Electronic Supplementary Material (ESI) for Green Chemistry.

Double-metal cyanide as an acid and hydrogenation catalyst for the highly selective ring-rearrangement of biomass-derived furfuryl alcohol to cyclopentenone compounds

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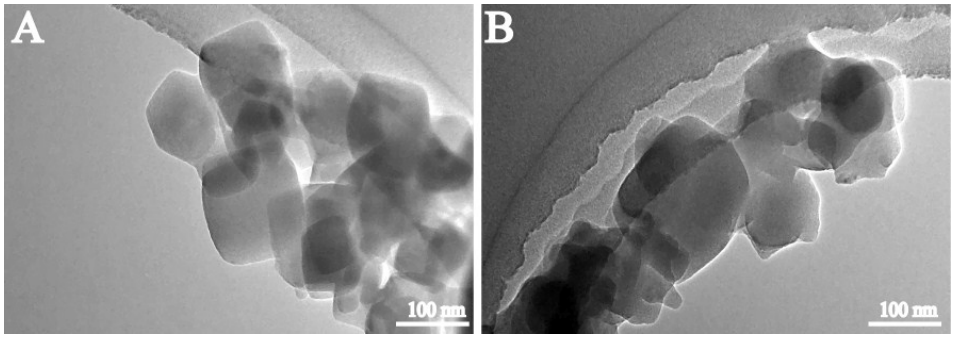

Figure S1. TEM micrographs of (A)FeZn, (B) FeZn-P.

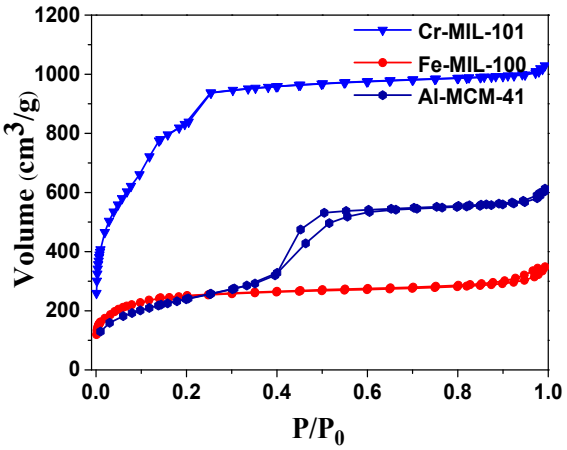

Figure S2. N_2 adsorption-desorption isotherms of Cr-MIL-101，Fe-MIL-100, Al-MCM-41.

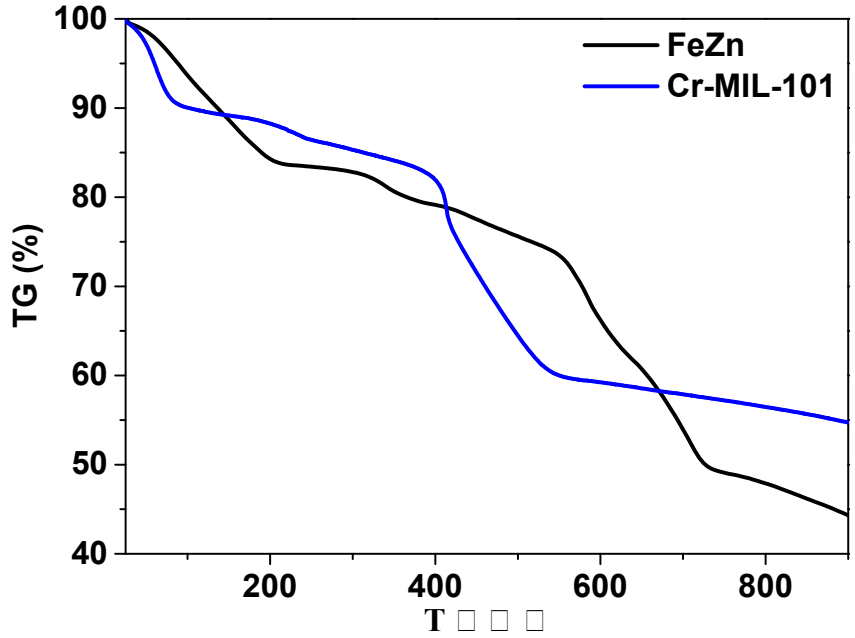

Figure S3. Thermal gravimetric analysis profiles of FeZn-DMC and Cr-MIL-101 catalysts.

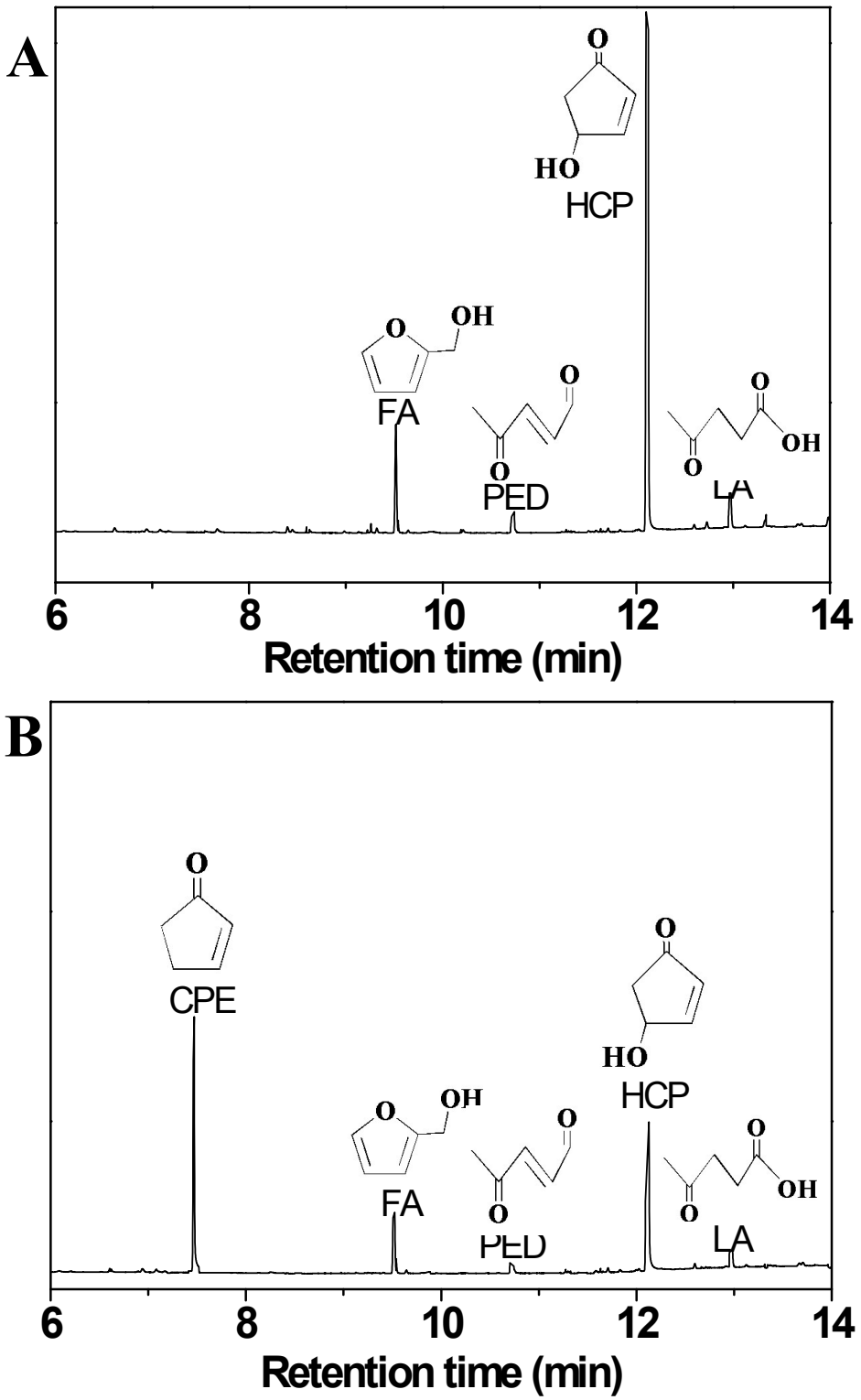

Figure S4. GC patterns for the synthesis reactions of (A) 4-hydroxy-2-cyclopentenone (HCP) and (B) 2-cyclopentenone (CPE).

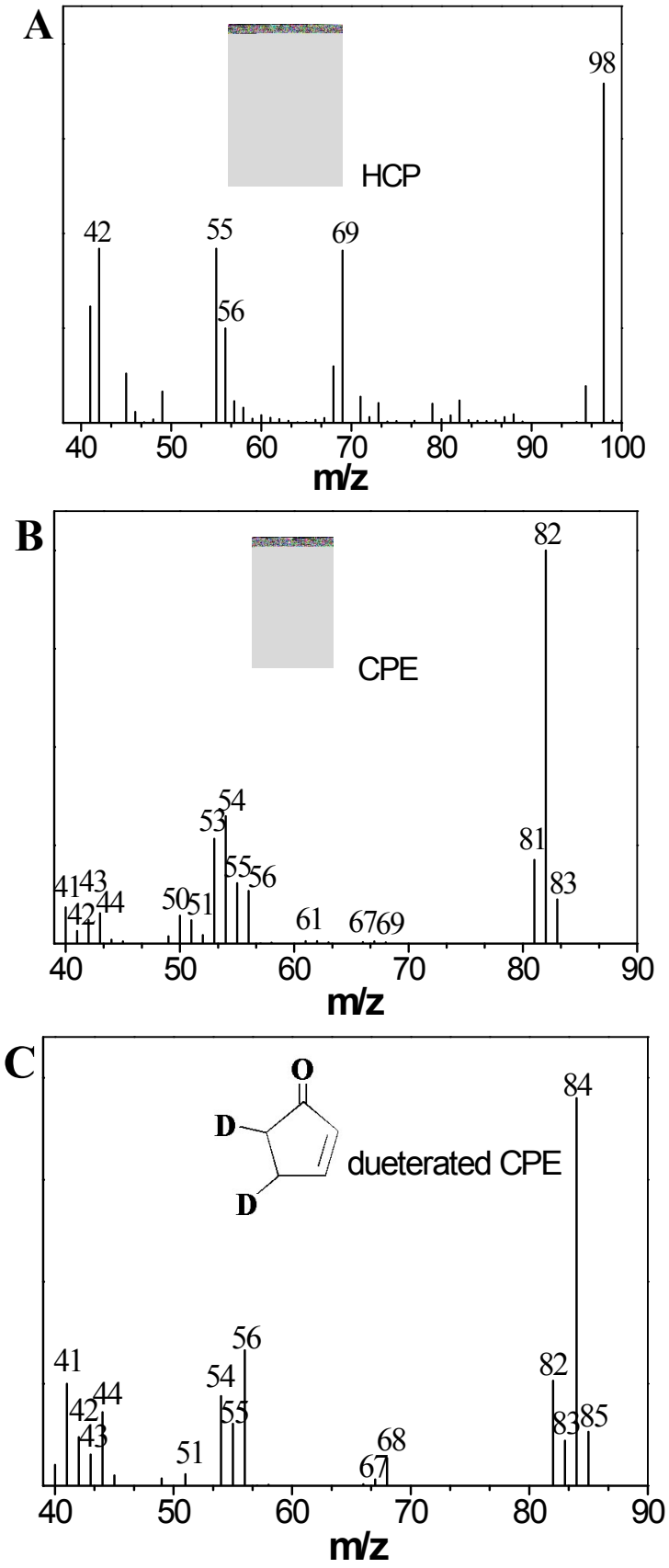

Figure S5. MS patterns for (A) HCP, (B) CPE and (C) dueterated CPE.

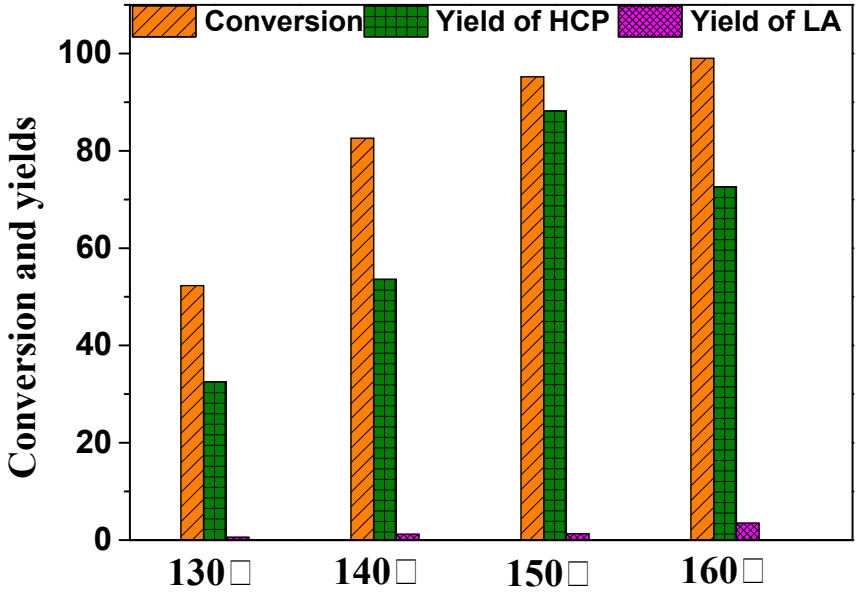

Figure S6. Effect of reaction temperature on FA conversion and product yields over FeZn-P. Reaction conditions: FA (10.2 mmol), catalyst 0.1 g, 20 mL water and 20ml n-hexane, 4.0 MPa N_2 pressure, time 6 h.

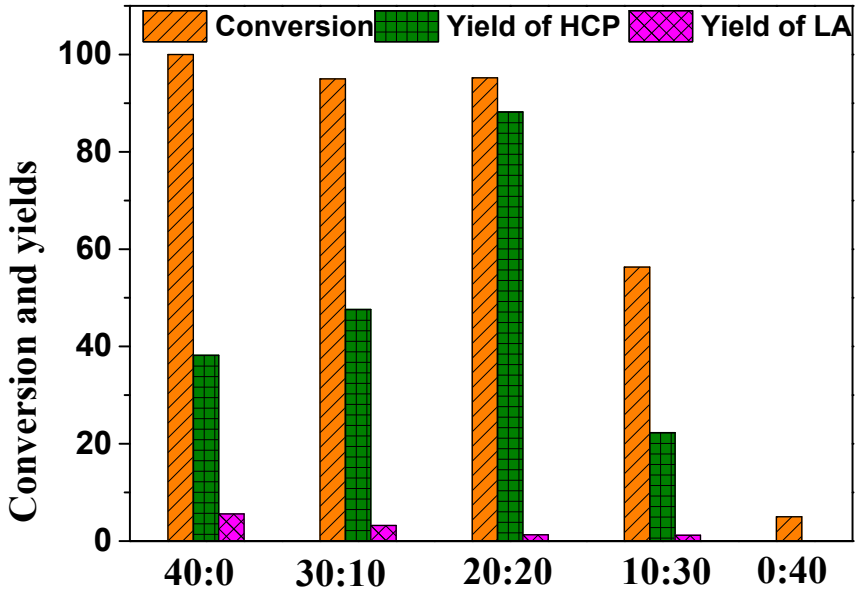

Figure S7. Effect of volume ratio of water/n-hexane on FA conversion and product yield over FeZn-P. Reaction conditions: FA (10.2 mmol), catalyst 0.1 g, temperature 150 °C, 4.0 MPa N_2 pressure, time 6 h.

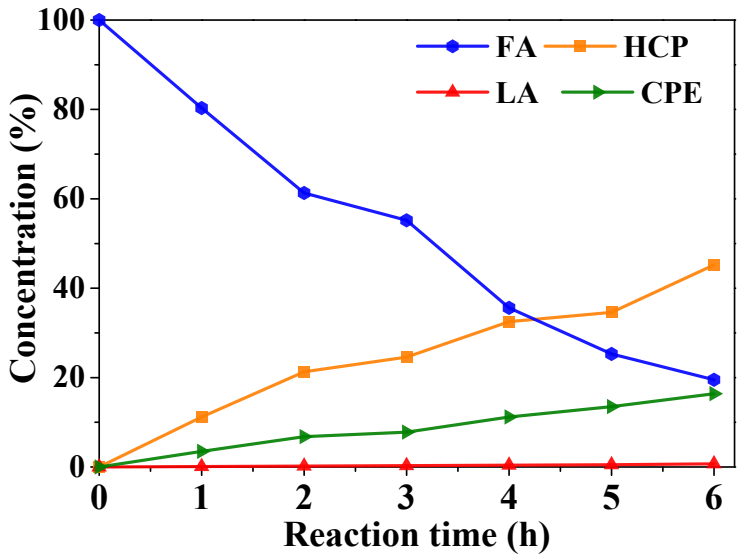

Figure S8. Time-dependent product distribution using FeZn-P, Reaction conditions: FA (10.2 mmol), catalyst (0.1 g), water (40 mL), 150 °C, 2.0 MPa H_2 pressure.

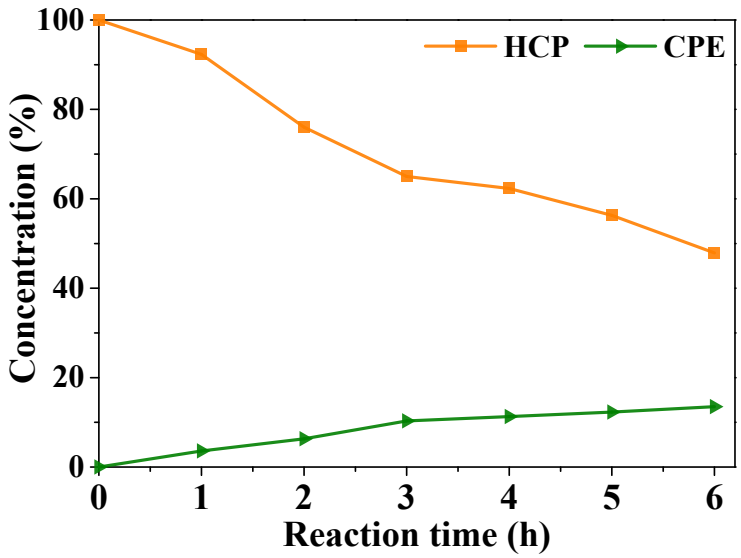

Figure S9. Time-dependent product distribution using FeZn-P. Reaction conditions: HCP (10.2 mmol), catalyst (0.1 g), water (40 mL), 150 °C, 2.0 MPa H_2 pressure.

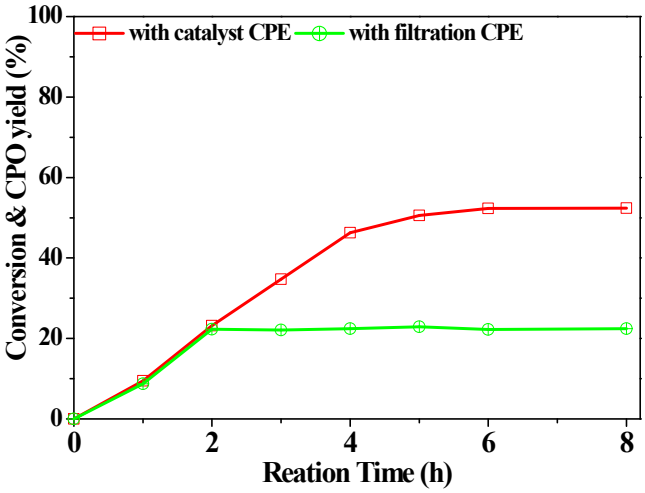

Figure S10. Fast hot catalyst filtration test in FA hydrogenative rearrangement using FeZn-P. Reaction conditions: FA (10.4 mmol), FeZn-P (0.1 g), water (40 mL), 4.0 MPa H_2, temperature 150 °C.

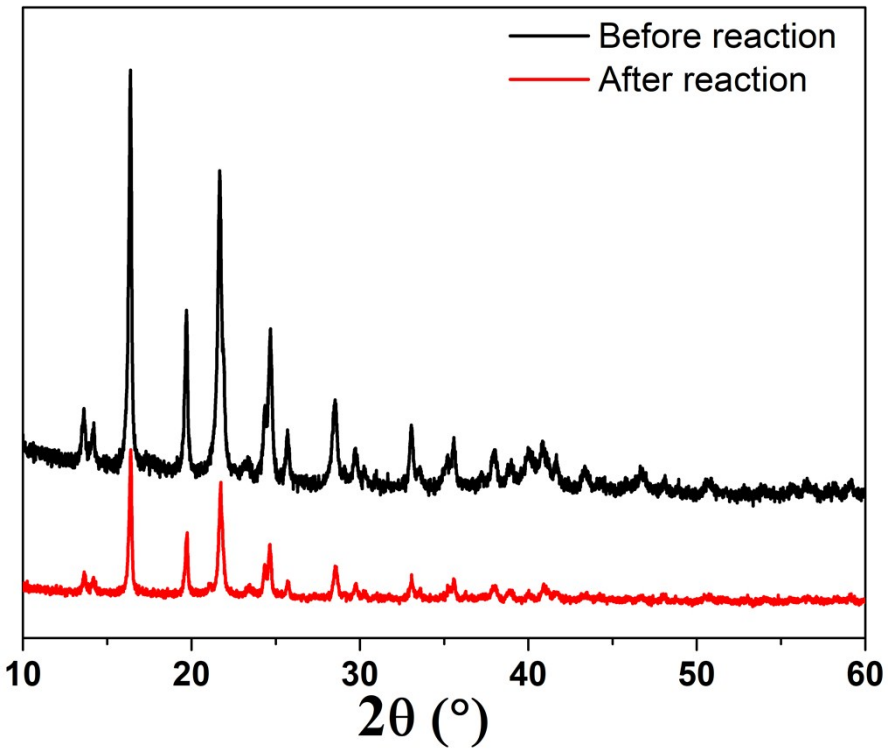

Figure S11. XRD diffraction patterns of FeZn-P before and after five catalytic runs.

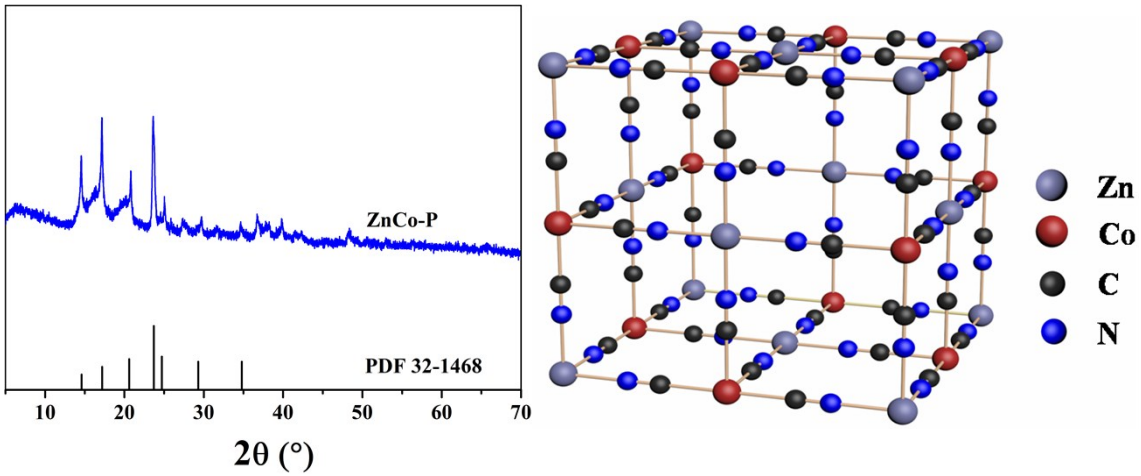

Figure S12. X-ray diffraction patterns and crystal structure of ZnCo-DMC.

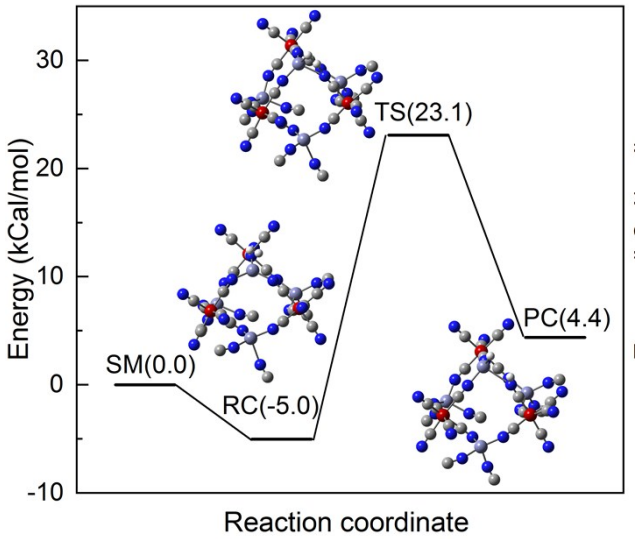

Figure S13. DFT calculated reaction free energies of H_2 heterolysis on tri-coordinative Zn^{2+} site ($Zn(N)_3$).

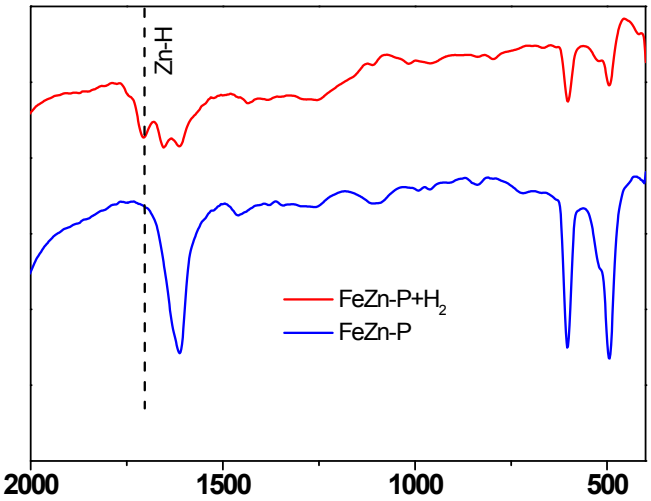

Figure S14. The FTIR spectra of the FeZn-P and H_2-actived FeZn-P.

Table S1. Catalytic performance of DMC with HCP as a reactant. Reaction conditions: HCP (10.2 mmol), catalyst 0.1 g, reaction temperature 150 °C, time 6 h.

Catalyst	H_2 pressure (MPa)	Conversion (%)	Yield of CPE (%)
-	4.0	-	-
FeZn	4.0	56.8	17.6
ZnCo-P	4.0	54.2	16.5
FeZn-P	2.0	52.1	13.5
FeZn-P	3.0	53.3	16.8
FeZn-P	4.0	61.4	38.3
FeZn-P	5.0	68.4	41.2
FeZn-P	6.0	73.6	53.9
FeZn-P	7.0	72.9	53.2

Table S2. Physicochemical properties of catalysts. [a] represents the recycled sample

Samples	S_{BET} (m^2/g)	V_{total} (cm^3/g)
FeZn-P	42.6	0.068
FeZn-P[a]	28.6	0.048