

Figure S1. N_2 adsorption-desorption isotherms (A) and pore size distributions (B).

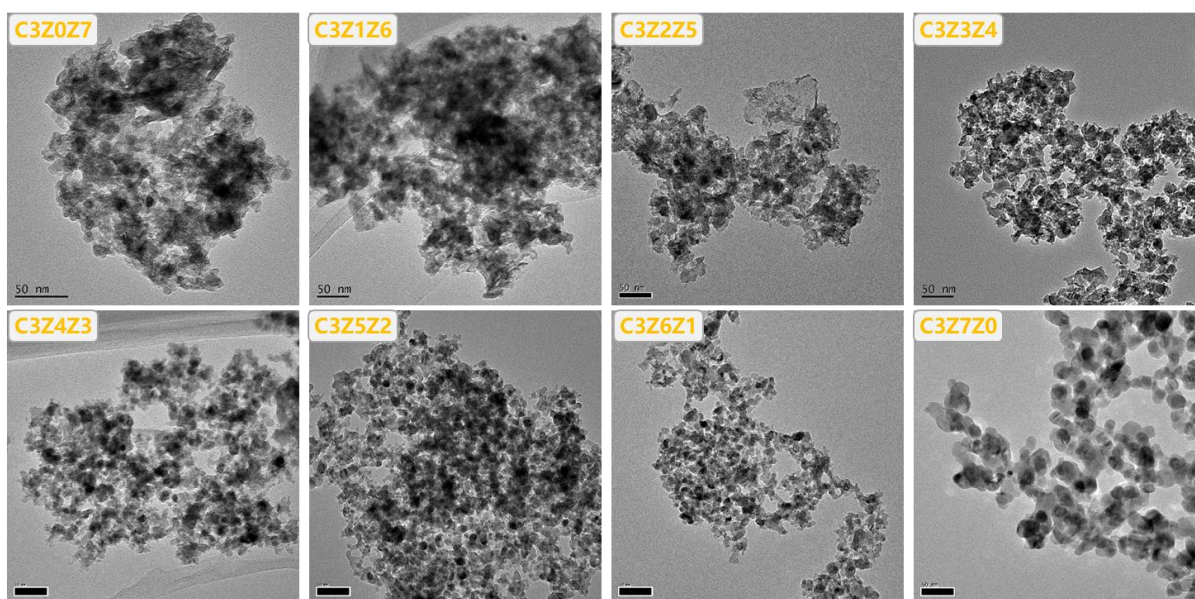


Figure S2. TEM images of reduced catalysts.

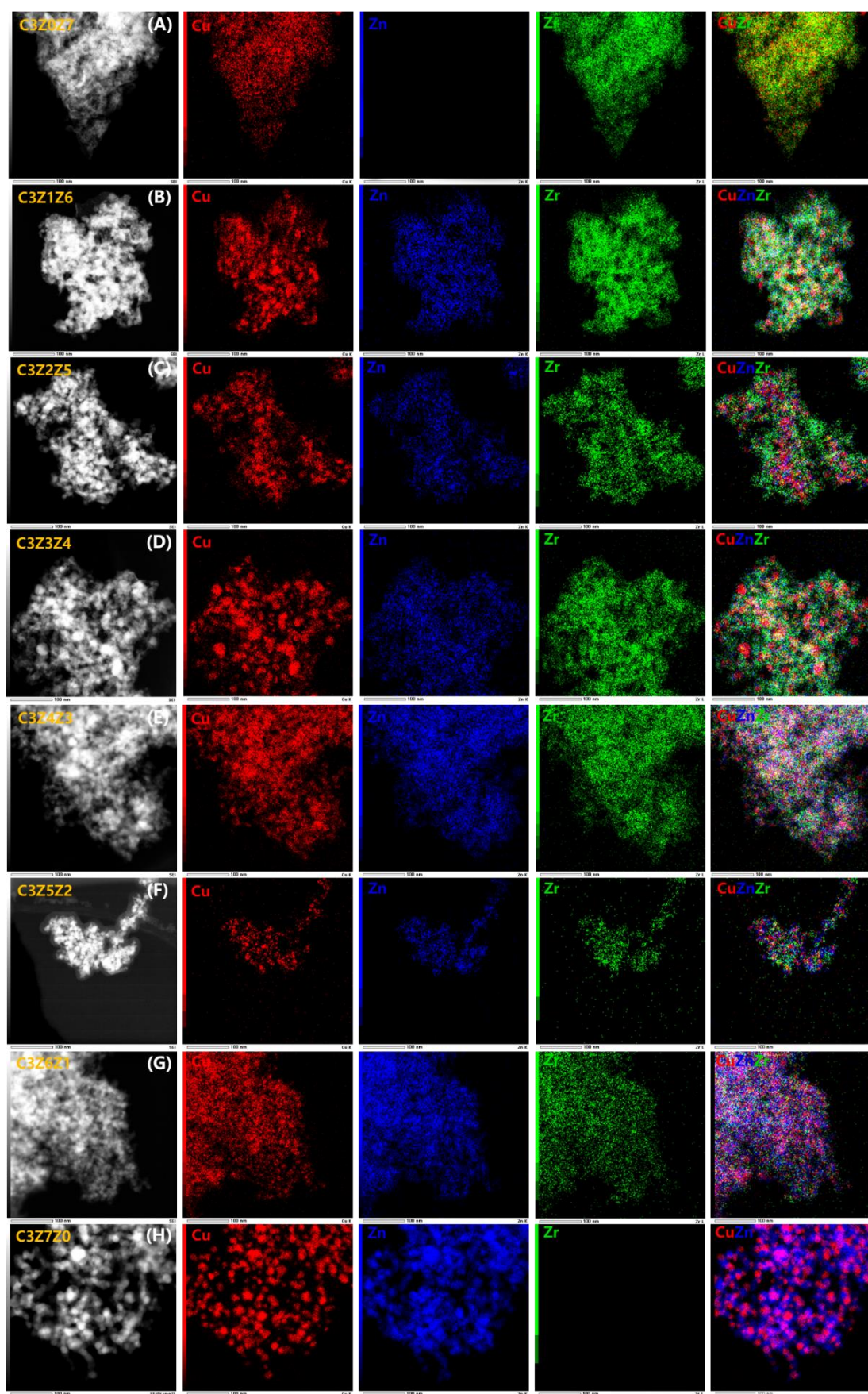


Figure S3. EDS-mapping images of reduced catalysts.

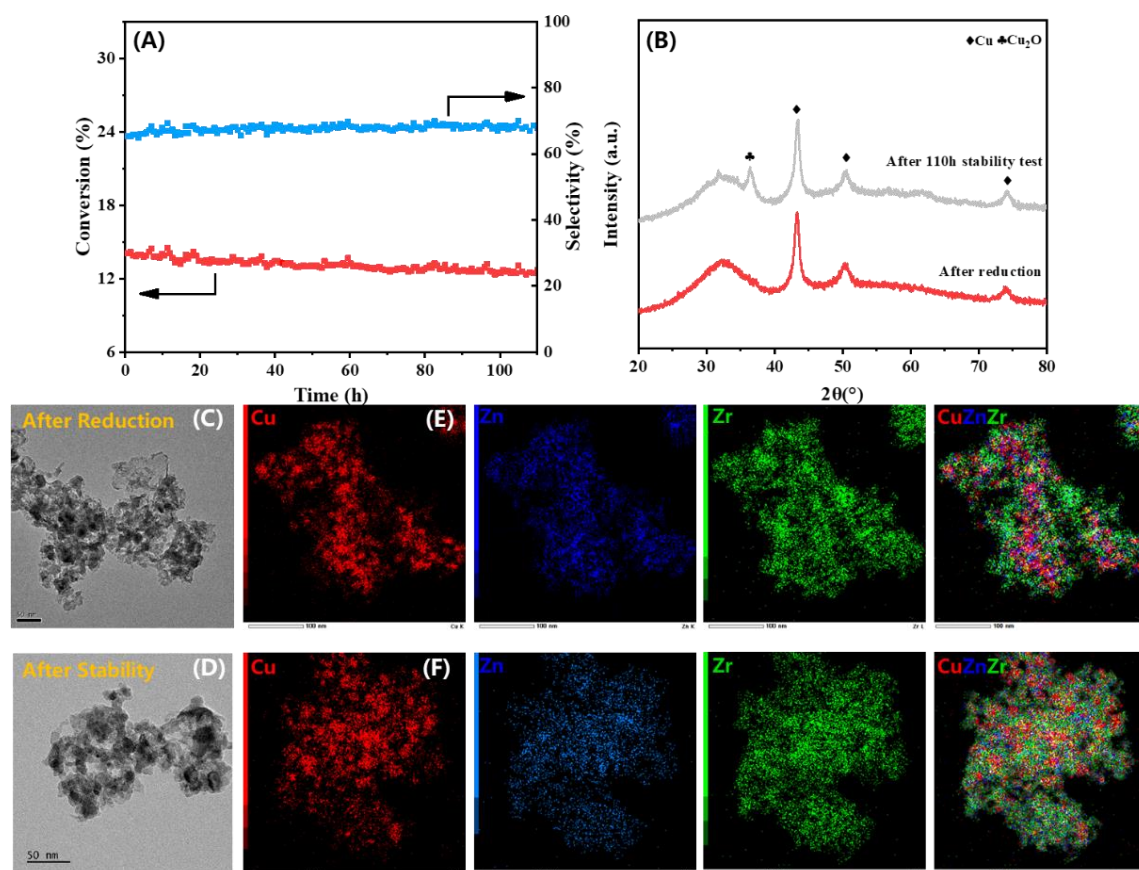


Figure S4. C3Z2Z5 (A) 110 h stability test, (B) XRD pattern after reduction and stability test, TEM image (C) after reduction and (D) stability test, EDS-mapping images (E) after reduction and (F) stability test.

Table S1. Catalytic performance of Cu-based catalysts for CO₂ hydrogenation to methanol

Catalyst	Reaction condition		Catalytic performance		
	T (°C), P (MPa)	WHSV/GHSV	CO ₂ Conversion (%)	Methanol Selectivity (%)	STY (g _{methanol} /kg _{cat} /h)
This work	240, 3.0	18000 mL/g _{cat} /h	15.5	60.6	610.8
Cu-ZrO ₂ [29]	220, 3.0	9600 mL/g _{cat} /h	6.7	69.6	161.5
Cu/a-ZrO ₂ [39]	240, 3.0	-	5.1	58.1	81.3
CuZr _{0.9} @SiO ₂ [49]	230, 2.5	12000 mL/g _{cat} /h	-	-	23.3
Cu _{0.8} ZrO ₂ [50]	230, 2.5	12400 mL/g _{cat} /h	<1	75	12.4
FSP- 60Cu/ZrO ₂ [51]	230, 1.0	6000 mL/g _{cat} /h	2.9	59.5	28.6
CZ-8-350[52]	230, 1.0	8400 mL/g _{cat} /h	2.1	71.5	44.8
Cu ₄₀ /ZrO ₂ [53]	240, 5.0	-	6.6	68.0	-
CZ-450[54]	220, 3.0	3600 h ⁻¹	4.2	53.9	45.7
100CZZ[55]	240, 3.0	3600 h ⁻¹	5.8	68.1	-
CuO-ZnO- ZrO ₂ /SAPO-11[56]	275, 3.0	-	8.1	98	-
Cu ₃₂ -ZnO-ZrO ₂ [5]	200, 1.0	8800 mL/g _{cat} /h	2.2/1.2	83.0/85.5	-
CuZnZr[57]	200, 3.0	19200 mL/g _{cat} /h	8.4	74	-
CZAZ-USP[58]	230, 3.0	10000 mL/g _{cat} /h	22.5	22.6	-
CZAZ-5Al[59]	250, 5.0	4000 mL/g _{cat} /h	25.2	60.6	-