Supporting information for "Active, Selective, and Stable Manganese Oxide Supported Atomic Pd Catalyst for Aerobic Oxidation of 5-Hydroxymethylfurfural"

1. Calculation of TOF values based on the interface of Pd/MnO_2

For the interface as active sites, the TOF values can be calculated according to the reference [1] by the specific rate in terms of the length of the perimeter of Pd/MnO_2 by assuming half sphere of Pd nanoparticles. For atomic Pd catalyst, the number of Pd atoms at the perimeter can be obtained from the loading amount.

The TOF based on the interface length between Pd and MnO_2 can be calculated according to the equation (1).

$$TOF=r_{FDCA}\times n_{Pd}\times N_A/N_{Pd} \qquad (1)$$

n_{Pd} was the weight percentage of Pd in the catalyst. N_A is Avogadro constant.

The number of Pd atoms at the perimeter (N_{Pd}) can be calculated according to the equation (2).

$$N_{Pd} = L/d \qquad (2)$$

L can be calculated according to the equation (3).

$$L = 2\pi R\times N \qquad (3)$$

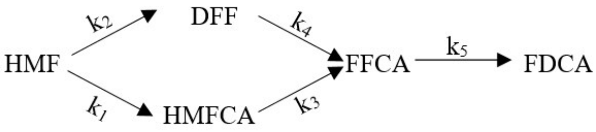
The number of Pd particle at the interface (N) can be calculated according to the equation (4).

$$N = 1.32\times 10^{19}\times(4/3\pi\, r^3/A)\,/(1/2\times 4/3\pi\, R^3) \qquad (4)$$

R and r represent the radius of Pd particle (~1.00 nm) and Pd atom (0.179 nm), respectively. A is the volume correction factor of 0.74 (space utilization of the closed-pack atoms in metal nanoparticles).

2. Reaction kinetic model for Pd-species-dependent HMF oxidation

By following the evolution of the reaction with time, different products were detected in Figure 4 (a and b) of the text. The catalytic oxidation of HMF can expressed from the proposed mechanistic model (Scheme 1) with the assumption that the first oxidation of HMF gives both DFF and HMFCA.



Scheme 1. Reaction pathway for HMF oxidation to FDCA.

Equations (1)−(5) give the rate equations for each species consumed and produced, where C_{HMF}, C_{HMFCA}, C_{FFCA}, and C_{FDCA} are the concentrations of each compound, and k_1−k_5 are the rate constants of each reaction step [2, 3].

$$\frac{dC_{HMF}}{dt} = -(k_1+k_2)C_{HMF} \tag{1}$$

$$\frac{dC_{HMFCA}}{dt} = k_1 C_{HMF} - k_3 C_{HMFCA} \tag{2}$$

$$\frac{dC_{DFF}}{dt} = k_2 C_{HMF} - k_4 C_{DFF} \tag{3}$$

$$\frac{dC_{FFCA}}{dt} = k_3 C_{HMFCA} + k_4 C_{DFF} - k_5 C_{FFCA} \tag{4}$$

$$\frac{dC_{FDCA}}{dt} = k_5 C_{FFCA} \tag{5}$$

The least squares fitting algorithm of MATLAB lsqcurvefit was used to estimate the kinetic parameters, with the assumptions that:

1) the reaction temperature is regulated and assumed to be stable throughout the experiment at 100 ^{o}C;

2) the properties and the amount of the active species of the catalyst remain constant during the catalytic reaction the amount of the active species of the catalyst is constant;

3) the gem-diol form of the aldehyde group is unstable, and the equilibrium is shifted to carbonyl form;

4) all dehydrogenation reactions are irreversible;

5) the oxygen concentration is constant in the liquid phase and oxygen is sufficiently available.

Results

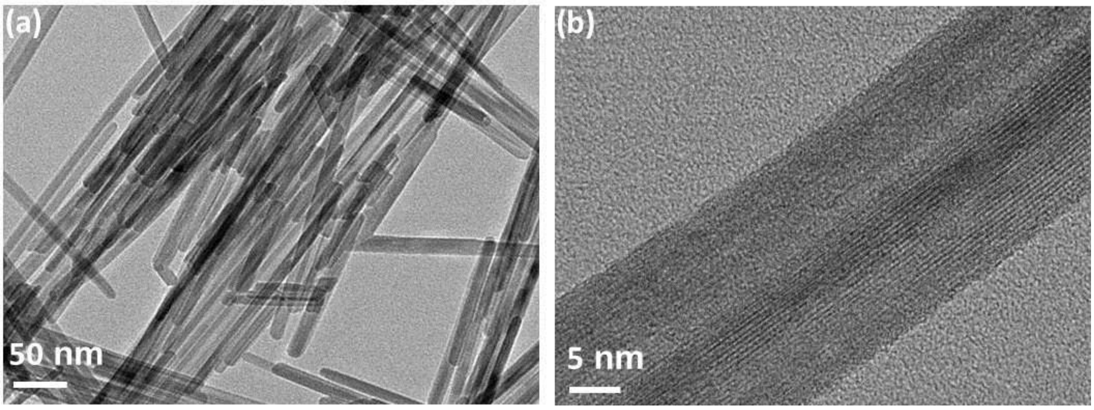


Figure S1. TEM (a) and HRTEM (b) image of α-MnO_2.

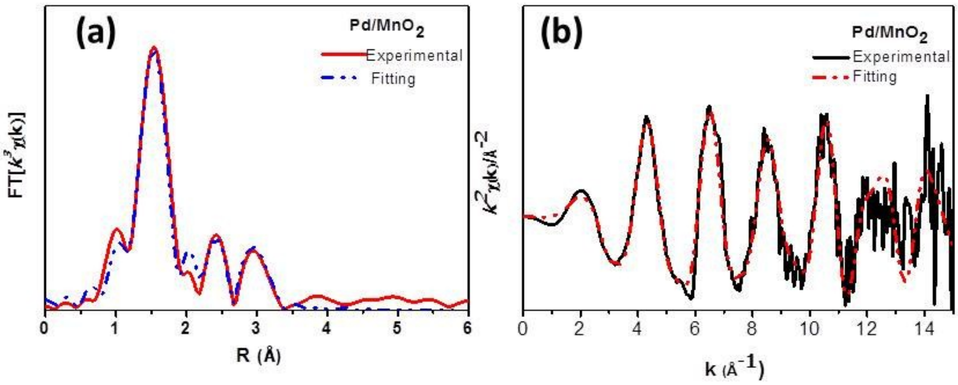


Figure S2. The magnitude R-space experimental EXAFS data and fitting curve of Pd/MnO_2 (a). The EXAFS oscillation functions at the Pd K-edge of Pd/MnO_2 (b).

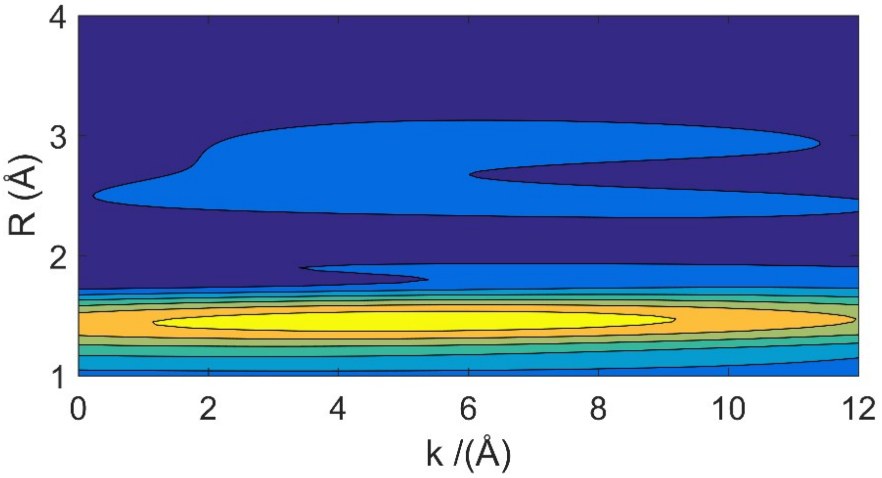


Figure S3. Full WT plot of Pd/MnO_2.

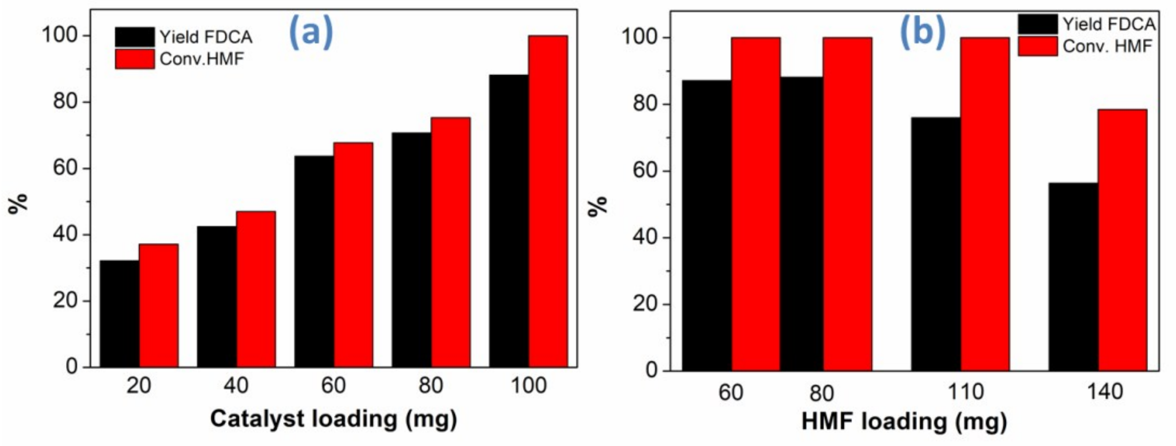


Figure S4. Effects of catalyst loading (a) and HMF dosage (b) on HMF oxidation. Reaction conditions: n(HMF): n(K_2CO_3) = 1:4, water as solvents, t=4 h, T=100 ^oC, with an O_2 flow rate of 25 mL.min^{-1}.

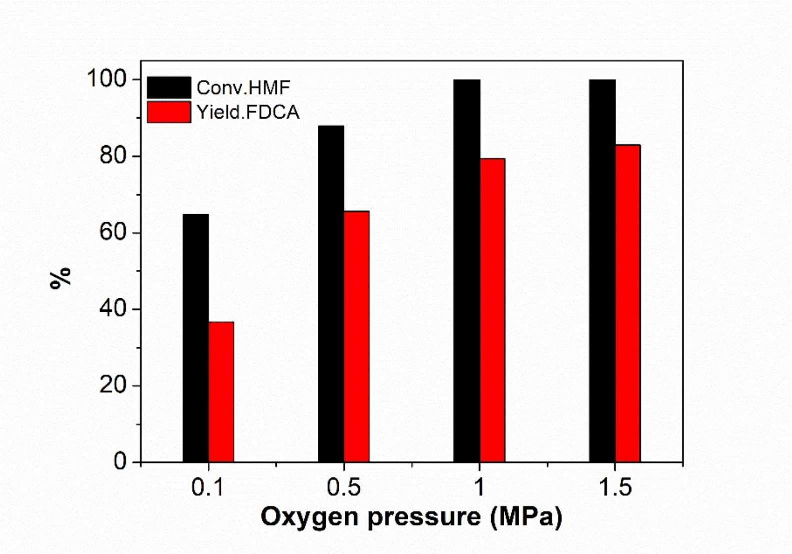


Figure S5. Influence of O_2 pressure on HMF oxidation. Reaction conditions: m(HMF)/m(cat.) = 0.8 mg, n(HMF): n(K_2CO_3) = 1:4, water as solvents, t=2 h, T=100 ^{o}C.

Table S1. Structural parameters of Pd foil, PdO, and Pd-MnO_2 SA samples derived from quantitative EXAFS curve-fitting using the IFEFFIT software.

Sample	Shell	N	R	ΔE_0(eV)	σ^2(10^{-3} Å^2)
Pd foil	Pd-Pd	12	2.82	0.7±0.5	4.6±0.5
PdO	Pd-O	4	2.01	-	-
	Pd-Pd	4	3.02	-	-
Pd/MnO_2	Pd-O	4.5±0.4	2.00±0.01	-1.4±1.3	2.4±1.0
	Pd-Pd	1.5±1.0	2.71±0.03	3.2±4.0	8.4±7.2
	Pd-Mn-1	1.5±0.6	3.00±0.04	3.2±4.0	7.0
	Pd-Mn-2	2.9±1.1	3.48±0.08	-4.4	7.0

Table S2. Pd 3d, O 1S, and Mn 3s spectrum analysis of MnO_2, Pd/MnO_2 and PdNP/MnO_2.

Sample	Pd $_{3d}$ (eV)	AOS of Mn $_{3s}$	O_{lat} (%)	O_{ad} (%)	O_{ad}/O_{lat} (%)
MnO_2	-	3.84	82.0	13.0	0.158
Pd/MnO_2	337.8	3.67	67.9	27.1	0.398
PdNP/MnO_2	336.9	3.80	69.8	20.7	0.297

Table S3. Kinetic parameters estimated for Pd-MnO_2 and PdNP/MnO_2 catalysts.

Catalyst	Rate constant (h^{-1})				
	k_1	k_2	k_3	k_4	k_5
Pd-MnO_2	0.13	0.45	1.42	6.74	1.72
PdNP/MnO_2	0.11	0.24	0.30	208.90	1.39

Table S4. Comparison of normalized FDCA Productivity by the number of bulk Pd atoms, exposed Pd atoms, and Pd-MnO_{2-x} interfacial sites.

Sample	Pd atoms (mmol. $h^{-1} \cdot g_{Pd}^{-1}$)	Exposed Pd atoms (mmol. $h^{-1} \cdot g_{Pd}^{-1}$)	Interfacial Pd-MnO_{2-x} sites (mmol. $h^{-1} \cdot g_{Pd}^{-1}$)
Pd/MnO_2	100.91	100.91	0.042
PdNP/MnO_2	45.57	75.07[a]	0.019

[a] normalized to number of Pd surface atoms calculated from average Pd particle size, determined by TEM.

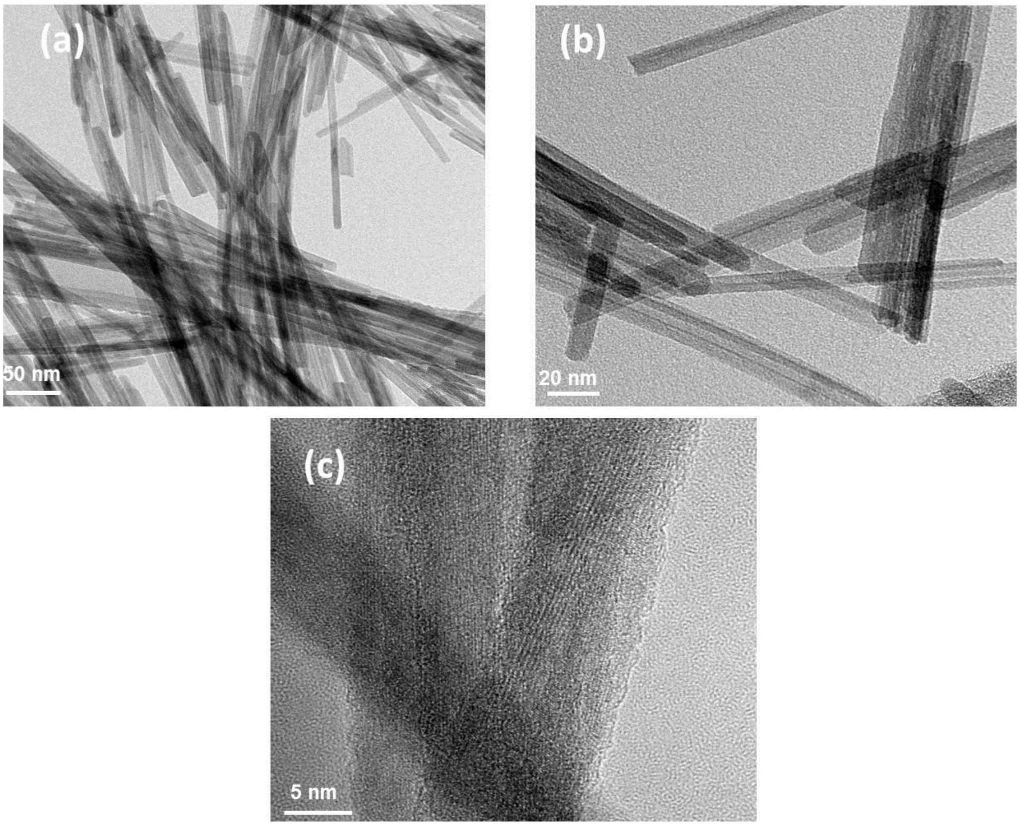


Figure S6. TEM images of Pd/MnO_2 after 5 catalytic cycles.

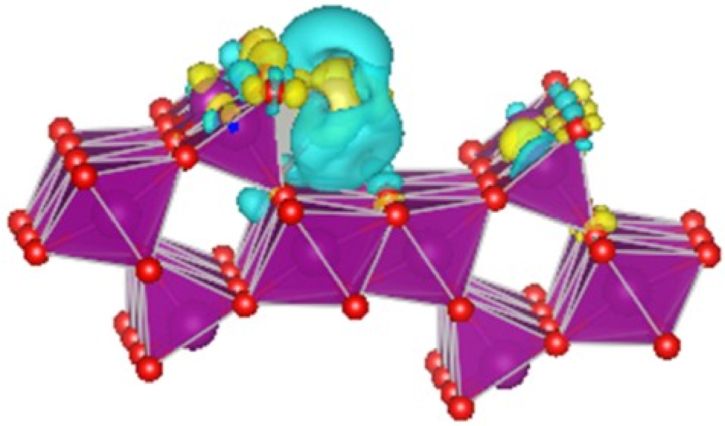


Figure S7. The charge density distribution of Pd-MnO_2. Mn atom (purple), Pd atom (silver) and O atom (red). The yellow and the blue color represent the accumulation and depletion of electrons, respectively.

References

[1] Y. Chen, J. Lin, L. Li, B.T. Qjao, J.Y. Liu, Y. Su, X.D. Wang, ACS Catal. 2018, 8, 859.
[2] H.A. Rass, N. Essayem, M. Besson, ChemSusChem, 2015, 8, 1206.
[3] A.B. Gawade, A.V. Nakhate, G.D. Yadav, Catal. Today, 2018, 309, 119.