Boosting the Activity of Catalytic Oxidation of 5-Hydroxymethylfurfural to 2,5-Diformylfuran Over Nitrogen-Doped Manganese Oxide Catalysts with a Strong Nonmetal-Metal Oxide Interaction

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S1 Experimental Section

S1.1 Materials

Oxalic acid dehydrate (AR grade), manganese (II) acetate tetrahydrate (AR grade) and cobalt (II) acetate tetrahydrate (99%) were purchased from Adamas Reagent, Ltd. (China). 5-Hydroxymethylfurfural (99%), MnO (99.5% metal basis), and polyvinylpyrrolidone (PVP, mw=1300000) and MnO_2 (99.5% metal basis) were obtained from Aladdin Industrial Corporation (China). Other reagents were purchased from Other commercially available reagents were purchased from Acros, Sigma-Aldrich and Alfa Aesar Chemical Company.

S1.2 Synthesis of N-MnO_2 catalyst

N-MnO_2 was prepared as following procedure: A homogeneous mixture was prepared by vigorously stirring urea (20-100 mmol), ultrapure water (30 mL, 18 mΩ/cm), ethylene glycol (30 mL), manganese (II) acetate tetrahydrate (20 mmol) and PVP (1 mmol) at room temperature. The mixtures were stirred for 1 h at room temperature and transferred into an autoclave for hydrothermal crystallization at 180 °C for 5h. After filtration, a powder was dried at 80 °C for 12h. Then the final black catalysts were obtained by calcination under air atmosphere at 350 °C for 4h. The obtained catalysts were denoted as N-MnO_2(X), where X refers to 20, 40, 60, 80 OR 100 of the urea used.

S1.3 Synthesis of N-MeO_X catalyst

N-CeO_2, N-CuO, N-FeO_x amd N-PdO was prepared as following procedure: A homogeneous mixture was prepared by vigorously stirring urea (80 mmol), ultrapure water (30 mL, 18 mΩ/cm), ethylene glycol (30 mL), metal salt (20 mmol) and polyvinylpyrrolidone (PVP, mw=1300000, 1 mmol) at room temperature. The mixtures were stirred for 1 h at room temperature and transferred into an autoclave for hydrothermal crystallization at 180 °C for 5 h. After filtration, a powder was dried at 80 ºC for 12 h. Then the final black catalysts were obtained by calcination under air atmosphere at 350 ºC for 4h. The obtained catalysts were denoted as N-MeO_X (Me, Me=Ce, Cu, Fe).

S1.4 Synthesis of Mn_2O_3 catalyst

Mn_2O_3 was prepared as following procedure: A homogeneous mixture was prepared by vigorously stirring oxalic acid dehydrate (90 mmol), ultrapure water (25 mL, 18 mΩ/cm) and ethanol (25 mL) at room temperature. A solution consisting of ultrapure water (25 mL), manganese (II) acetate tetrahydrate (20 mmol) was added into the mixture under vigorously stirring to form MnO_x precursors. The precursors were stirred for 5 h at room temperature, aged for 10 h at 50 ºC. After filtration, a pink powder was dried at 80 ºC for 10 h. Then the final black catalysts were obtained by calcination under air atmosphere at 500 ºC for 4h. The obtained catalysts were denoted as Mn_2O_3.

S1.5 Synthesis of Co_3O_4 catalyst

Co_3O_4 was prepared as following procedure: A homogeneous mixture was prepared by vigorously stirring oxalic acid dehydrate (90 mmol), ultrapure water (75 mL, 18 mΩ/cm) and ethanol (75 mL) at room temperature. A solution consisting of ultrapure water (75 mL), cobalt (II) acetate tetrahydrate (30 mmol) was added into the mixture under vigorously stirring to form CoO_x precursors. The precursors were stirred for 6 h at room temperature, aged for 10 h at 50 ºC. After filtration, a pink powder was dried at 80 ºC for 12 h. Then the final black catalysts were obtained by calcination under air atmosphere at 350 ºC for 4h. The obtained catalysts were denoted as Co_3O_4.

S1.6 Synthesis of P-N-MnO_2(80) catalyst

N-MnO_2 was prepared as following procedure: A homogeneous mixture was prepared by vigorously stirring urea (80 mmol), ultrapure water (30 mL, 18 mΩ/cm), ethylene glycol (30 mL), manganese (II) acetate tetrahydrate (20 mmol) and PVP (1 mmol) at room temperature. The mixtures were stirred for 1 h at room temperature and transferred into an autoclave for hydrothermal crystallization at 180 °C for 5 h. After filtration, a powder was dried at 80 ºC for 12 h. Then the final black catalysts were obtained by calcination under oxygen atmosphere at 350 ºC for 4h. The obtained catalysts were denoted as P-N-MnO_2(80).

S1.7 H_2-TPR experiments

H_2-TPR experiments: Typically, 20 mg samples were placed in a quartz cell and then heated in a 5% H_2/N_2 flow (30 mL/min). The temperature ramped from 298 to 923 K at a rate of 10 K/min. The consumption of H_2 was calibrated by the reduction in pure CuO powder.

S1.8 General procedure of the oxidation of HMF

Typically, the mixtures of HMF (60 mg, 0.5 mmol), catalyst (150 mg), and toluene (2 mL) were added in a 10 mL Schlenk tube at 25±2 °C for 6-8h, the oxygen with flux of 8 mL/min was bubbled in the tube by Internal pipeline. Afterwards, the catalyst was separated from the mixture by filtration. The crude products without further purification, and their reactant conversions and product selectivities were determined by a chromatograph-mass spectrometer (Agilent 7890B, USA), and ^1H NMR spectra recorded on a BrukerALX400 spectrometer operating at 400 MHz.

S1.9 Control experiments

Reaction under nitrogen atmosphere: Mixtures of HMF (60 mg, 0.5 mmol) and toluene (2 mL) were added in a 10 mL Schlenk tube at 25±2 °C for 6-8h, the nitrogen with flux of 8 mL/min was bubbled for 1 h before adding N-MnO_2(80) catalyst (150 mg) in the tube by Internal pipeline. Afterwards, the catalyst was separated from the mixture by filtration. The crude products without further purification, and their reactant conversions and product selectivities were determined by a chromatograph-mass spectrometer (Agilent 7890B, USA), and the spent catalyst was dried under vacuum drying oven.

FTIR studies for CO_2 adsorption: 150 mg of N-MnO_2(80) was calcined at 350 °C for 2h under nitrogen atmosphere. Then cooling to room temperature, the as-prepared sample was placed under CO_2 atmosphere for 2h. The final sample sealed in a bottle for IR characterization.

FTIR studies for HMF adsorption: Mixtures of HMF (60 mg, 0.5 mmol), catalyst (150 mg), and toluene (2 mL) were added in a 10 mL Schlenk tube at 25±2 °C for 1 h, the oxygen with flux of 8 mL/min was bubbled in the tube by Internal pipeline. Afterwards, the catalyst was separated from the mixture by filtration and washed with toluene with 3-5 cycles for removing the physical adsorbed. And the spent catalyst was vacuum dried at 40 °C for 24 h before IR characterization.

S1.10 Characterization

Products were characterized by using ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectroscopy using $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. The mesoporous volumes and Brunauer-Emmett-Teller (BET) surface areas were determined by using a surface area and porosity analyzer (ASAP 2020, Micromeritics Inc., USA). Conversion of the reactant and selectivity of the product were obtained on a Agilent 7890B chromatography (Agilent, USA) equipped with a flame ionization detector and a HP-5 column (30 m×0.25 mm). The amounts of metal oxides element in samples were determined from ICP-AES (Varian 710-ES, Varian Co. Palo Alto, USA). Scanning electron microscope (SEM) images of the prepared catalysts were obtained on an SU8010 SEM (Hitachi, Japan). X-ray photoelectron spectroscopy (XPS) spectra were measured with a PHI-5000C ESCA system (Perkin-Elmer, USA) with Al Kα radiation (hν = 1486.6 eV) for the X-ray source; the binding energies were calibrated using C 1s as a reference set at 284.6 eV. Co and Mn k-edge adsorption spectra (EXAFS) were performed on the BL14W1 beamline at the Shanghai Synchrotron Radiation Facility (SSRF), Shanghai Institute of Applied Physics, China, operated at 3.5 GeV with injection currents of 140–210 mA, and the 1W1B beamline of the Beijing Synchrotron Radiation Facilityoperated at 200 mA and 2.2 GeV. On both beamlines, a Si(111) double-crystal monochromator was used to reduce the harmonic component of the monochrome beam. Transmission electron microscopy (TEM) was performed on a JEOL JEM 2100 microscope. The H_2-TPR of the catalysts was detected on an Auto Chem II 2920 with a thermal conductivity detector.

Table S1. Structural parameters of various catalysts**.**

Sample	S_{BET} (m^2/g)	S_{EXT} (m^2/g)	V_{meso} (cm^3/g)
MnO_2	11.2	2.2	0.01
Mn_2O_3	10.2	--	0.13
N-MnO_2(20)	108.4	109.7	0.25
N-MnO_2(40)	115.7	118.6	0.26
N-MnO_2(60)	103.5	104.7	0.26
N-MnO_2(80)	111.5	116.5	0.25
N-MnO_2(100)	118.5	125.0	0.26
P-N-MnO_2(80)	110.7	114.9	0.26

Table S2. Assignment of N 1s species in XPS profile.

Sample	Pyridinc N / eV	Pyrrolic N / eV	Graphitic N / eV
Reference[1]	398.6	400.0	401.0
N-MnO_2(80)	398.6	400.0	401.0

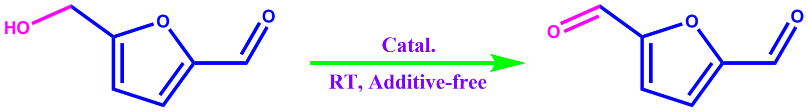
[1] Y. Sun, H. Ma, X. Jia, J. Ma, Y. Luo, J. Gao, J. Xu, *ChemCatChem* **2016**, *8*, 2907-2911.

Table S3 Assignment of Mn 2p species in XPS profile.

Sample	$Mn^{3+}(2p_{1/2})$ / eV	$Mn^{3+}(2p_{3/2})$ / eV	$Mn^{4+}(2p_{1/2})$ / eV	$Mn^{4+}(2p_{3/2})$ / eV
Reference[2]	653.1	641.2	654.2	643.2
MnO_2	652.6	641.1	653.7	642.3
N-MnO_2(80)	652.7	641.1	653.8	642.4
Spent N-MnO_2(80) under oxygen	652.3	640.8	653.3	642.2
Spent N-MnO_2(80) under Nitrogen	652.7	641.0	653.8	642.6

[2] T. Zhang, L. Zhang, X. Liu, Z. Mu and S. Xing, *Dalton Transactions*, **2019**, 48, 3045-3051.

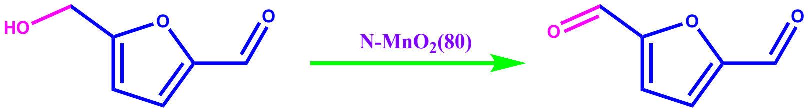
Table S4. Catalytic activity of oxidation of HMF to DMF over various catalysts.



Entry	Catalyst	Conv.%	Sel.%	Yield%	TOF(h^{-1})
1	—	n.d.[a]	—	—	N/A
2	Mn_2O_3	n.d.	—	—	N/A
3	MnO_2	n.d.	—	—	N/A
4	N-MnO_2(40)	99.1	>99.9	99.1	0.05
5	N-MnO_2(60)	99.6	>99.9	99.6	0.05
6	N-MnO_2(80)	100	>99.9	>99.9	0.05
7	N-MnO_2(100)	98.3	>99.9	98.3	0.05
8[b]	N-MnO_2(80)	100	>99.9	>99.9	0.19
9	N-CoO_x	15.7	>99.9	15.7	1×10^{-3}
10	N-CeO_x(80)	11.7	>99.9	11.7	1×10^{-3}
11	N-FeO_x(80)	9.1	>99.9	9.1	1×10^{-3}
12	N-CuO_x(80)	15.5	>99.9	15.5	1×10^{-3}

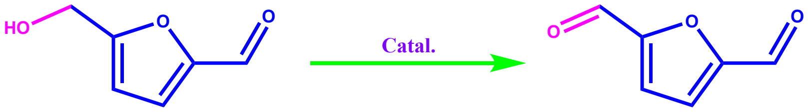
Reaction conditions: HMF (0.5 mmol), catalyst (150 mg), MeCN OR toluene (2 mL), room temperature (25±2 °C), 6 h. [a]n.d. refers to no prodcut detected by GC. [b]Reacted using 100 mg catalyst under 60 °C for 2 h. TOF=TON/time (h), and TON refers to number of moles of HMF converted to DFF per mol of catalyst.

Table S5. Catalytic performance of N-MnO$_2$(80) under different conditions.



Entry	Catalyst mass/mg	Solvent	oxidant	Temperature /°C	Time /h	Conv. /%	Sel. /%	Yield /%
1	40	toluene	1 bar O_2	60	2	31.1	>99.9	31.1
2	80	toluene	1 bar O_2	60	2	61.1	>99.9	61.1
3	100	toluene	1 bar O_2	60	2	70.6	>99.9	70.6
4	150	toluene	1 bar O_2	60	2	>99.9	>99.9	>99.9
5	150	toluene	1 bar O_2	25	2	65.3	>99.9	65.3
6	150	toluene	1 bar O_2	25	4	84.4	>99.9	84.4
7	150	toluene	1 bar O_2	25	6	>99.9	>99.9	>99.9
8	150	toluene	1 bar N_2	25	6	22.1	>99.9	22.1
9	150	water	1 bar O_2	25	6	60.1	>99.9	60.1
10	150	DMSO	1 bar O_2	25	6	73.1	>99.9	73.1
11	150	MeCN	1 bar O_2	25	6	98.3	>99.9	98.3

Table S6. A Comparison of catalytic performance of N-MnO$_2$(80) catalyst with the previously typical catalysts.



Entry	Catalyst	Additive/oxidant	Temperature /°C	Time /h	Conv. /%	Sel. /%	Yield /%	TOF /h^{-1}	Ref
1	N-MnO$_2$(80)	—/8 mL/min O_2	25	6	100	>99.9	>99.9	0.05	This work
2	N-MnO$_2$(80)	—/8 mL/min O_2	60	2	100	>99.9	>99.9	0.19	This work
3	5% Mn/CoO$_x$	—/1 bar Air	130	4	80	96	76.8	0.18	[3]
4	Rh/C	8 MPa CO_2	150	2	100	100	100	—	[4]
5	α-CuV$_2$O$_6$	—/1 bar O_2	130	3	>99.9	>99.9	>99.9	—	[5]
6	f-Ce$_9$Mo$_1$O$_\delta$	—/10 mL/min O_2	120	8	100	>99.9	>99.9	—	[6]
7	Graphene oxide	TEMPO/1 bar Air	100	18	100	99.6	99.6	—	[7]
8^b	MgO●CeO$_2$	—/9 bar O_2	100	15	100	>99.9	>99.9	0.19	[8]
9	FeN$_x$/C-900	—/5 bar O_2	100	10	99.5	97.3	96.8	7	[9]

[3] S. Biswas, B. Dutta, A. Mannodi-Kanakkithodi, R. Clarke, W. Song, R. Ramprasad, S. L. Suib, *Chemical Communications* **2017**, *53*, 11751-11754.

[4] M. Chatterjee, T. Ishizaka, A. Chatterjee, H. Kawanami, *Green Chemistry* **2017**, *19*, 1315-1326.

[5] W. Hou, Q. Wang, Z. Guo, J. Li, Y. Zhou, J. Wang, *Catalysis Science & Technology* **2017**, *7*, 1006-1016.

[6] Z. Yang, W. Qi, R. Su, Z. He, *ACS Sustainable Chemistry & Engineering* **2017**, *5*, 4179-4187.

[7] G. Lv, H. Wang, Y. Yang, T. Deng, C. Chen, Y. Zhu, X. Hou, *ACS Catalysis* **2015**, *5*, 5636-5646.

[8] M. Ventura, F. Lobefaro, E. de Giglio, M. Distaso, F. Nocito, A. Dibenedetto, *ChemSusChem* **2018**, *11*, 1305-1315.

[9] J. Zhang, S. Nagamatsu, J. Du, C. Tong, H. Fang, D. Deng, X. Liu, K. Asakura and Y. Yuan, *J. Catal.*, **2018**, 367, 16-26.

Table S7. EXAFS fitting parameters at the Mn K-edge for various samples (S_0^2=0.813).

Sample	Shell	N^a	R(Å)^b	σ^2(Å^2)^c	ΔE_0(eV)^d	R factor
Mn foil	Mn-Mn	12	2.66	0.0027	8.0	0.0338
	Mn-Mn	4	2.80	0.0027		
MnO	Mn-O	6	2.19	0.0087	-8.3	0.0001
	Mn-Mn	12	3.13	0.0086		
MnO_2	Mn-O	6	1.89	0.0013	2.2	0.0055
	Mn-Mn	6	2.87	0.0068		
	Mn-O	6	3.37	0.0013		
	Mn-Mn	12	3.45	0.0068		
	Mn-O	6	3.58	0.0013		
Mn_2O_3	Mn-O	5.4	1.92	0.0029	-3.7	0.0006
	Mn-Mn	12.8	3.11	0.0074		
	Mn-O	7.0	3.59	0.0074		
N-MnO_2(80)	Mn-O	5.9	1.90	0.0026	-3.1	0.0014
	Mn-Mn	4.0	2.86	0.0075		
	Mn-O	4.2	3.41	0.0026		
	Mn-Mn	4.3	3.48	0.0075		
	Mn-O	3.9	3.70	0.0026		

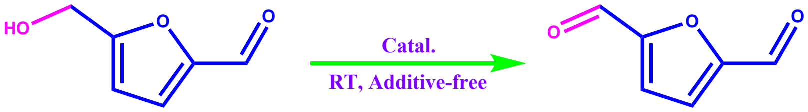
$^a N$: coordination numbers; $^b R$: bond distance; $^c \sigma^2$: Debye-Waller factors; ^{d} ΔE_0: the inner potential correction. R factor: goodness of fit. S_0^2 was set to 0.813, according to the experimental EXAFS fit of MnO reference by fixing CN as the known crystallographic value.

Table S8 Assignment of O1s species in XPS profile.

Sample	O_l / eV	O_d / eV	O_w / eV
Reference[10]	529.7	531.2	532.6
MnO_2	528.6	530.4	532.1
N-MnO_2(20)	529.8	531.2	532.2
N-MnO_2(40)	528.8	530.5	532.2
N-MnO_2(80)	528.8	530.7	532.2
Spent N-MnO_2(80) under oxygen	528.7	530.3	532.2

[10] J. Bao, X. Zhang, B. Fan, J. Zhang, M. Zhou, W. Yang, X. Hu, H. Wang, B. Pan, Y. Xie, *Angewandte Chemie* **2015,** *127*, 7507-7512.

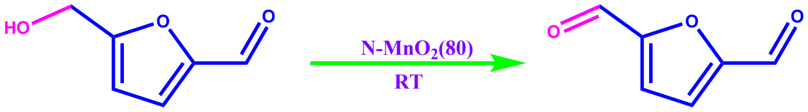
Table S9. Control experiments of the Catalytic activity of oxidation of HMF to DMF over various catalysts.



Entry	Catalyst	Conv.%	Sel.%	Yield%	TOF(h^{-1})
1	N-MnO_2(20)	62.5	>99.9	62.5	0.03
2	P-N-MnO_2(80)	91.8	>99.9	91.8	0.04
3[a]	MnO_2(80)	22.1	>99.9	22.1	0.01

Reaction conditions: HMF (0.5 mmol), catalyst (150 mg), toluene (2 mL), room temperature (25±2 °C), 6 h. [a]Reaction proceed under nitrogen atmosphere.

Table S10. Control experiments of the Catalytic activity of oxidation of HMF to DMF over MnO_2(80).



Sample	1		2	
Additive	—	BHT[a]	—	BHT
Time	2h	Another 2h	1h	Another 3h
Yield/%	65.3	82.0	46.2	85.5

Reaction conditions: HMF (0.5 mmol), catalyst (150 mg), toluene (2 mL), room temperature (25±2 °C).
[a] BHT, 2,6-di-tert-butyl-e-methylphenol.

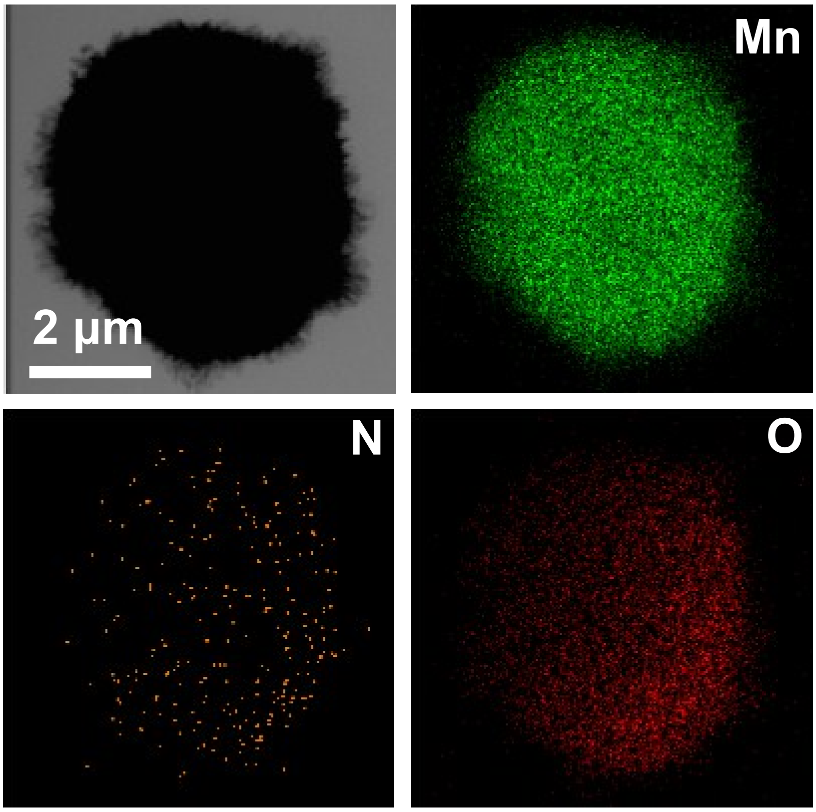


Figure S1. EDS mapping analysis of N-MnO_2(80) samples. Different colors are clearly observed in the EDS mapping images: orange-N-K, green-Mn-K and red-O-K.

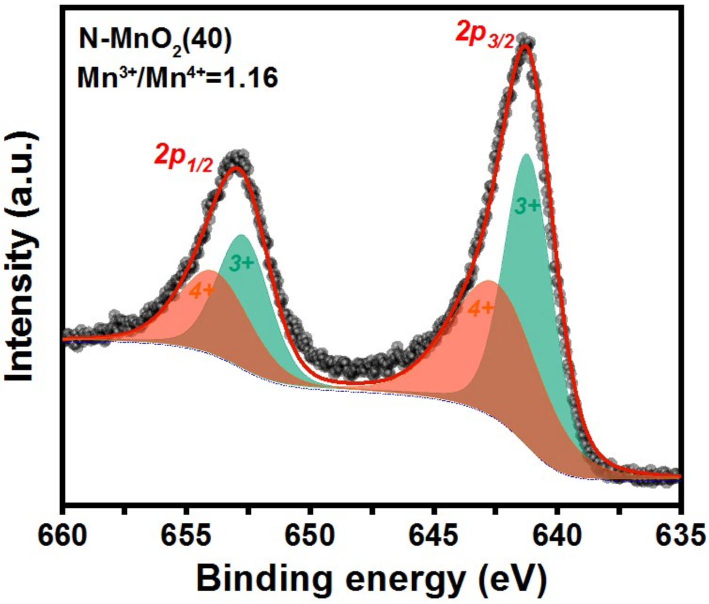


Figure S2. Mn 2P XPS spectrum of N-MnO_2(40) catalyst.

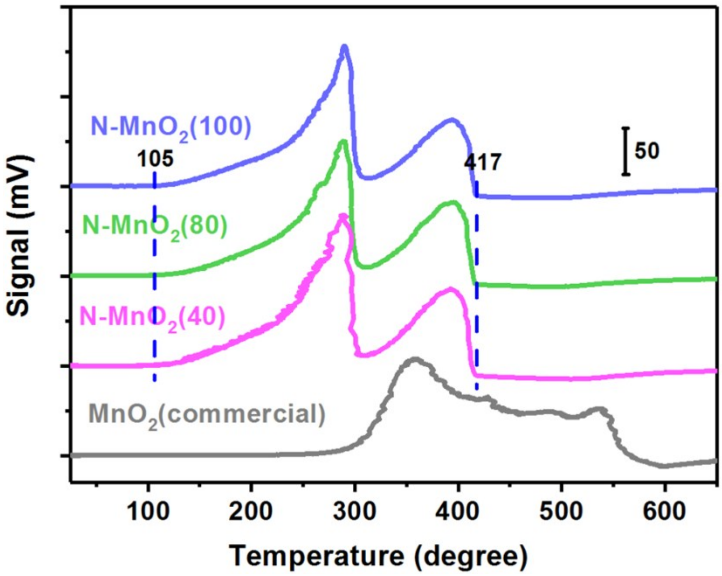


Figure S3. H_2-TPR profiles of N-MnO$_2$(40-100) and MnO$_2$ samples.

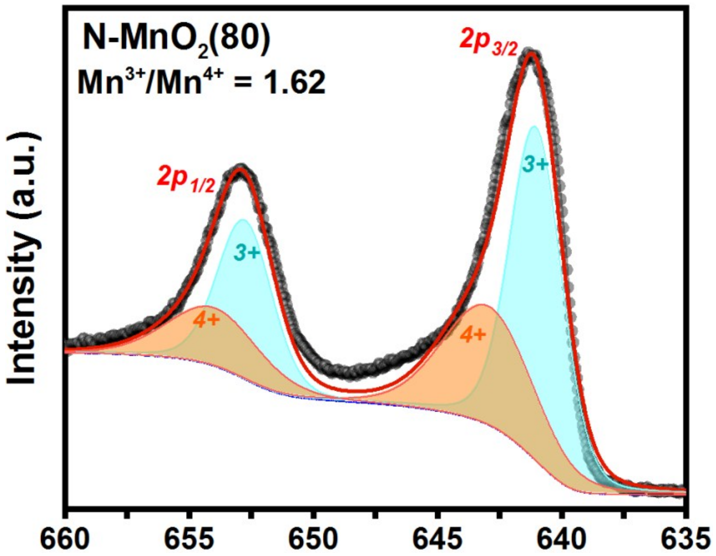


Figure S4. XPS core-level spectra of Mn 2p of spent N-MnO$_2$(80) catalyst under nitrogen atmosphere.

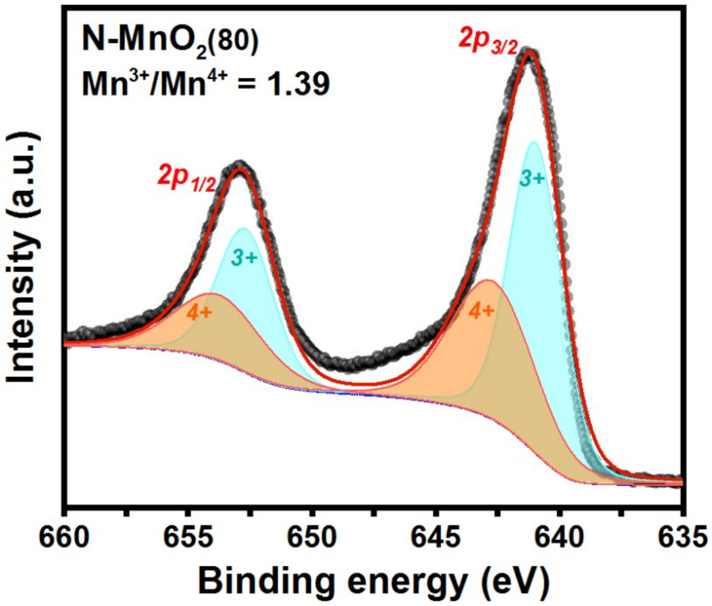


Figure S5. XPS core-level spectra of Mn 2p of spent N-MnO_2(80) catalyst under oxygen atmosphere.

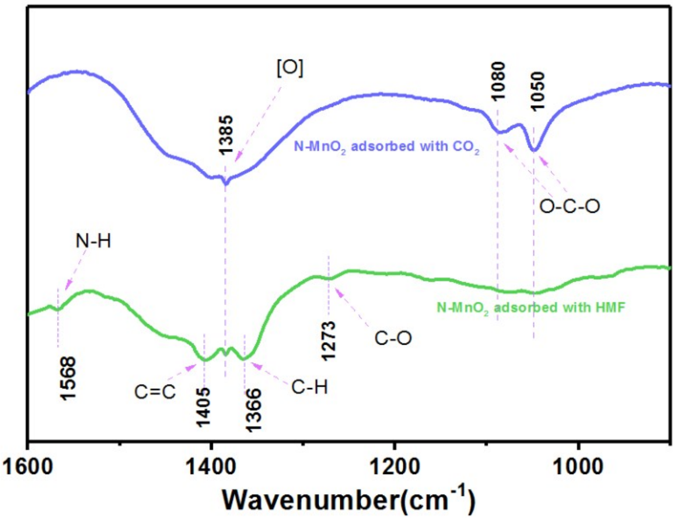
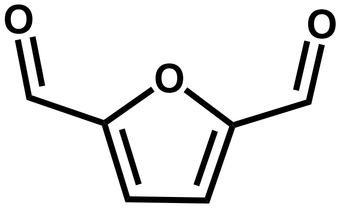


Figure S6. FT-IR profiles of N-MnO_2(80) adsorbed with HMF (under reaction condition) OR CO_2 (adsorption condition shown in experimental section).

S2 NMR data

(1) 2,5-Diformylfuran



White Solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.87 (s, 2H), 7.35 (d, *J* = 3.7 Hz, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 179.22 (s), 154.24 (s), 119.24 (s).