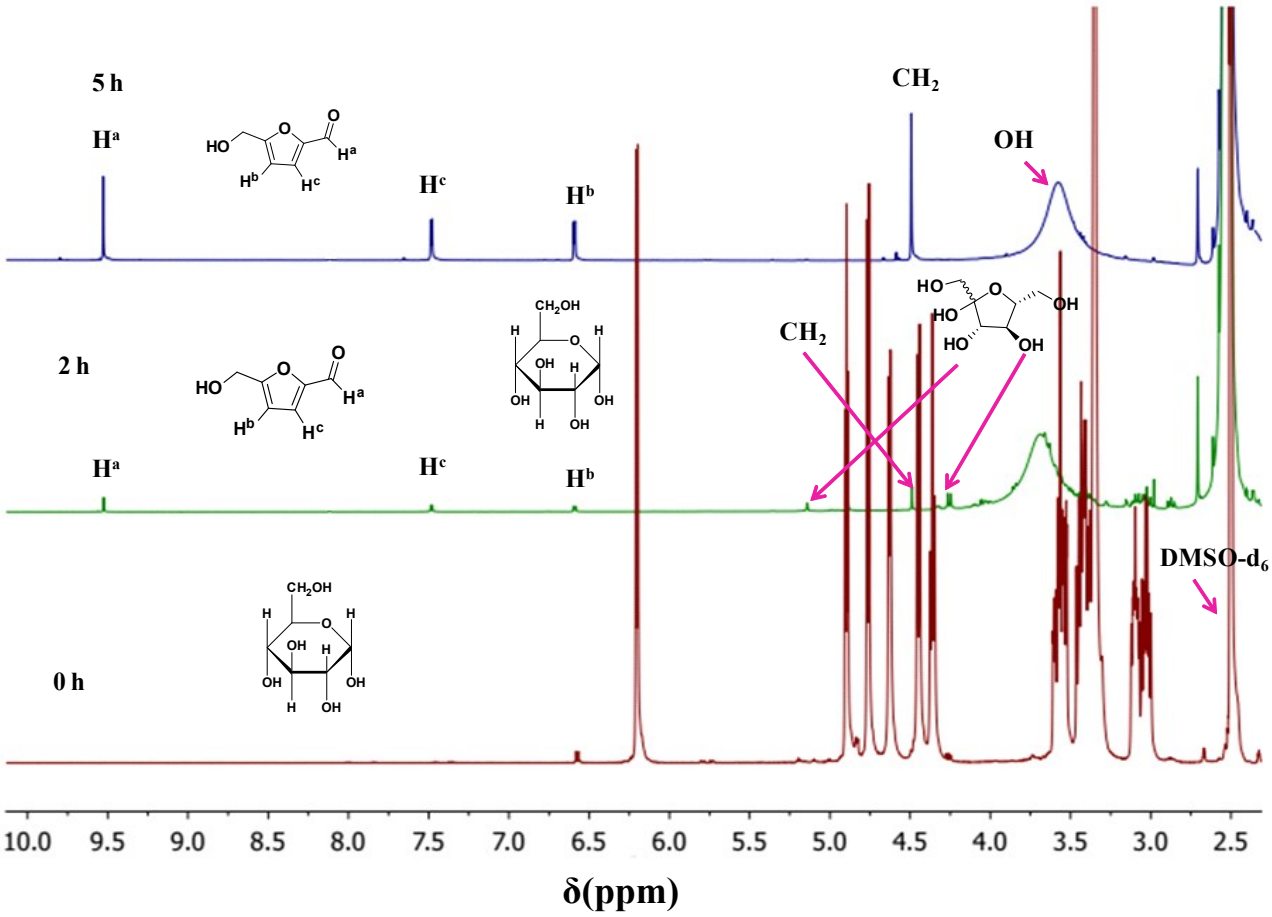


Fig. S10 ^{1}H NMR spectra recorded during one-pot conversion of glucose to HMF.

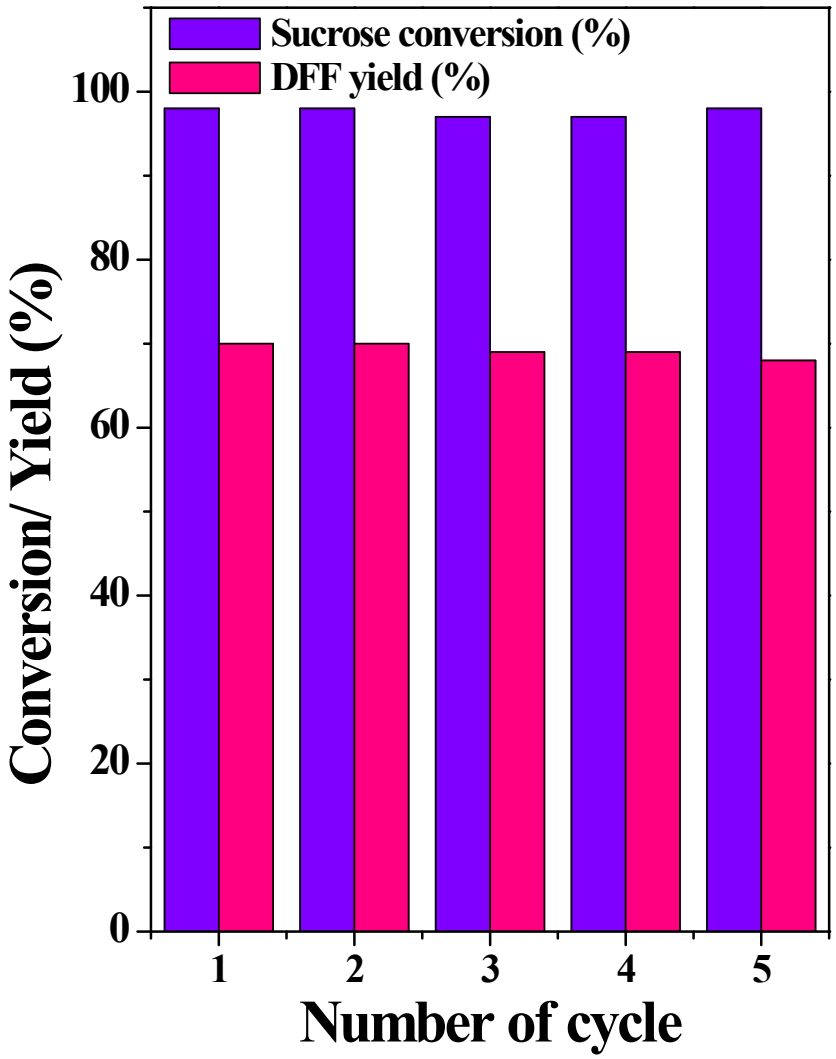


Fig. S11 Recycling of catalyst Ru(3%)/H-Beta during the one-pot conversion of sucrose to DFF.

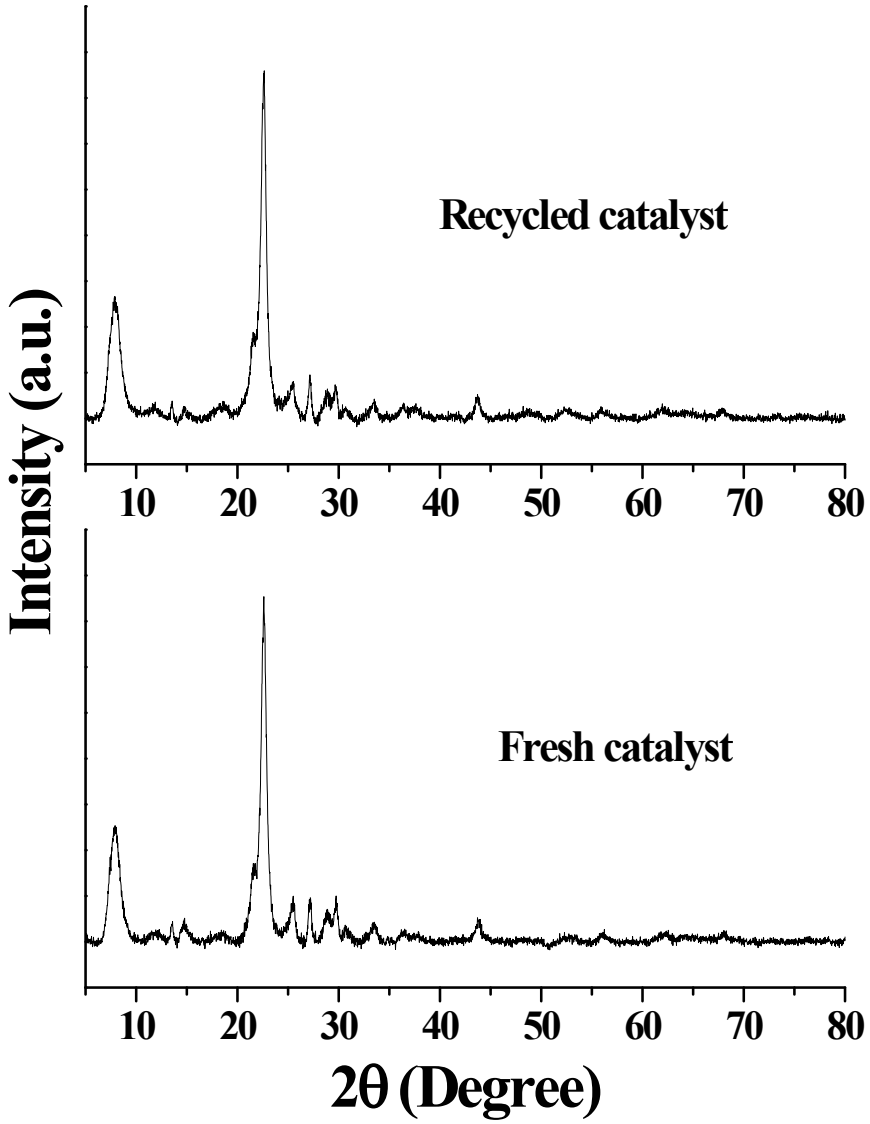
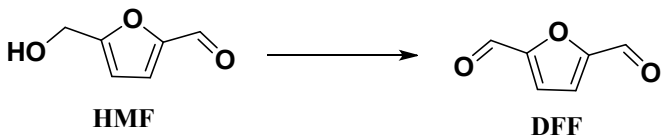


Fig. S12 XRD patterns of fresh and recycled Ru(3%)/H-Beta recovered after fifth cycles after 5th recycle.

Table S1 Comparative catalytic activity of various reported Ruthenium supported heterogeneous catalysts in the transformation of HMF to DFF.

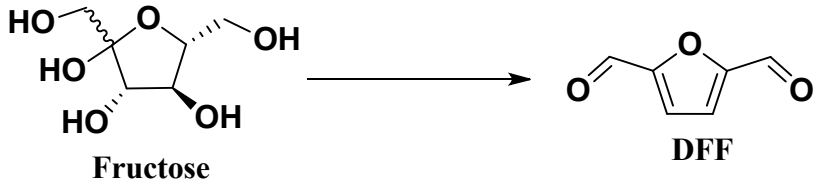


S. N	Reaction condition	DFF yield (%)	Reference
1	HMF (2.0 mmol), catalyst [Ru@mPMF, (Ru content = 4.20%), poly-melamine formaldehyde polymer (mPMF) (50 mg)], toluene (10 mL), O_2 (2 MPa, 12 h, 378 K.	84.6	50
2	HMF (1 mmol), DMF (3 mL), 393 K, 6 h, O_2 flow (20 mL/ min), catalyst [Ru/HT (4.4 wt % Ru) (0.1 g)]	92	31
3	HMF (1 mmol), DMF (3 mL), 393 K, 6 h, O_2 flow (20 mL/min), catalyst [Ru/Al_2O_3 (5 wt% Ru) (0.1 g)]	36	31
4	HMF (1 mmol), DMF (3 mL), 393 K, 6 h, O_2 flow (20 mL/min), catalyst [$Ru/Mg(OH)_2$, 4.2 wt% Ru) (0.1 g)]	72	31
5	HMF (1 mmol), DMF (3 mL), 393 K, 6 h, O_2 flow (20 mL/min), catalyst [Ru/C, 5 wt% Ru)]	76	31

6	γ-Fe_2O_3@HAP-Ru (150 mg), Ru content (2 wt %), HMF (100 mg), 4-chlorotoluene (7 mL), O_2 (20 mL/min^{-1}).	81.4	26
7	HMF (100 mg, 0.8 mmol) and catalyst Fe_3O_4@SiO_2-NH_2-Ru(III) (100 mg) (0.3 wt % Ru.) toluene (7 mL), 383 K, 12 h, O_2 flow (20 mL min^{-1})	85.9	51
8	[Catalyst (HMF/metal molar ratio= 40:1, CTF= covalent triazine framework, Ru content (3.71%)], 1 h, 353 K, air (20 bar) methyl t-butyl ether (MTBE) (15 mL).	63.6	21b
9	HMF (63 mg, 0.5 mmol) and catalyst SBA-15-Bisimidazole-Ru catalyst (2.0 wt% Ru) (50 mg). p-chlorotoluene (8 mL), 383 K, 12 h, O_2 (15 bar).	88.7	38
10	HMF (1.0 mmol), HMF/metal = 80/1 (mol/mol), toluene (10 mL), 383 K, O_2 (2.0 MPa), Catalyst (Ru/C).	28.86	52
11	HMF (0.5 mol), Ru/ γ-Al_2O_3 (200 mg, 1.8 wt% Ru), toluene (15 mL), O_2 (40 psi), 393 K, 4 h.	97.3	53
12	HMF (63 mg, 0.5 mmol), Ru-PVP/CNT (60 mg, 2.2 wt% Ru), DMF (5 mL), O_2 (2.0 MPa), 393	94	54

	K, 12 h.		
13	HMF (1 mmol), DMSO (5 mL), 413 K, 24 h, O_2 bubbling (20 mL/min), catalyst Ru(3%)/H-Beta, 2.75 wt% Ru (EDAX study) (120 mg).	90.2	This study

Table S2 Comparative catalytic activity of various reported heterogeneous catalysts in the transformation of fructose to 2,5-diformylfuran (DFF).



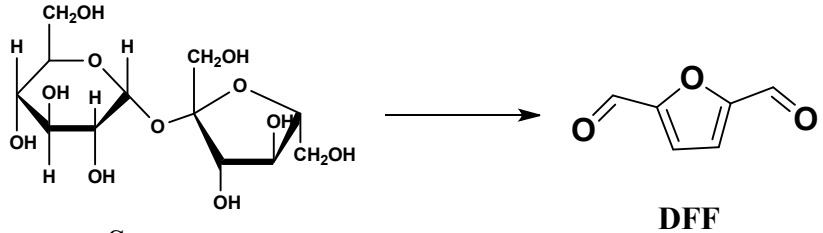
Fructose **DFF**

S. N	Reaction condition	DFF yield (%)	Reference
1	Fructose (0.2 g), DMSO (2 mL), N_2 atmosphere (2 h), O_2 (20 mL min^{-1}, 17 h), carbonaceous catalyst $CCSO_3H$-NH_2 (60 mg).	69	55
2	Fructose (1.11 mmol, 0.2 g), DMF (3 mL), 373 K, 3 h, N_2 flow (20 mL/min), catalyst Amberlyst-15 (0.1 g), Ru/HT (0.2 g).	49	31
3	Fructose (0.1 g) (~0.1 equiv) Fe_3O_4-SBA-SO_3H, 0.1 g (~0.75 equiv) K-OMS-2 (0.1 g), DMSO (3 mL), 10 mL min^{-1} O_2, 2 h in air, 383 K, O_2 flow for 8 h.	80	25
4	Fructose (1 mmol), solvent (DMSO, 3 mL), O_2 balloon (1 bar), 408 K, 3.5 h, catalyst, (PIJEVPI-Br and α-CuV_2O_6 (50 mg and 90 mg)	63.1	43
5	Fructose (0.5 mmol), catalyst (SBA-15-Biimidazole-Ru catalyst) (120 mg), of DMSO (1 mL) at 383 K, p-chlorotoluene (7 mL), 2 h, and then 12 h under 20 bar O_2 pressure.	72.4	38
6	Fructose (0.8 mmol, 143 mg), DMSO (1 mL) and 4-chlorotoluene (4 mL), catalyst Fe_3O_4@SiO_2SO_3H (150 mg), 383 K, second step: γ-Fe_2O_3@HAP-Ru (150 mg), with an O_2 flow rate of 20 mL/min.	79.1	26

7	Fructose (145 mg), DMSO and 4-chlorotoluene, temperature 383 K, for 2 h; catalyst polyaniline–$VO(acac)_2$ (80 mg), 383 K, O_2 flow (30 mL/min), time (14 h).	70	27
8	Fructose (1.11 mmol, 200 mg), catalyst $Cs_3H_2PMo_{10}V_2O_{40}$ (150 mg), DMSO (2 mL), 2 h at 383 K under N_2 (0.1 MPa), then reaction was further performed at 393 K for 6 h under O_2 (0.1 MPa).	89	28
9	Fructose (0.5 mmol, 90 mg), catalyst Fe_3O_4-GO-SO_3H (50 mg, 0.078 mmol SO_3H), DMSO (1 mL), 383 K for 2 h under an air atmosphere. Fe_3O_4-RGO-SO_3H was separated using magnet. Finally, $ZnFe_{1.65}Ru_{0.35}O_4$ (0.128 mmol Ru, 100 mg), DMSO (1 mL), and 1 mL H_2O, and then stirred for 16 h at 403 K, O_2 flow (20 mL/ min).	74	41
10	Fructose (2 mmol, 360 mg); DMSO (4 mL); catalyst, GO (20 mg); 413 K; N_2 or O_2 (20 mL/min).	72.5	30
11	Fructose (200 mg), catalyst, V-g-C_3N_4 (H+) (100 mg), DMSO (2 mL), 403 K, After 2 h reaction under N_2 (0.1 MPa), and O_2 (0.1 MPa).	63	29
12	Fructose (1.2 mmol), catalyst Fe/C-S (metal 20 mol%), ethanol (2 mL), 393 K, N_2 (3 bar) for 2 h and then changed to O_2 (1 bar) for 3 h, 6 h and then changed to O_2 (3 bar) for 8 h	99	40
13	Fructose (45.0 mg), catalyst PMo_{12} HPA. (2.5 mg), DMSO (1 mL), 433 K, 2 h, in air.	60	56
14	Fructose (200 mg), DMSO (5 mL), O_2= 20 mL /min, Catalyst Cr-MIL-101-Encapsulated Keggin Phosphomolybdic Acid (40 mg), 423 K, 7 h,	75	37
15	Fructose (200 mg); DMSO, 5 mL; catalyst Sulfonated MoO_3–ZrO_2 (10 mg); O_2 = 20 mL/min; 423 K; 10 h.	74	32

16	Fructose (200 mg), catalyst MoO_3-containing protonated nitrogen doped carbon (20 mg), DMSO (5 mL), O_2 (20 mL/min), 423 K, 9 h.	77	33
17	Fructose (180 mg), Catalyst bifunctional f-$Ce_9Mo_1O_\delta$, (Mo loading 6 mol %), DMSO (4 mL), 393 K, N_2 10 mL min^{-1}, and O_2 10 mL min^{-1}.	74	42
18	Fructose (1.0 mmol), catalyst [100 mg, 0.04 mmol,VO(salen) and 0.025 mmol tungstic acid], H_2O_2 (1.0 mmol, added after 1 h), isopropanol (solvent), 353 K (for initial 1 h) and 333 K (for subsequent 15 h).	70	36
19	Fructose, (90 mg); H_2SO_4 (0.05 M); V_2O_5/ceramic (100 mg); DMSO (4 mL); O_2 (40 mL/min), 5 h.	68.4	35
14	Fructose (1 mmol), DMSO (5 mL), temperature (393 K), time (1 h) under N_2 flow (10 mL/min), first step no catalyst. For second step, catalyst Ru(3%)/Beta (120 mg) was added and reaction was carried out at 413 K for 24 h at an O_2 flow rate of 10 mL/min.	79.7	This study

Table S3 Comparative catalytic activity of present catalyst systems and Ru(3%)/H-Beta for the one-pot two-step conversion of sucrose to 2,5-diformylfuran over various reported catalysts.



Sucrose **DFF**

E.N	Reaction condition	DFF yield (%)	Reference
1	Sucrose (45.0 mg), catalyst $PMo_{12}HPA$ (2.5 mg), DMSO (1 mL), 433 K, 2 h, in air.	28	70
2	Sucrose (0.1 g), of V-containing Beta catalyst (0.1 g), of H_2SO_4 (0.15 g), 403 K, and O_2 balloon, 6 h.	39.5	71
3	Sucrose (1 mmol), DMSO (5 mL), temperature (393 K), time (6 h), Ru(3%)/H-Beta (120 mg) under N_2 flow (10 mL/min). Second step was carried out at 413 K for 24 h at an O_2 flow rate of 10 mL/min.	66.8	This study