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Supporting information

Temperature-responsive dissolution/recrystallization of Zn MOF enables the maximum efficiency and recyclability of catalysts

Xiao Chen,‡[a] Huan Zhang,‡[a,b] Mingkai Zhang,[a] Yong Zou,[a] Sai Zhang[a]* and Yongquan Qu[a]*

[a] Center for Applied Chemical Research, Frontier Institute of Science and Technology and School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an, 710049, China.
[b] Western Metal Materials Co., Ltd, Xi'an, 710201, China.
‡ These authors contributed equally to this work.
Email: yongquan@mail.xjtu.edu.cn and zhangsai058@mail.xjtu.edu.cn

Experimental section

Materials

All of the starting reagents for the synthesis and reactions were commercially available and were used as received. Zinc nitrate hexahydrate (Energy Chemical, 99%), Zinc formate (Alfa Aesar, 98%), DMF (N, N-Dimethylformamide, Sigma-Aldrich, 99.8%, with molecular sieves, water ≤ 50 ppm), D_2O (Energy Chemical, 99.9% D, for NMR). Formic acid (Sigma-Aldrich, ≥ 95%), Toluene (Chron Chemicals, 99.5%), Triethylamine (Energy Chemical, 99.5%), Methanol (Sigma-Aldrich, ACS reagent, ≥ 99.8%), n-heptane (Energy Chemical, 98.5%), Bromocresol green (Aladdin, ACS reagent, 95%).

Sample preparation and characterization

Synthesis of DMZnF MOFs

To synthesize the DMZnF MOFs, $Zn(NO_3)_2 \bullet 6H_2O$ (3 mmol) was added into the mixture of DMF (40 mL) and H_2O (1.676 mL). The solution was deaerated by bubbling argon through a needle for 20 min before heating. After reaction at 120 ^oC for 8 h, the white solids of ZnO was removed by hot filtration and the liquid supernatant was kept standing for 12 h in Ar atmosphere for crystal separating, and the MOFs were collected for the dehydrogenation reaction. The collected materials needed avoiding exposed to air.

Characterization

The structure and composition of the samples were monitored by powder X-ray diffraction (PXRD, Cu Kα radiation, Shimadzu XRD-6000), using a CuK radiation. Transmission electron microscopy (TEM, Hitachi HT-7700) with an accelerating voltage of 120 kV and high-resolution TEM (FEI Tecnai G2 F20 S-TWIN) with an accelerating voltage of 200 kV were performed to analyze the microstructures of ZnO. The yield of hydrogen and carbon dioxide was analyzed by gas-chromatography (Hydrogen was detected by TCD detector, GC-7900, Techcomp Instrument. Carbon dioxide was detected by FID detector, GC-1690, Hangzhou Jiedao Instrument.). The mass spectra of generated gas were identified by gas analysis system with model of GSD 320 O2 (Pfeiffer Vacuum, D-35614 Asslar). The Zn^{2+} content was identified by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer NexION 350D). The crystal structure and image of DMZnF were collected by Bruker SMART CCD diffractometer with MoKα radiation (λ = 0.71073 Å) and solved by direct methods and refined on F2 using SHELXTL. The FT-IR spectra (Fourier-transform infrared spectroscopy) of DMZnF catalysts were collected by NIOLET 6700 (Thermo Scientific) with wavenumber range of 650-4000 cm^{-1} and Raman spectra were tested with the wavenumber range of 100-3200 cm^{-1} (Renishaw inVia Raman Microscope). The TGA (Thermogravimetric Analysis) and DSC (Differential Scanning Calorimeter) curves (35 – 800 ^oC) were simultaneously characterized by TGA/DSC 3^+ STAR System (Mettler Toledo) with a heating rate of 10 ^oC/min in Ar atmosphere. The Brunauer-Emmett-Teller (BET) specific surface area of DMZnF are measured from the nitrogen adsorption-desorption isotherms at 77 K (BeiShiDe Instrument, 3H-2000PS2 static volume method). The pore size distribution was analysed by BJH method.

Catalytic activity tests

DMF-H_2O system: Under the general reaction condition, 40 mg DMZnF and a mix solution of 4 mL DMF and 0.2 mL H_2O was added in the reaction vessel (30 mL), the reaction vessel was sealed by a rubber plug and degassed by Ar for 20 min, and then the reaction was carried on the heating plate with magnetic stirring at 60, 80, 100, 120 °C with reflux condensation. For quantifying the generated gas, 100 µL of gas was taken out from the vessel and analyzed by GC at intervals. Stability reactions were conducted under the same condition, except that the reaction vessel needed degassed by Ar when the solution was cooled to room temperature after every cycle. The Zn^{2+} concentration of the origin reaction solution was analyzed by ICP-MS with 0.041 mmol/mL.

HCOOH system: 1) 0.3 mmol $Zn(NO_3)_2$•$6H_2O$ was added in a mix solution of 3 mmol formic acid and 4 mL toluene. 2) 1 mmol Et_3N was added in a mix solution of 3 mmol formic acid and 4 mL toluene. 3) 0.3 mmol $Zn(HCOO)_2$•$2H_2O$ was added in a mix solution of 3 mmol formic acid and 4 mL toluene. 4) 0.3 mmol $Zn(NO_3)_2$•$6H_2O$ and 1 mmol Et_3N was added in a mix solution of 3 mmol formic acid and 4 mL toluene. The mixed solution was first added in four reaction vessel respectively, and then sealed by a rubber plug, and degassed by Ar for 20 min. Afterwards, the reaction was carried on the heating plate with magnetic stirring at 120 °C with reflux condensation. For quantifying the generated gas, 100 µL of gas was removed from the vessel and analyzed by GC at intervals.

DMF system: 10 mg DMZnF was added into the mixture of 2 mL DMF and 5 µL H_2O in the reaction vessel, which was sealed with a rubber plug. Then the solution was degassed with Ar for 20 min, after that the reaction was carried on the heating plate with magnetic stirring at 120 °C with reflux condensation. After the halted stage, another 5 µL H_2O was injected to the cooled reaction solution and degassed for 20 min, and then the reaction was still carried on at 120 °C. For quantifying the generated gas, 100 µL of gas was taken out from the vessel and analyzed by GC at intervals. The final amount of generated H_2 (0.27 mmol) was consistent with the amount of 5 µL water.

The calculation of gas generated in the reaction system.

The mole of hydrogen production:

$$n_{H_2} = S_{\text{area of GC}} \times V_{\text{gas dispersed in reaction bottle}}/(a \times 22.4 \times 100) \ \ (\text{mmol})$$

The hydrogen production rate:

$$v_{H2} = n_{H2}/t \ \ (\text{mmol h}^{-1})$$

The hydrogen production rate normalized to Zn^{2+} active sites:

$$v_{\text{normalized to Zn active sites}} = v_{H2}/n_{Zn} \ \ (\text{mol}_{H_2}\ \text{mol}_{Zn}^{-1}\text{h}^{-1})$$

a was the slope of H_2 standard curve which identified by GC.

The mole of carbon dioxide production:

$$n_{CO2} = S_{\text{area of GC}} \times V_{\text{gas dispersed in reaction bottle}}/(b \times 22.4 \times 100) \ \ (\text{mmol})$$

b was the slope of CO_2 standard curve which identified by GC.

The calculation of TOF values in the reaction system.

$$\text{TOF} = \frac{\text{the mole of products}}{\text{the mole of active sites } \times t} \ (\text{h}^{-1})$$

In this reaction system, the active sites of the catalysts are Zn^{2+}, and the amount of Zn^{2+} in the reaction solution represents the number of active sites. Thus, the values of v_{H2} are equal to the values of TOF.

Table S1. Crystallographic data for DMZnF

DMZnF	
Empirical formula	$C_{15} H_9 N_3 O_{18} Zn_3$
Formula weight (g mol^{-1})	715.36
Crystal system	Trigonal
Space group	R-3c
T (K)	296.15 K
a [Å]	8.182(5)
b [Å]	8.182(5)
c [Å]	22.20(2)
α [°]	90
β [°]	90
γ [°]	120
V [Å^3]	1287(2)
Z	2
ρ_{calcd} [Mg m^{-3}]	1.846
F (000)	708
Reflections collected/Unique	3373/255
Limiting indices	-9<=h<=9, -9<=k<=9, -26<=l<=26
Crystal size [mm]	0.2x0.15x0.14
R_{int}	0.1368
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	255/0/25
GOF	1.235
R_1 [all data]	0.0618
R_1 [I>2sigma(I)]	0.0610
wR_2 (all data)	0.1434
wR_2 (I>2sigma(I))	0.1433
Largest diff. peak/hole [e Å^{-3}]	1.414/-0.791

Table S2. Bond lengths [A] and angles [deg] for DMZnF

Zn(1)-O(1)	2.106(4)	O(1)#5-Zn(1)-O(1)#2	180.0(2)
Zn(1)-O(1)#1	2.106(4)	O(1)#3-Zn(1)-O(1)#5	88.34(18)
Zn(1)-O(1)#2	2.106(4)	O(1)#3-Zn(1)-O(1)#1	88.34(18)
Zn(1)-O(1)#3	2.106(4)	O(1)#4-Zn(1)-O(1)#5	88.34(18)
Zn(1)-O(1)#4	2.106(4)	O(1)#2-Zn(1)-O(1)#1	88.34(18)
Zn(1)-O(1)#5	2.106(4)	O(1)-Zn(1)-O(1)#2	88.34(18)
O(1)-C(1)	1.254(7)	O(1)#5-Zn(1)-O(1)#1	91.66(18)
O(1)-C(1)#6	1.254(7)	C(1)-O(1)-Zn(1)	126.1(5)
C(1)-H(1)	0.9300	O(1)#6-C(1)-O(1)	124.7(9)
C(2)-N(1)#7	1.429(18)	O(1)-C(1)-H(1)	117.7
C(2)-N(1)	1.429(18)	O(1)#6-C(1)-H(1)	117.7
C(2)-N(1)#8	1.429(18)	N(1)-C(2)-N(1)#7	53.3(15)
N(1)-C(2)#9	1.429(18)	N(1)-C(2)-N(1)#8	53.3(15)
N(1)-N(1)#8	1.28(5)	N(1)#7-C(2)-N(1)#8	53.3(15)
N(1)-N(1)#7	1.28(5)	C(2)#9-N(1)-C(2)	117.6(19)
O(1)-Zn(1)-O(1)#3	180.0	N(1)#7-N(1)-C(2)	63.3(8)
O(1)#4-Zn(1)-O(1)#2	91.66(18)	N(1)#8-N(1)-C(2)#9	63.3(8)
O(1)#4-Zn(1)-O(1)#1	180.0(3)	N(1)#8-N(1)-C(2)	63.3(8)
O(1)-Zn(1)-O(1)#4	88.34(18)	N(1)#7-N(1)-C(2)#9	63.3(8)
O(1)-Zn(1)-O(1)#1	91.66(18)	N(1)#8-N(1)-N(1)#7	60.000(4)
O(1)#3-Zn(1)-O(1)#4	91.66(18)		
O(1)#3-Zn(1)-O(1)#2	91.66(18)		
O(1)-Zn(1)-O(1)#5	91.66(18)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+y,-x,z #2 y,-x+y,-z #3 -x,-y,-z
#4 x-y,x,-z #5 -y,x-y,z #6 x-y+1/3,-y+2/3,-z+1/6
#7 -y+1,x-y,z #8 -x+y+1,-x+1,z #9 y+1/3,x-1/3,-z+1/6

Table S3. The FT-IR frequencies (in cm^{-1}) of DMZnF and suggested assignment. [1]

IR Frequencies (cm^{-1})	Assignment
3054	ν (NH_2)
2790	ν (NH_2)
2490	$\rho(NH_2)+\delta(NH_2)$
1630	$\delta(NH_2)$
1577	$\nu_4(HCOO^-)$
1472	$\delta_{as}(CH_3)$
1457	$\delta_{as}(CH_3)$
1442	$\delta_{as}(CH_3)$
1360	$\nu_2(HCOO^-)$
1341	$\nu_2(HCOO^-)$
1251	$\rho(CH_3)$
1028	ν_{as} (CNC)
937	$\rho(NH_2)$
895	ν_s (CNC)
797	$\nu_3(HCOO^-)$

Table S4. The Raman frequencies (in cm^{-1}) of DMZnF and suggested assignment. [1]

Raman Frequencies (cm^{-1})	Assignment
3055	$\nu_{as}(CH_3)$
3039	$\nu_{as}(CH_3)$
2978	$\nu_s(CH_3)$
2940	$\delta_{as}(CH_3)$
2866	$\nu_1(HCOO^-)$
2844	$\nu_1(HCOO^-)$
1459	$\delta_{as}(CH_3)$
1367	$\nu_5(HCOO^-)$
1344	$\nu_2(HCOO^-)$
897	ν_s (CNC)
795	$\nu_3(HCOO^-)$

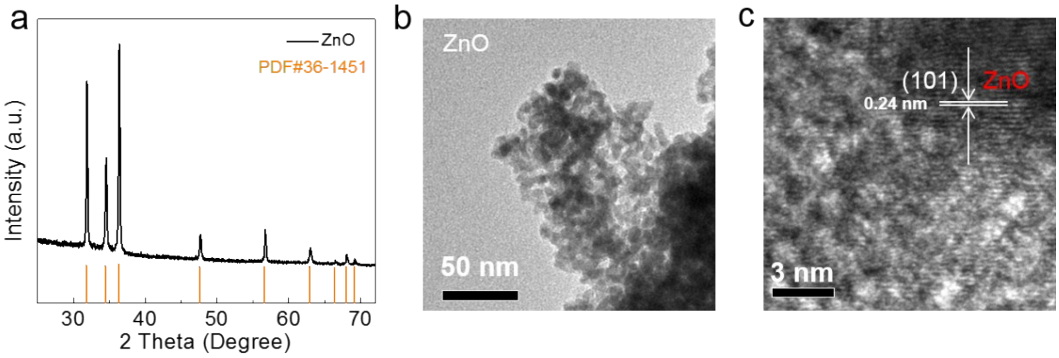

Figure S1. (a) The XRD pattern, (b) TEM and (c) HRTEM of ZnO generated in the solution.

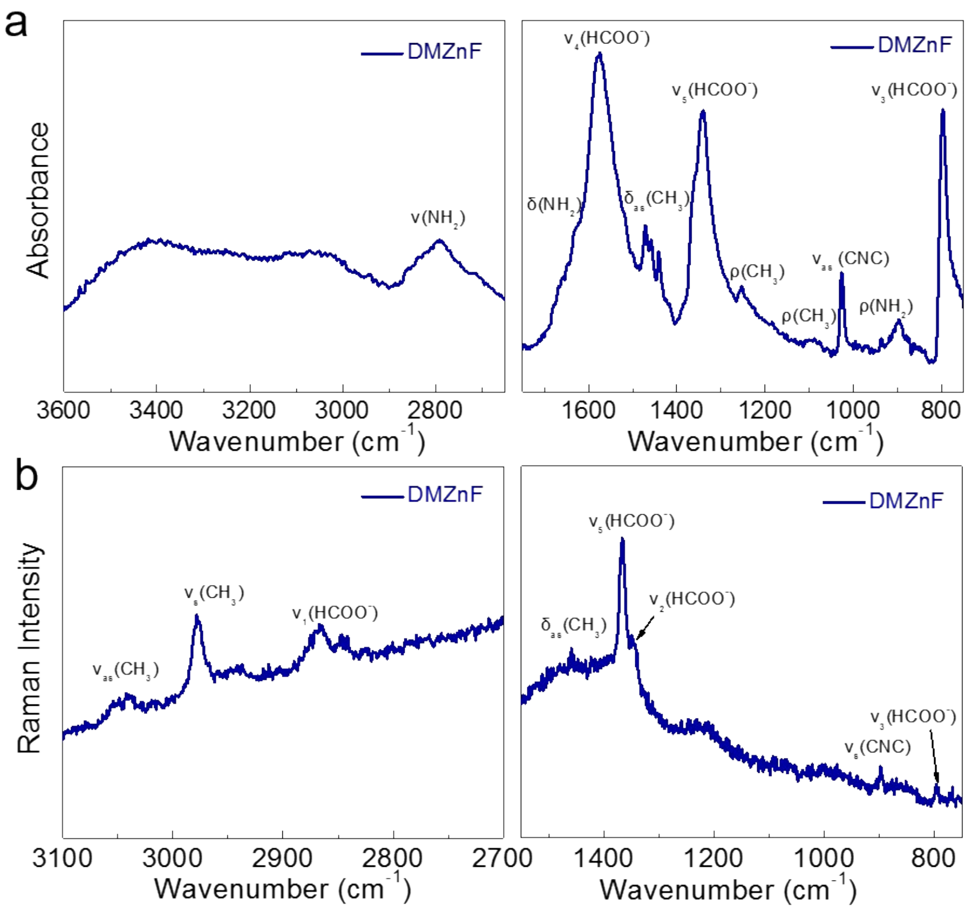

Figure S2. (a) The FT-IR spectra and (b) Raman spectra of as-synthesized DMZnF catalysts recorded at 298 K.

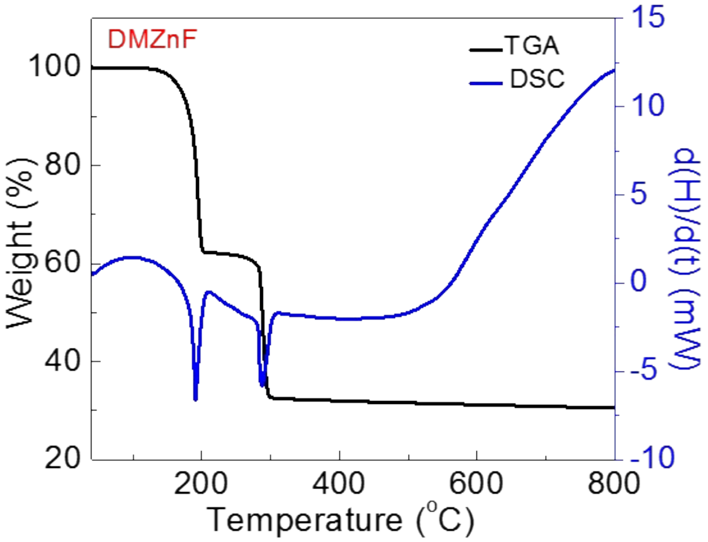

Figure S3. TGA -DSC curves of as-synthesized DMZnF from 50 to 800 °C with Ar atmosphere.

The structure of the DMZnF catalysts could be further determined by the simultaneous thermogravimetric analysis-differential scanning calorimeter (TGA-DSC) analysis. The 36.4% mass loss at the temperature range of 120-200 °C could be attributed to the departure of a dimethylammouium cation and formate anion with a theoretical weight of 36.9% in each chemical formula unit. The second stage occurred in the temperature range of 230-300 °C, corresponding to the decomposition of formate ligands. At this stage, the mass loss of 29.4 % was also consistent with their theoretical value of 30.0 %. Thus, a high correlation was found between the experimental and theoretical values for DMZnF, revealing the structural correctness of DMZnF catalysts.

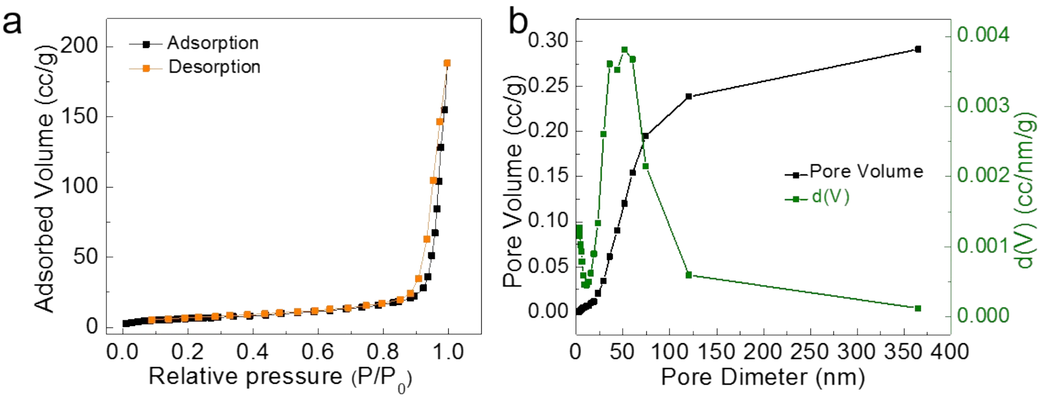

Figure S4. (a) N_2 adsorption-desorption isotherms and (b) pore size distribution of as-synthesized DMZnF at 77K.

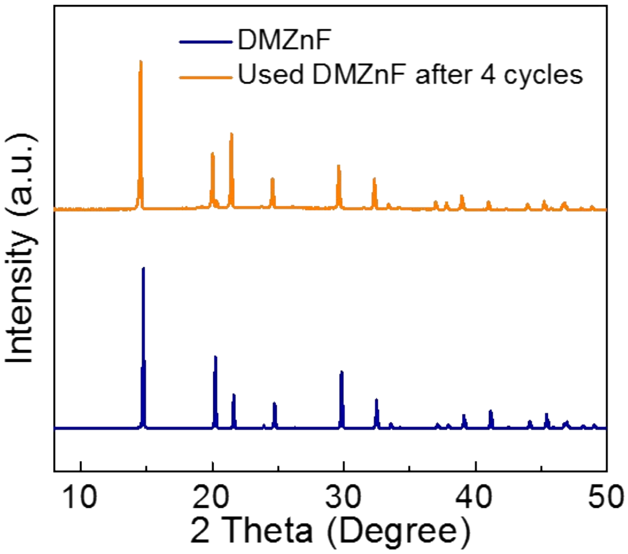

Figure S5. The XRD patterns of as-synthesized DMZnF and used DMZnF.

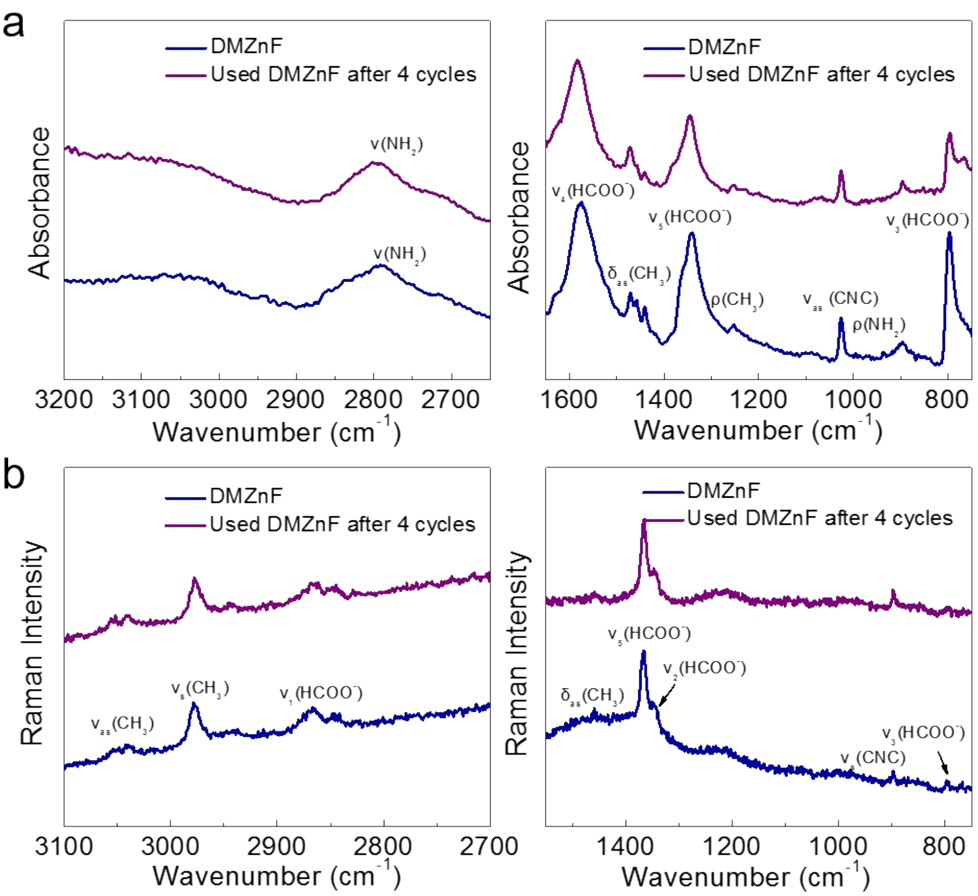

Figure S6. (a) The FT-IR spectra and (b) Raman spectra of as-synthesized DMZnF and used DMZnF.

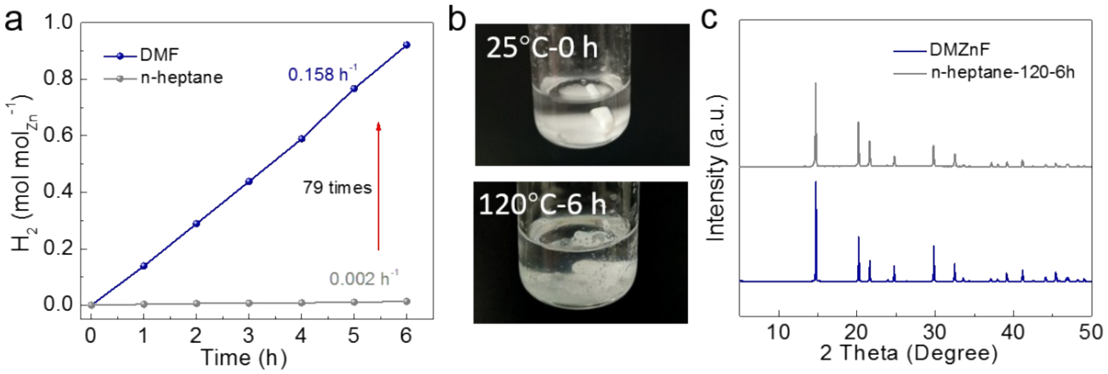

Figure S7 (a) Catalytic performance of DMZnF with various solvents. **Reaction conditions**: 40 mg DMZnF, 4 mL DMF and 0.2 mL H_2O, 120 ^oC, Ar./ 40 mg DMZnF, 4 mL n-heptane, 0.2 mL DMF and 0.01 mL H_2O, 120 ^oC, Ar. (b) the photo images of reaction solution with n-heptane at different temperatures. (c) The XRD patterns of as-synthesized DMZnF and used DMZnF (n-heptane as solvent).

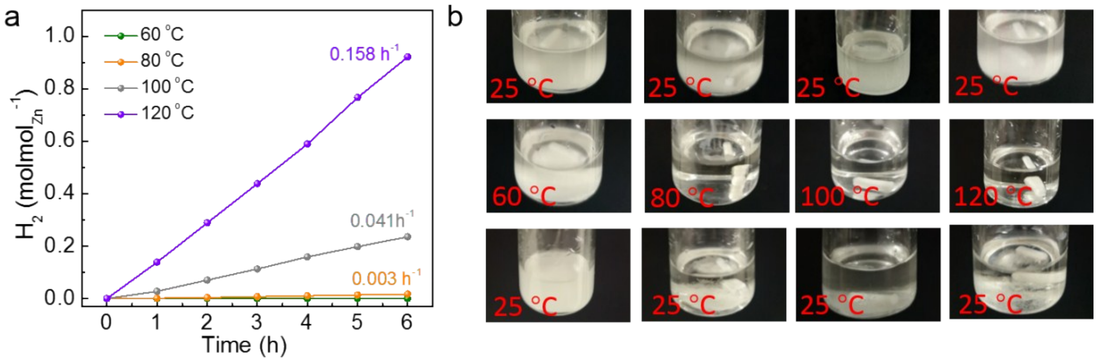

Figure S8. (a) The catalytic performance of DMZnF at various temperatures in DMF-H_2O system. **Reaction conditions**: 40 mg DMZnF, 4 mL DMF and 0.2 mL H_2O, 60, 80, 100, 120 ^oC, Ar. (b) Photo images of the dissolution and recrystallization of DMZnF catalysts at various temperatures.

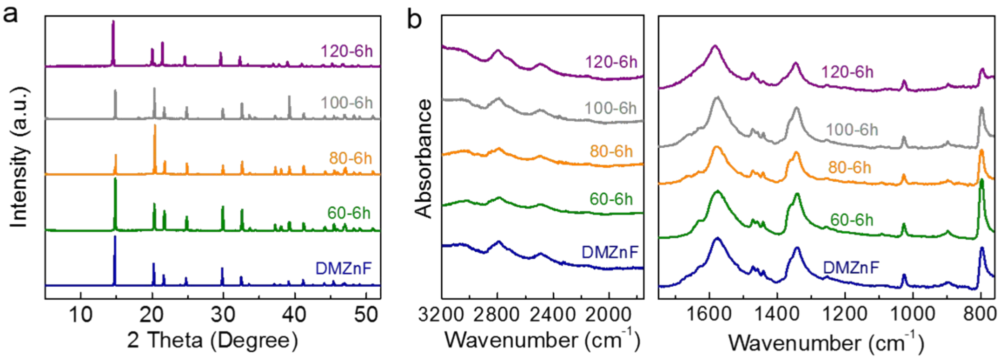

Figure S9. (a) The XRD patterns and (b) FT-IR spectra of as-synthesized DMZnF and the used DMZnF catalysts.

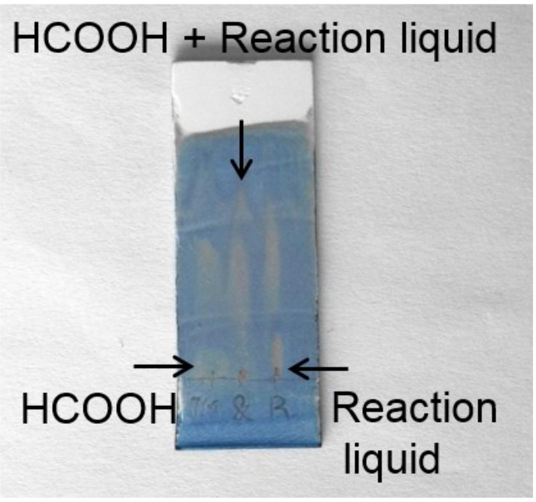

Figure S10. Detection of formic acid in the reaction liquid by thin layer chromatography. (Developing solvent: $H_2O/CH_3OH=4/1$, Coloring agent: bromocresol green)

In thin layer chromatography, formic acid, mixed solution of HCOOH and reaction fluid (after 5 h reaction) as well as the reaction solution was pointed in the silica gel plate by capillary, respectively. Water/methanol with a ratio of 4:1 was used as developing solvent. After drying at room temperature, the silica gel plate was dipped in bromocresol green.

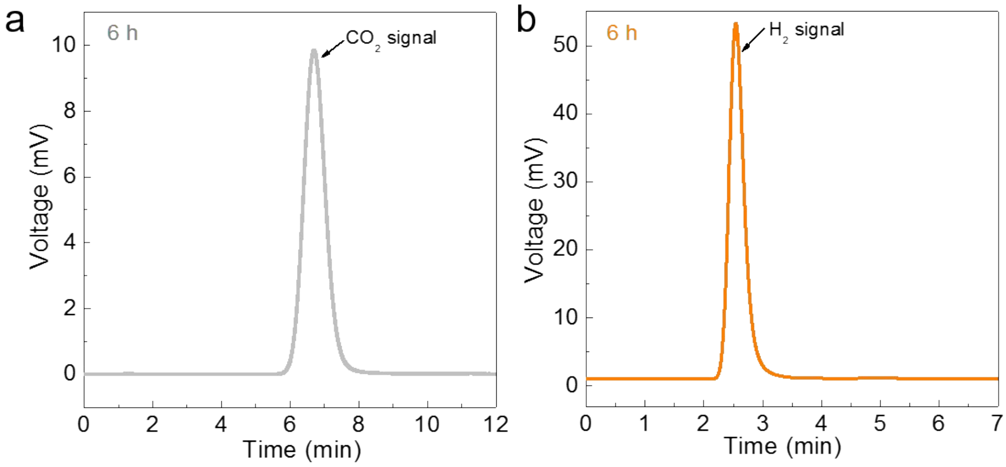

Figure S11. The gas signal of (a) CO_2 and (b) H_2 after 6 h reaction characterized by GC. **Reaction conditions:** 40 mg DMZnF, 4 mL DMF, 0.2 mL H_2O, 120 ^oC, Ar. The CO and CO_2 peak position was at 1.3 and 6.7 min, which were detected by FID detector, GC-1690. The H_2 peak position was at 2.5 min, detected by TCD detector, GC-7900.

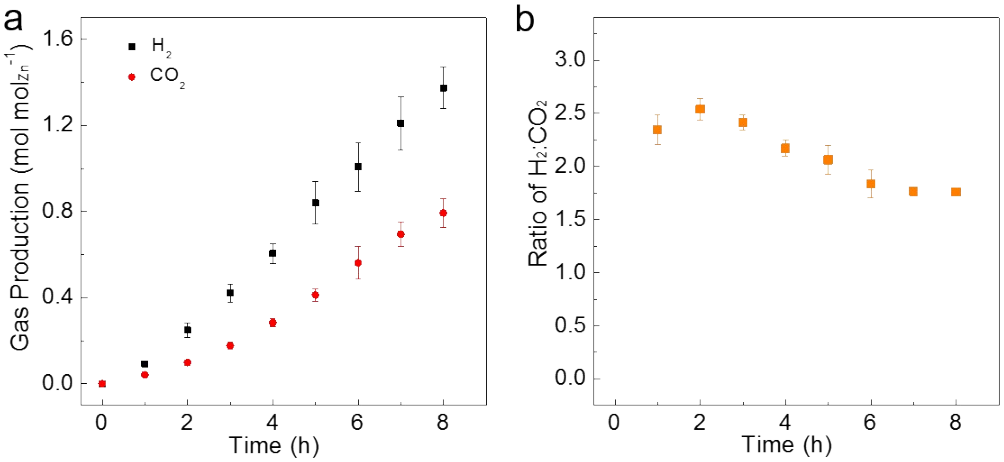

Figure S12. (a) The gas production of H_2 and CO_2 during the reaction from DMF-H_2O system. (b) The molar ratio of H_2 and CO_2 during the reaction from DMF-H_2O system. **Reaction condition**: DMZnF (40 mg), DMF (4 mL), H_2O (0.2 mL), 120 °C and Ar atmosphere.

References:

1. M. Maczka, M. Ptak and L. Macalik, *Vib. Spectrosc*, 2014, **71**, 98-104.
2. J. Ban, G. C. Xu, L. Zhang, H. Lin, Z. P. Sun, Y. Lv and D. Z. Jia, *J. Solid State Chem.*, 2017, **256**, 151-157.