Electronic Supplementary Information

Phase Competition Driven Formation of Hierarchical FeNiZn-MIL-88B on MOF-5 Octapods with High Selectivity for RWGS Reaction

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EXPERIMENTAL SECTION

Materials. Iron(III) acetylacetonate ($Fe(acac)_3$) and Nickel(II) acetylacetonate ($Ni(acac)_2$) were bought from Aladdin Industrial Corp. Zinc nitrate hexahydrate ($Zn(NO_3)\cdot 6H_2O$) and polyvinylpyrrolidone (PVP, Kw=30) were purchased from Sinopharm Chemical Reagent Co., Ltd. Benzenedicarboxylic acid (H_2BDC), N,N-Dimethylformamide (DMF) and ethanol were purchased from Beijing Chemical Reagent Factory. All chemical reagents were at analytical purity level without additional purification.

Synthesis. For a typical synthesis of octapods-FeNiZn MOF materials, $Fe(acac)_3$ (120 mg), $Ni(acac)_2$ (60 mg), $Zn(NO_3)\cdot 6H_2O$ (92.8 mg), H_2BDC (38.4 mg) and PVP (650 mg) were dissolved in the DMF-ethanol mixture ($V_{DMF}/V_{ethanol}$ = 32 mL/19.2 mL) with magnetic stirring for 30 min to form a uniform solution. The Fe^{3+}/Ni^{2+} molar ratio was 1.5/1. Then, the mixture solutions were transferred into a 100 mL Teflon-lined stainless-steel autoclave and heated at 100 ^oC for 6 h. After cooling naturally at room temperature, the products were collected and washed with DMF and ethanol via centrifugation at 10000 rpm for several times. The products were dried in a vacuum oven at 70 ^oC for 12 h. Meanwhile, when tuning Fe^{3+}/Ni^{2+} molar ratio with 2/1 ($Fe(acac)_3/Ni(acac)_2$ = 164 mg/60 mg), flower-FeNiZn MOFs were successfully prepared. Adjusting Fe^{3+}/Ni^{2+} molar ratio with 1/2 ($Fe(acac)_3/Ni(acac)_2$ = 82 mg/120 mg), cube-FeNiZn MOFs were synthesized. Other reaction conditions were in agreement with octapods-FeNiZn MOFs synthesis procedure. As for the synthesis of the contrast samples, the preparation of FeZn MOFs and NiZn MOFs were carried out without adding $Ni(acac)_2$ or $Fe(acac)_3$ based on the octapods-FeNiZn MOFs synthesis. The FeNiZnOx materials were prepared by calcining the mixture of $Fe(acac)_3$ (120 mg), $Ni(acac)_2$ (60 mg), $Zn(NO_3)\cdot 6H_2O$ (92.8 mg) and PVP (650 mg) in the Muffle furnace at 350 ^oC for 2 h.

Characterization. The phase composition information of as-prepared materials were collected from powder X-ray diffraction (XRD) measurements on a Bruker D8 diffractometer with Cu Kα source. The shape and size of materials were observed on Transmission electron microscope (TEM) (HT7700) and Scanning electron microscope (SEM) (Hitachi S4700). The elemental mapping images were obtained on JEOL-JEM-2100F transmission electron microscope equipped with energy dispersive X-ray spectrometer (EDS) system. The surface compositions of samples were gathered from X-ray photoelectron spectroscopy (XPS) results, recorded on a Thermo Fisher ESCALAB XPS system at Al Kα X-ray source. The Fourier transform infrared (FT-IR) spectra were performed using Bruker TENSOR27 FTIR Spectrometric analyzer at room temperature. The thermogravimetric (TG) analysis were measured under nitrogen flows with a heating rate of 10^{o}/min from 30 ^{o}C to 800 ^{o}C using TGA Q500.

Activity test of catalysts. The RWGS reactions were conducted in a continuous fixed-bed flow reactor. Inside, the catalyst bed was packed up at a constant temperature section with quartz sand supported. Reaction gas mixture were composed of 14.9% CO_2, 60.2% H_2 and 24.9% Ar. Before reactions, all the catalysts were activated under H_2 (99.999%) flow of 25 mL/min at 350 ^{o}C for 2 h. After pretreatments, with the temperature cooling below 200 ^{o}C, the gas mixture was switched with 10 mL/min in the reaction system. The catalytic performance of as-prepared samples were measured every 50 ^{o}C based on 200 ^{o}C until 400 ^{o}C. Finally, the gas products were monitored on line using Varian CP-3800 with thermal conductivity detector (TCD) using an internal standard method. The analyzing conditions were as follows: column temperature, 100 ^{o}C; detector temperature, 150 ^{o}C; carrier gas, helium.

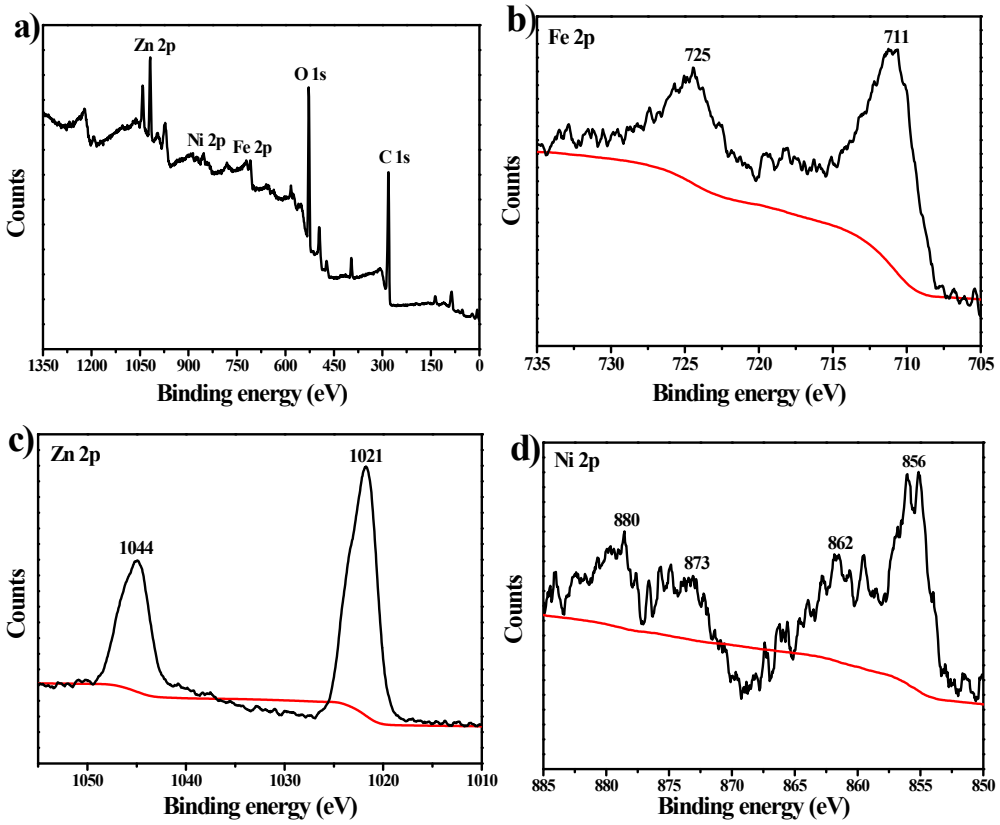

Fig. S1 XPS spectra of octapods-FeNiZn MOFs. (a) the survey spectrum; (b) Fe 2p spectrum; (c) Ni 2p spectrum and (d) Zn 2p spectrum.

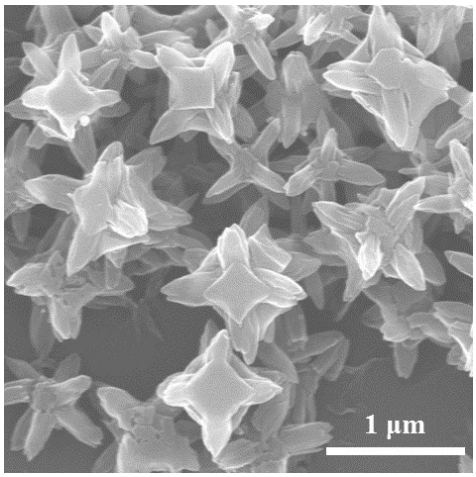

Fig. S2 SEM image of octapods-FeNiZn MOFs

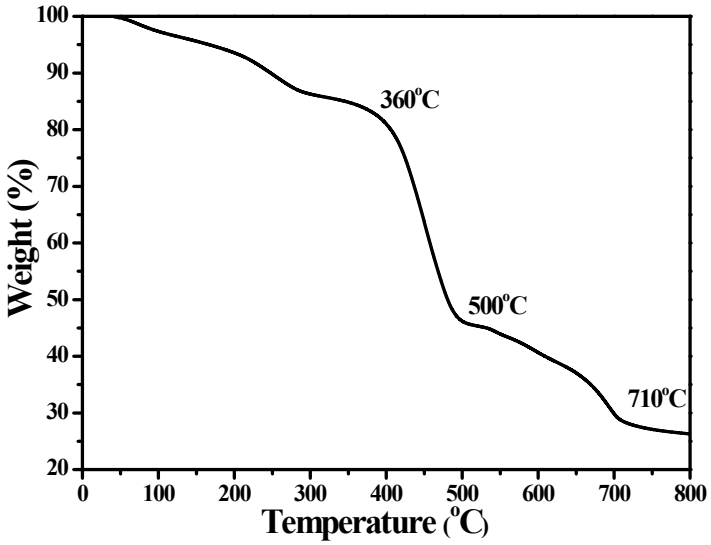

Fig. S3 TG curve of octapods-FeNiZn MOFs.

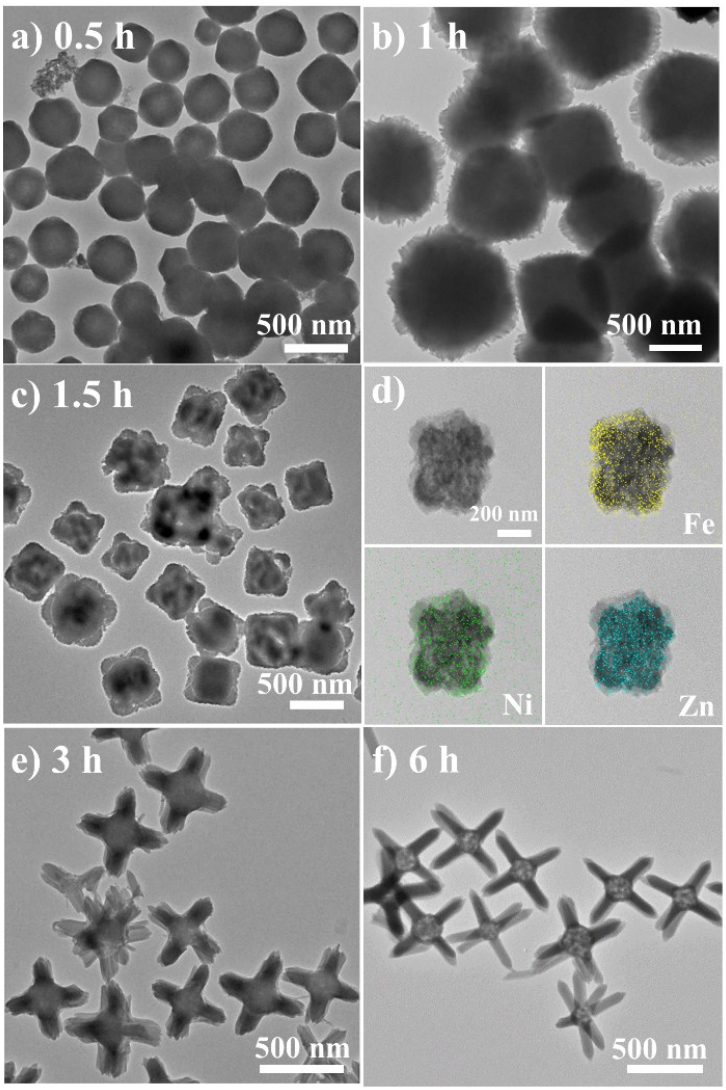

Fig. S4 TEM images of octapods-FeNiZn MOFs prepared under different reaction times. (a) 0.5 h, (b) 1 h, (c) 1.5 h, (d) EDX mapping analysis of 1.5 h samples, (e) 3 h, (f) 6 h.

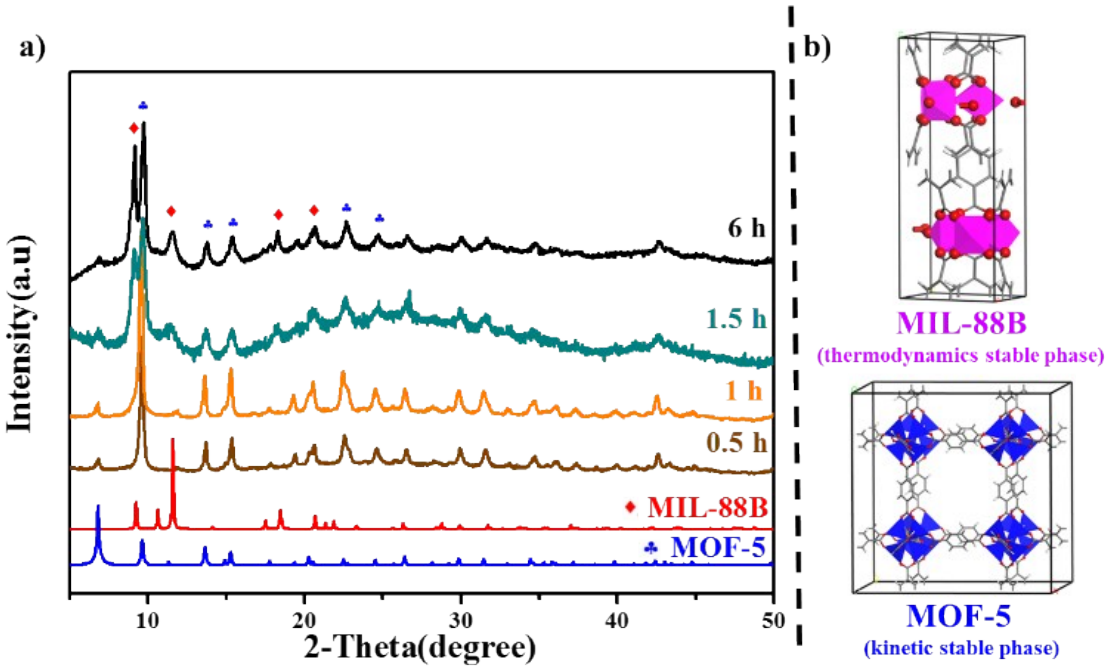

Fig. S5 (a) XRD patterns of octapods under different reaction times. (b) the schematic model of structure evolution.

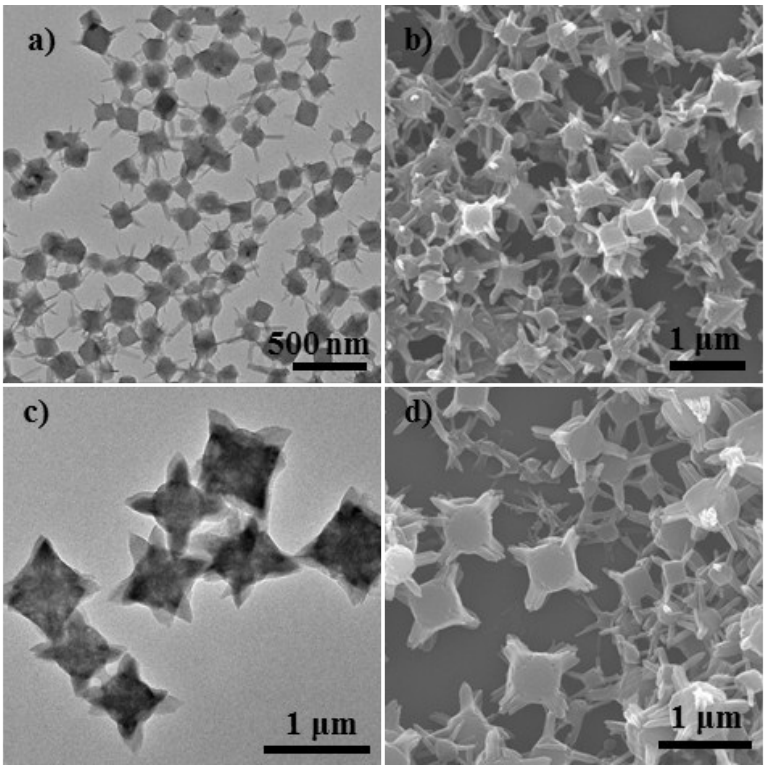

Fig. S6 TEM and SEM images of samples preprared with different Fe^{3+}/Ni^{2+} molar ratio (a-b) 1/1, (c-d) 1/1.5.

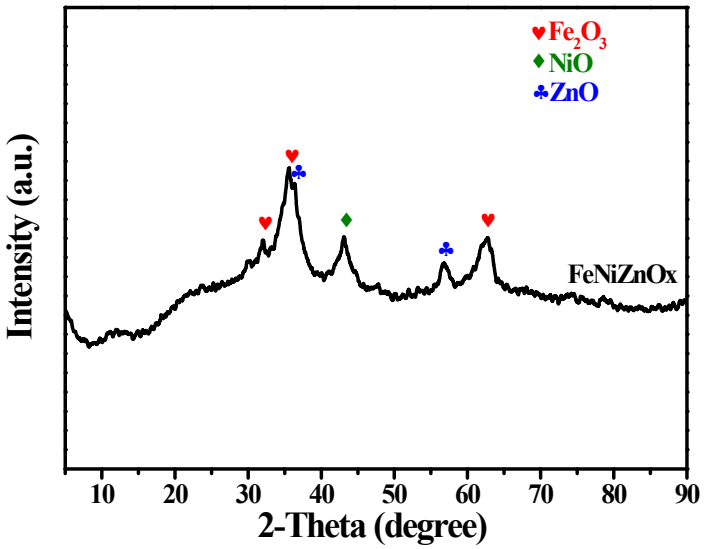

Fig. S7 XRD pattern of FeNiZnOx sample.

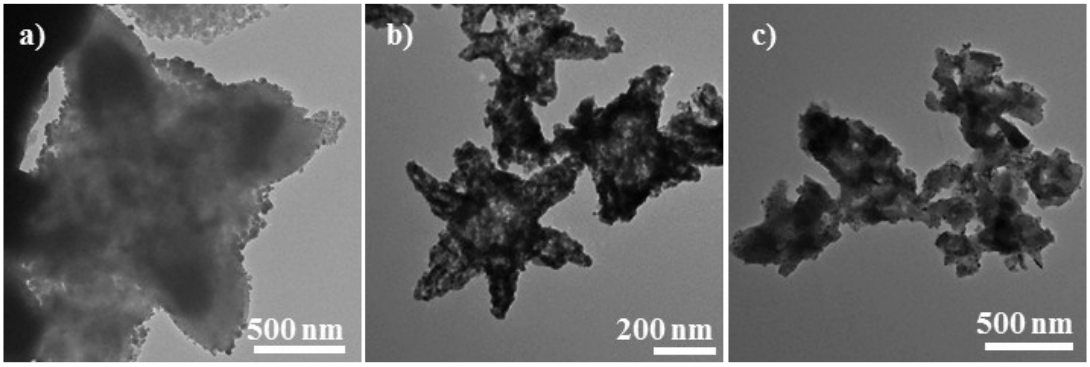

Fig. S8 TEM images after H_2 pretreatment at 350 °C for 2 h (a) flower-FeNiZn MOFs. (b) octapods-FeNiZn MOFs. (c) cube-FeNiZn MOFs.

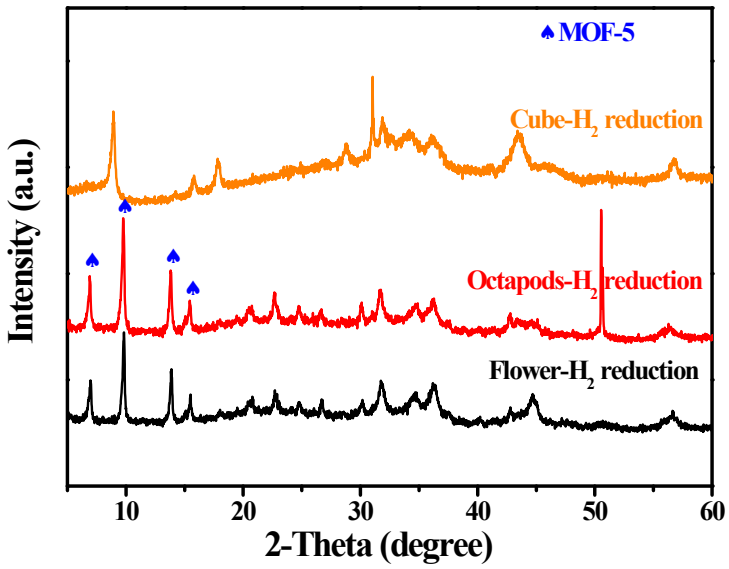

Fig. S9 XRD patterns of samples after H_2 reduction at 350 °C for 2 h.

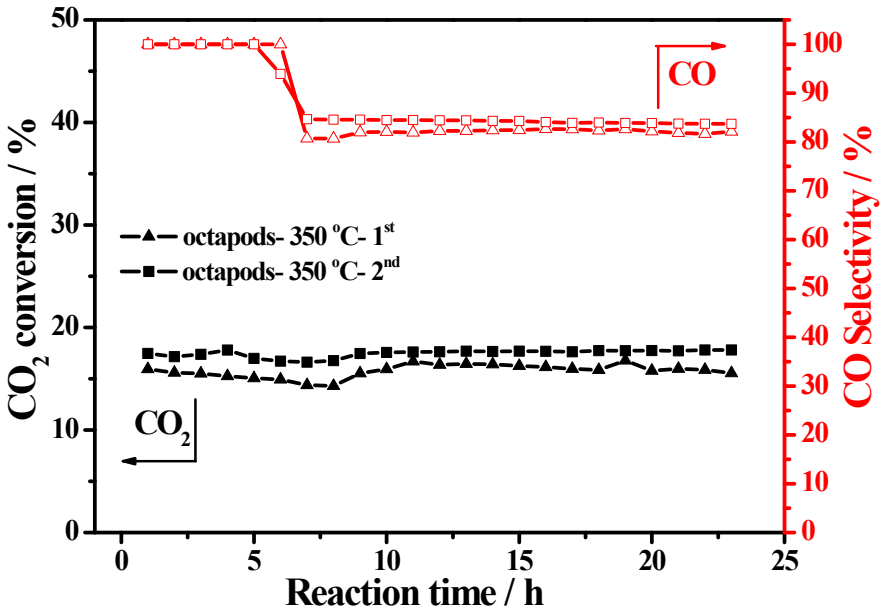

Fig. S10 Long-term stability tests of octapods-FeNiZn MOFs at 350 °C for 22 h.

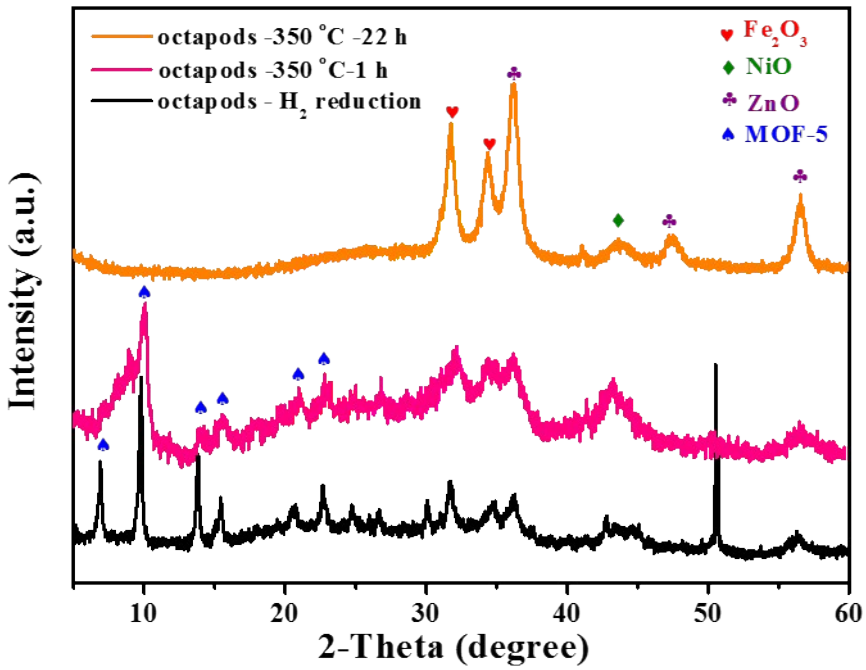

Fig. S11 XRD patterns of octapods after H_2 reduction, reacting 1 h at 350 °C and long-term tests for 22 h at 350 °C.

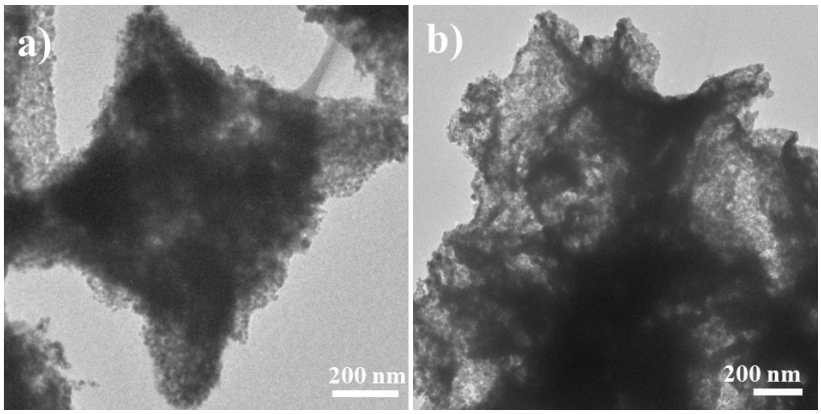

Fig. S12 TEM images (a) octapods-FeNiZn MOFs after reacting 1 h at 350 °C, (b) octapods-FeNiZn MOFs after long-term tests for 22 h at 350 °C.

Table S1. Comparison of RWGS catalytic performance of the reported catalysts.

Catalyst	T (°C)	P (MPa)	H_2/CO_2	CO_2 conversion (%)	CO selectivity (%)	Ref.
CuSiO/CuOx	350	0.1	3/1	2.2	/	1
Pt/MOF-74	350	2	3/1	1.9	100	2
4-Pt/Au@Pd@1Co	350	2	3/1	9.38	76.3	3
1.6%Ru@mSiO_2-N	350	/	4/1	9.4	88.1	4
CuOx/CeO_2	400	0.1	1/1	16	100	5
10%Pd/Al_2O_3	400	/	3/1	35	11.4	6
10%Co/CeO_2	400	/	1/1	10	93	7
Pt/Au@Pd@UIO-66	400	2	3/1	27.3	73	8
Au@UIO-67-H_2	408	0.1	3/1	3	/	9
Co/Mo_2C	300	/	2/1	9.5	/	10
Octapods-	350	0.1	3/1	16.51	100	this work
FeNiZn MOF	400	0.1	3/1	29.9	81.05	this work
Cube-	350	0.1	3/1	11.29	95.46	this work
FeNiZn MOF	400	0.1	3/1	23.93	90.24	this work
Flower-	350	0.1	3/1	6.9	100	this work
FeNiZn MOF	400	0.1	3/1	14.74	79.69	this work
	350	0.1	3/1	38.13	24.16	this work
FeNiZnOx	400	0.1	3/1	41.58	30.17	this work

References

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