

Supplementary Material (ESI)

Supporting Information

Base-free conversion of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid over Ru/C catalyst

Guangshun Yi, Siew Ping Teong, and Yugen Zhang*

Institute of Bioengineering and Nanotechnology, 31 Biopolis Way, The Nanos, Singapore 138669
Email: ygzhang@ibn.a-star.edu.sg

Experiments

Materials: HMF, DFF, FDCA, AlCl₃ and Ru/C (5 wt% metal) were purchased from Sigma-Aldrich. Isopropanol, THF, sulfuric acid (95-97%), hydrochloric acid (37%) were purchased from Merck. All the chemicals were used directly without any pretreatment.

Product analysis: HMF, FFCA, DFF and FDCA were analysed by HPLC (Agilent Technologies, 1200 series) and confirmed with isolation yield. HPLC working conditions: column (Agilent Hi-Plex H, 7.7 × 300 mm, 8 μm), solvent 10mM H₂SO₄, flow rate 0.7 ml/min, 25 °C, DAD detector (280 nm for HMF, DFF and FFCA; 254 nm for FDCA and HFCA). The retention time for detected compounds were 20.7 min, 24.4 min, 29.4 min, 36.5 min, and 46.5 min for FDCA, HFCA, FFCA, HMF and DFF, respectively. Fructose and glucose conversion were measured using a Sugar Analyzer (DKK-TOA Corporation, Japan. Model: SU-300).

Characterization: The product was characterized by ¹H and ¹³C NMR (Bruker AV-400). Ru/C catalyst was characterized by TEM (FEI Tecnai F20) and XRD (PANalytical X-ray diffractometer, X'pert PRO, with Cu Kα radiation at 1.5406 Å).

Conversion of HMF to FDCA with base

HMF (1 mmol, 126 mg), equivalent amount of base (for HT, 0.2 g), H₂O (10 mL), Ru/C catalyst (5 wt%, equivalent to 5 mol%, 0.1 g) were charged to a 50 ml Parr reactor. The reactor was purged with O₂ thrice and the final pressure was 0.2 MPa. The reactor was heated to 120 °C in silicon oil bath, with stirring speed of 500 rpm. After 5 h, the reaction was cooled down to room temperature.

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Base-free conversion of HMF to FDCA

HMF (1 mmol, 126 mg), H₂O (10 mL), Ru/C catalyst (5 wt%, 0.2 g, equivalent to 10 mol%) were charged to a 50 ml Parr reactor. The reactor was purged with O₂ thrice and final pressure was 0.2 MPa. The reactor was heated to 120 °C in silicon oil bath, with stirring speed of 700 rpm. After 10 h, the reaction was cooled down to room temperature.

The obtained FDCA in white precipitates were separated from the mixture by centrifugation. Methanol (10 mL) was added to dissolve the FDCA under sonication. After filtration and washed twice with methanol, the solution was evaporated to obtain white solids. Isolated yield is 78%. The remaining FDCA was found mainly in water.

For HPLC testing, Na₂CO₃ (1 mmol, 0.106 g) was added to the reaction solution, FDCA precipitates was dissolved as FDCA sodium salt and CO₂ bubbles were released from the solution. The Ru/C catalyst was filtered out, followed by washing with enough 90°C hot water. The solution was collected and aliquots of solution were taken out for HPLC testing.

One-pot 2-step method for the conversion of HMF to FDCA

HMF (1 mmol, 126 mg), H₂O (10 mL), Ru/C catalyst (0.2 g) were charged to a 50 ml Parr reactor. The reactor was purged with O₂ thrice and final pressure was 0.2 MPa. The reactor was heated to 120 °C for 1.2 h.

After that, the catalyst was separated by filtration, the filtrate was evaporated, and re-dissolved in *t*BuOH/EtOAc mixture solution (5 ml/5 ml), and peracetic acid (1 mol.L⁻¹) was added through a syringe pump at room temperature over 12 h. FDCA was obtained as white precipitate, as shown in Figure S5.

FDCA promoted conversion of fructose and glucose to HMF

1 mmol of fructose, 1 mmol of FDCA, 4.85 ml anhydrous isopropanol and 0.15 ml of H₂O (or 4.5 ml THF with 0.5 ml H₂O) were added into an 8 ml thick wall glass tube. The reactor was heated up to 170 °C for reaction.

For glucose conversion, 1 mmol glucose, 1 mmol FDCA, 0.05 mmol AlCl₃, or 0.1 g Sn-Beta were added to 5 ml *i*PrOH/H₂O solution (4.85/0.15 ml). The reaction was conducted at 170 °C.



Figure S1. FDCA in acid form was directly obtained as white precipitate in base-free condition

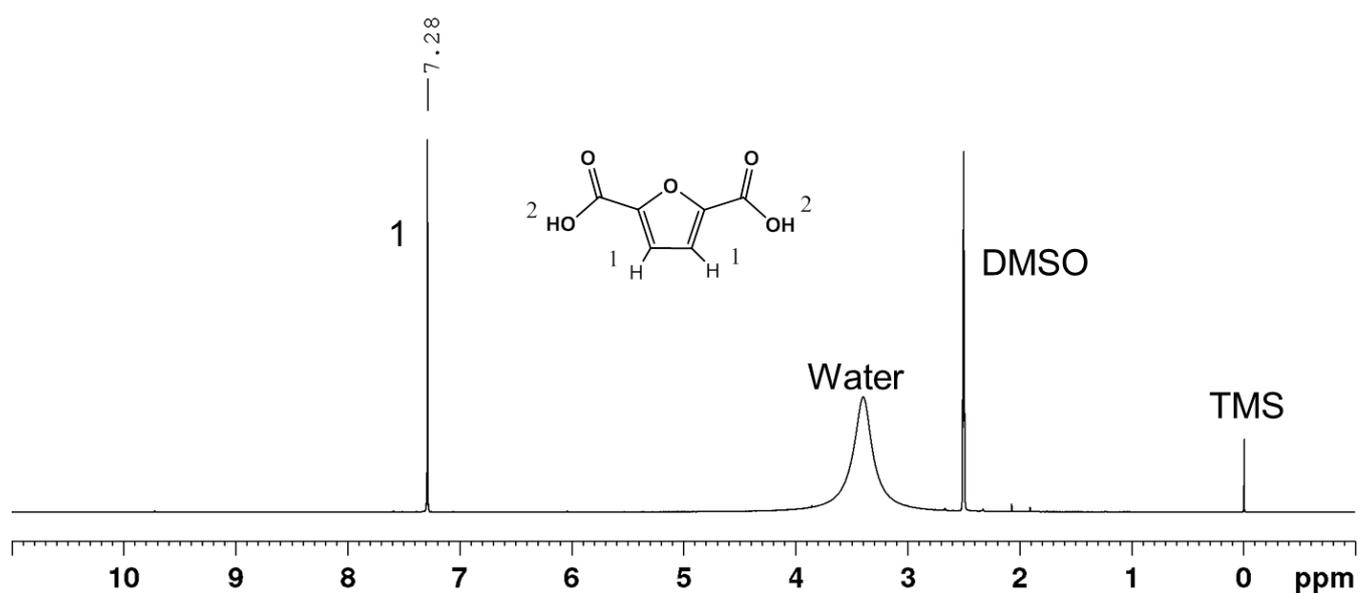


Figure S2. NMR spectrum of FDCA obtained in base-free reaction. Solvent: DMSO

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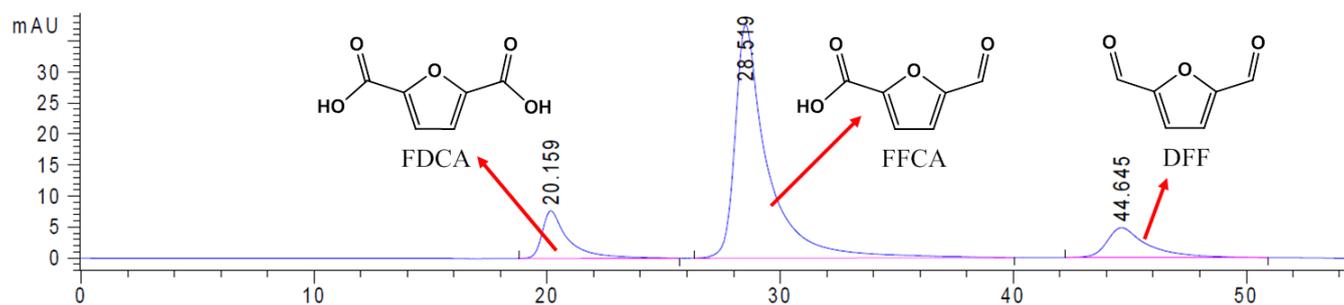
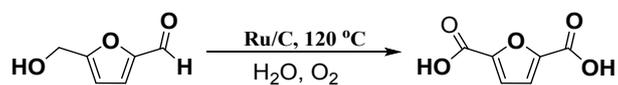


Figure S3. HPLC results for base-free conversion of HMF in water (120 °C for 5 h with 0.1 g Ru/C, 0.2 MPa O₂). HMF (36.5 min) was fully converted

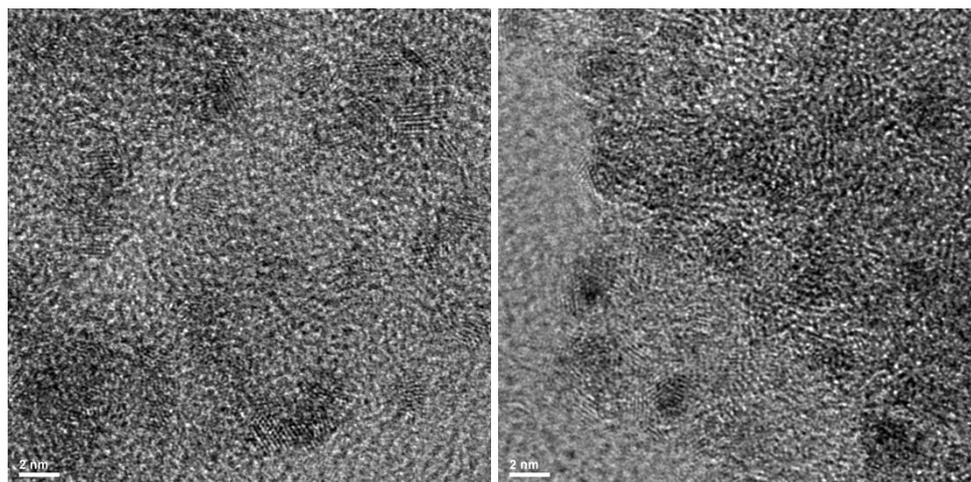
Table S1. Recyclability of the catalyst ^a



Entry	Runs	Conv. (%)	FDCA (%)	FFCA (%)	DFF (%)
1	1 st	100	88	0	0
2	2 nd	100	87	0	0
3	3 rd	100	87	0	0
4	4 th	100	78	7	0
5	5 th	100	76	11	0
6 ^b	6 th	100	88	0	0

^a Reaction conditions: 1 mmol HMF, 10 ml H₂O, 0.2 g Ru/C (10 mol%), 0.2 MPa O₂, 120 °C. ^b Reactivated catalyst. Reactivation conditions: 10% H₂/Ar flow, 350 °C, 4 h.

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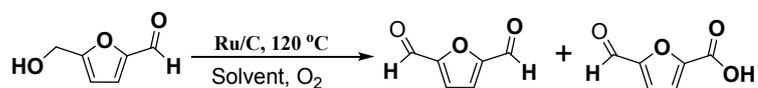


(A)

(B)

Figure S4. TEM image of Ru/C catalyst (A) before and (B) after 5 rounds of reaction

Table S2. Base-free conversion of HMF to DFF/FFCA over Ru/C



Entry	Solvent	HMF 100% Conv. Time (h)	DFF Yield (%)	FFCA Yield(%)	Total DFF/FFCA (%)
1	H ₂ O	1.2	13	84	97
2	MeCN	5	97	2	99
3	HOAc	5	95	3	98
4	MeOH	5	95	1	96

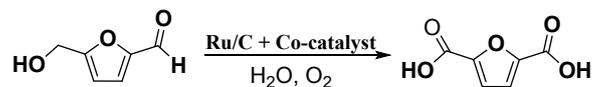
Reaction Conditions: 1 mmol HMF, 10 ml H₂O, 0.2 g Ru/C (10 mol%), 0.2 MPa O₂, 120 °C.

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Figure S5. DFF/FFCA solution with and without AcOOH addition.

Table S3. Effect of co-catalyst on the base-free conversion of HMF to FDCA



Entry	Catalyst	Co-Catalyst	Conversion (%)	Yield (%)	Reaction Rate
1	Ru/C		100	88	
2	Ru/C	Co(OAc) ₂	100	87 (FDCA)	Same
3	Ru/C	Mn(OAc) ₂	100	74 (FDCA) + 12 (FFCA)	Lower
4	Ru/C	Co(OAc) ₂ + Mn(OAc) ₂	100	85 (FDCA)	Same

Reaction Conditions: 1 mmol HMF, 10 ml H₂O, 0.2 g Ru/C (10 mol%), 0.015 g Mn(OAc)₂ and/or Co(OAc)₂, 0.2 MPa O₂, 120 °C.

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Table S4. FDCA catalysed glucose to HMF

Entry	Catalyst	Reaction time (h)	Glucose Conversion (%)	HMF Yield (%)
1	FDCA + Sn-Beta	0.5	99	23
2	FDCA + Sn-Beta	1	100	25
3	FDCA + Sn-Beta	2	100	30
4	FDCA + Sn-Beta	5	100	26
5	FDCA + AlCl ₃	0.5	100	14
6	FDCA + AlCl ₃	1	100	15
7	FDCA + AlCl ₃	2	100	20
8	FDCA + AlCl ₃	5	100	36

Reaction Conditions: 1 mmol glucose, 1 mmol FDCA, AlCl₃ (0.05 mmol), or Sn-Beta (0.1 g), *i*PrOH/H₂O (4.85/0.15 ml), 170 °C.
