Electronic Supplementary Information for

Catalytic conversion of 5-hydroxymethylfurfural into 2,5-furandiamidine dihydrochloride

Xiuquan Jia,^{a,b}⁺ Jiping Ma,^a⁺ Min Wang,^a Hong Ma,^a Chen Chen^a and Jie Xu^{*a}

^aState Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy,

Dalian 116023, P. R. China. E-mail: xujie@dicp.ac.cn.

^bUniversity of the Chinese Academy of Sciences, Beijing 100049, P. R. China.

‡ These authors contributed equally.

Contents:

- 1. Materials and Characterization (pp.2-5)
- 2. General experimental procedure (pp. 6-7)
- 3. Products Analysis (pp.7)
- 4. Additional Results (pp.8-17)
- 5. GC, MS and NMR Traces (pp.18-23)

1. Materials and Characterization

1.1 Materials

All chemicals were of analytical grade and used as received unless otherwise stated. MeOH, aq. NH₃, Co₃O₄, Fe₂O₃, Al₂O₃, KMnO₄, MnSO₄, NH₄Cl and MnCl₂ were purchased from Tianjin Kermel Chemical Reagent Co. Ltd.. CeO₂ and Mn₃O₄ were obtained from Aladdin Chemistry Co. Ltd.. HMF was purchased from Wutong Aroma Chemicals Co. Ltd.. 2,5-Dicyanofuran was purchased from TCI Shanghai. γ -MnO₂ was obtained from Alfa Aesar. β -MnO₂ ^[S1] and δ -MnO₂ ^[S2] were prepared according to the literature procedures.

1.2 Preparation of β-MnO₂

β-MnO₂ was prepared according to the literature procedure (see below).^[S1] A 60 mL aqueous solution containing stoichiometric amount of MnSO₄ (18 mmol) and KMnO₄ (3 mmol) was loaded in a 100 mL Teflon-lined autoclave, which was sealed and maintained at 140 °C for 12 h. After naturally cooling to room temperature, the resulting solid was collected by centrifugation, washed repeatedly with distilled water, and finally dried overnight in air at 80 °C.

1.3 Preparation of δ -MnO₂

 δ -MnO₂ was prepared according to the literature procedure (see below).^[S2] An aqueous solution (A) was prepared by dissolving 0.04 mol of KMnO₄ and 1.2 mol of NaOH in 400 mL of water. Afterward, another aqueous solution (B) was prepared by

dissolving 0.112 mol of $MnCl_2 \cdot 4H_2O$ in 400 mL of water. Solution B was added dropwise to solution A with vigorous stirring in an ice bath. The resulting precipitate was statically aged at room temperature for 1 day and then washed and dried at 90 °C.

1.4 Preparation of OMS-2

OMS-2 was prepared according to the literature procedure (see below).^[S3] KMnO₄ (5.89 g) in water (100 mL) was added to a solution of $MnSO_4 \cdot H_2O$ (8.8 g) in water (30 mL) and conc. HNO₃ (3 mL). The solution was refluxed at 100 °C for 24 h. Then, the dark brown solid was filtered off, washed with a large amount of water (ca. 3 L), and dried at 120 °C to afford 8.2 g of OMS-2.

- [S1] F. Y. Cheng, T.R. Zhang, Y. Zhang, J. Du, X. P. Han, J. Chen, Angew. Chem. Int. Ed. 2013, 52, 2474.
- [S2] O. Ghodbane, J.-L. Pascal, and F. Favier, ACS Appl. Mater. Interfaces. 2009, 1, 1130.
- [S3] R. N. DeGuzman, Y.-F. Shen, E. J. Neth, S. L. Suib, C.-L. O'Young, S. Levine, J. M. Newsam, *Chem. Mater.* 1994, 6, 815.

1.5 Characterization of Catalysts

The X-ray powder diffraction (XRD) patterns were obtained using Rigaku D/Max 2500/PC powder diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm) at 40 kV and 200 mA in a scanning rate of 5 °/min.



Figure S1 XRD patterns of β -MnO₂.



Figure S2 XRD patterns of γ -MnO₂.



Figure S3 XRD patterns of δ -MnO₂.



Figure S4 XRD patterns of (a) fresh OMS-2; and (b) OMS-2 after the sixth use.

2. General experimental procedure

Catalytic reactions were performed in a 20 mL stainless steel autoclave equipped with a magnetic stirrer, a pressure gauge, and automatic temperature control apparatus. The reactor was connected to an oxygen cylinder for reaction pressure. In a typical experiment, HMF (31.5 mg, 0.25 mmol), aq. NH₃ (120 µL, 6 equiv.), MeOH (5 mL) and OMS-2 (0.1 g) were loaded into the reactor. After sealing and charging with O₂ (0.5 MPa), the autoclave was heated to the desired temperature (30 °C). After reaction, the autoclave was cooled. The solution was separated by centrifugation and analyzed by GC using the internal standard method. The catalyst was washed with alcohol 5 times and then regenerated at 250 °C in air for 7 h for the cycle experiments. To show the practical value of the present procedure, a gram-scale transformation of HMF (1.26 g, 10 mmol; 40-fold scale) was carried out. After reaction, the solution was separated by centrifugation. MeOH was removed by rotary evaporator and dichloromethane (20 mL) was added. The resulting yellow solution was washed with brine $(3 \times 5 \text{ mL})$ and dried by anhydrous sodium sulfate. The crude product was obtained after evaporation of dichloromethane. Then it was recrystallized from a MeOH-H₂O mixture giving white needles (1.34 g, 0.74 mmol) with a melting poit of 101-103 °C. ¹H NMR (400 MHz, [D₆]DMSO, 298 K): δ = 9.02 (2 H), 6.97 (2 H), 3.79 ppm (6 H); ¹³C NMR: δ = 53.10, 113.14, 146.25, 158.18 ppm (see Fig. S27-28). The elemental analysis of dimethyl furan-2,5-dicarboximidate is as follows: Found: C, 54.81; H, 5.62; N, 14.95. Calc. for C₈H₁₀N₂O₃: C, 52.74; H, 5.53; N, 15.38%.

2,5-Furandiamidine dihydrochloride was prepared by reaction of the methanolic

solution of dimethyl furan-2,5-dicarboximidate prepared *in situ* with 2 equivalent of ammonium chloride to the total imidate groups present. The reaction mixture was stirred for 0.5 h at 60 °C. After reaction, the solution was separated by centrifugation. MeOH was removed by rotary evaporator. The residue was extracted with alcohol to remove the residual ammonium chloride by centrifugation. The dissolved diamidine salts was recrystallized from alcohol-petroleum ether mixture giving yellow powder. ¹H NMR (400 MHz, [D₆]DMSO, 298 K): $\delta = 10.03$ (4 H), 9.57 (4 H), 8.07 ppm (2 H); ¹³C NMR: $\delta = 120.01$, 144.60, 153.22 ppm (see Fig. S29-30). The elemental analysis of 2,5-furandiamidine dihydrochloride is as follows: Found: C, 28.84; H, 5.39; N, 21.41. Calc. for C₆H₁₀N₄OCl₂·2H₂O: C, 27.60; H, 5.40; N, 21.46%.

3. Products Analysis

The products were identified by Agilent 6890N GC/5973MS as well as by comparison with the retention times to corresponding standards in GC traces. Gas chromatography measurements were conducted on Agilent 7890A GC with autosampler and a flame ionization detector. HP-5 capillary column (30 m × 530 μ m × 1.5 μ m) was used for separation of reaction mixtures. The temperature of the column was initially kept at 100 °C for 5 min, and then was increased at a rate of 20 °C min⁻¹ to 220 °C and kept for 10 min. 1,3,5-Trimethylbenzene was used as the internal standard. Elemental analysis of dimethyl furan-2,5-dicarboximidate and 2,5-furandiamidine dihydrochloride were conducted on HORIBA EMGA-930/EMIA-8100 analyzer.

The conversion of substrates and yield of products were evaluated as below.

Conversion = $(1 - \frac{\text{Moles of substrate}}{\text{Moles of substrate loaded initially}}) \times 100\%$

 $Yield = (\frac{Moles of product}{Moles of substrate loaded initially}) \times 100\%$

4. Additional Results



Figure S5 Synthesis of dimethyl furan-2,5-dicarboximidate from HMF over different metal oxides. Reaction conditions: 0.25 mmol HMF, 0.1 g catalyst, 120 μ L aq. NH₃ (6 equiv.), 5 mL MeOH, 0.5 MPa O₂, 30 °C, 12 h.

Table S1 Oxidative synthesis of DFF from HMF over different manganese oxides. ^[a]								
Entry	Catalyst	Conv. [%]	Yield [%]					
1	β-MnO ₂	41	36					
2	δ -MnO ₂	53	40					
3	γ -MnO ₂	94	54					
4 ^[b]	OMS-2	97	97					
[a] Reaction conditions: 0.25 mmol HMF, 0.1 g catalyst, 5 mL MeOH, 0.5 MPa O ₂ , 30 °C, 12 h. [b] 1.5 h.								



Figure S6 Image of dimethyl furan-2,5-dicarboximidate.



Figure S7 Recycling test of OMS-2: 0.25 mmol HMF, 0.1 g catalyst, 120 μ L aq. NH₃ (6 equiv.), 5 mL MeOH, 0.5 MPa O₂, 30 °C, 30 h.



polymers such as methanediamines as main products

Scheme S1 Main products derived from DFF and NH₃ over different manganese dioxides.



Figure S8 Kinetic profile of DFF conversion characterized by real-time in situ React FT-IR. Reaction conditions: 1.25 mmol DFF, 10 mL MeOH, 0.5 g OMS-2, 0.5 MPa O2, 30 °C, adding a.q. NH₃ at 0.5 h.



Figure S9 Kinetic profile of DFF conversion characterized by real-time in situ React FT-IR. Reaction conditions: 1.25 mmol DFF, 10 mL MeOH, 0.5 MPa O_2 , 30 °C, adding a.q. NH₃ at 0.5 h, removing polymer on the pobe at 4.1 h.

manganese oxides. ^[a]									
Entry	Catalyst	Yield [%]							
		4	5	6					
1	β-MnO ₂	16	2	1					
2	δ -MnO ₂	-	-	-					
3	γ -MnO ₂	-	6	-					
4	OMS-2	-	72	9					
[a] Reaction conditions: 0.25 mmol DFF, 0.1 g catalyst, 120 μL aq. NH ₃ (6 equiv.), 5 mL MeOH, 0.5 MPa O ₂ , 30 °C, 12 h. Conv. > 99%.									



Figure S10 GC trace for products from DFF. Reaction conditions: 0.25 mmol DFF,

0.1 g catalyst, 120 μL aq. NH_3 (6 equiv.), 5 mL MeOH, 0.5 MPa O_2, 30 °C, 0.5 h.



Figure S11 Kinetic profile of DFF conversion characterized by real-time in situ React FT-IR. Reaction conditions: 1.25 mmol DFF, 10 mL MeOH, 0.5 g β -MnO₂, 0.5 MPa O₂, 30 °C, adding a.q. NH₃ at 0.5 h, removing polymer on the pobe at 4.1 h.



Figure S12 Kinetic profile of DFF conversion characterized by real-time in situ React FT-IR. Reaction conditions: 1.25 mmol DFF, 10 mL MeOH, 0.5 g δ -MnO₂, 0.5 MPa O₂, 30 °C, adding a.q. NH₃ at 0.5 h, removing polymer on the pobe at 4.1 h.



Figure S13 Kinetic profile of DFF conversion characterized by real-time in situ React FT-IR. Reaction conditions: 1.25 mmol DFF, 10 mL MeOH, 0.5 g γ -MnO₂, 0.5 MPa O₂, 30 °C, adding a.q. NH₃ at 0.5 h, removing polymer on the pobe at 4.1 h.



Scheme S2 Stability test of dimethyl furan-2,5-dicarboximidate.

Table mangar	S3 Synthesis nese oxides. ^[a]	of 5 from	2,5-dicyanofuran	over	different	
Entry	Catalyst	Yield [%]				
		4	5	6		
1	-	1	98	-		
2	β -MnO ₂	7	85	-		
3	δ-MnO ₂	2	84	-		
4	γ -MnO ₂	2	96	-		
5	OMS-2	4	93	3		

[a] Reaction conditions: 0.25 mmol 2,5-dicyanofuran, 0.1 g catalyst, 120 μL aq. NH₃ (6 equiv.), 5 mL MeOH, 0.5 MPa O₂, 30 °C, 12 h. Conv. > 99%.



Figure S14 Kinetic profile of HMF conversion characterized by real-time in situ React FT-IR with wavenumber ranging from 1170-1285 cm⁻¹. Reaction conditions: 1.25 mmol HMF, 10 mL MeOH, 30 °C, then 600 μ L aq. NH₃ (6 equiv.) added at 0.5 h, 0.5 g OMS-2 and 0.5 MPa O₂ charged at 1.5 h.



Figure S15 Kinetic profile of HMF conversion characterized by real-time in situ React FT-IR with wavenumber ranging from 1610-1700 cm⁻¹. Reaction conditions: 1.25 mmol HMF, 10 mL MeOH, 30 °C, then 600 μ L aq. NH₃ (6 equiv.) added at 0.5 h, 0.5 g OMS-2 and 0.5 MPa O₂ charged at 1.5 h.



Figure S16 Kinetic profile of 2,5-dicyanofuran conversion to imidate characterized by real-time in situ React FT-IR. Reaction conditions: 1.25 mmol 2,5-dicyanofuran, 10 mL MeOH, 600 μ L aq. NH₃ (6 equiv.), 0.5 g OMS-2, 30 °C.



Figure S17 Kinetic profile of 2,5-dicyanofuran conversion to imidate characterized by real-time in situ React FT-IR. Reaction conditions: 1.25 mmol 2,5-dicyanofuran, 10 mL MeOH, 600 μ L aq. NH₃ (6 equiv.), 30 °C.



Figure S18 Relationship of peak height at 1197 ascribed to C-O stretching vibration of the imidate group and reaction time (t) of 2,5-dicyanofuran addition with MeOH. Reaction conditions: (a): 1.25 mmol 2,5-dicyanofuran, 10 mL MeOH, 600 μ L aq. NH₃ (6 equiv.), 0.5 g OMS-2, 30 °C; (b) is the same as (a) except without OMS-2 was added.

5. GC, MS and NMR Traces



Figure S19 GC trace for products from HMF (Table 1, entry 4 in main text).

The compounds correspond to retention time: 4.285 min (internal standard), 5.625 min (2), 5.744 min (4), 6.013 min (hexamethylenetetramine), 6.632 min (3), 7.058 min (5), 8.204 min (6).

MS: m/z (%): 123 (100) [M+], 106 (40), 68 (69), 51 (25), 31 (13)



Figure S20 Mass spectrum of 2.

MS: m/z (%): 155 (38) [M+], 125 (52), 94 (100), 69 (28), 41 (34)



Figure S21 Mass spectrum of 3.

MS: m/z (%): 150 (32) [M+], 119 (100), 92 (85), 64 (70), 37 (27)



Figure S22 Mass spectrum of 4.

MS: m/z (%): 182 (67) [M+], 151 (88), 138 (64), 94 (100), 58 (18)



Figure S23 Mass spectrum of 5.

MS: m/z (%): 168 (26) [M+], 138 (43), 124 (45), 94 (100), 39 (19)



Figure S24 Mass spectrum of 6.

MS: m/z (%): 125 (23) [M+], 94 (47), 41 (24), 32 (100)



Figure S25 Mass spectrum of aldimine.



Figure S26 GC spectrum of isolated 5.



Figure S27 ¹H NMR spectrum of isolated 5.



Figure S28 ¹³C NMR spectrum of isolated 5.



Figure S29 ¹H NMR spectrum of isolated 2,5-furandiamidine dihydrochloride.



Figure S30 ¹³C NMR spectrum of isolated 2,5-furandiamidine dihydrochloride.