

Supporting Information

Synthesis of durene by methylation of 1,2,4-trimethylbenzene with syngas over bifunctional CuZnZrO_x-HZSM-5 catalysts

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Table S1. Catalytic performance of 1,2,4-TriMB methylated with syngas in different ZZO and Z5 mass ratios.

Mass ratio	Conv. (%)	Product selectivity (%)														
		Non-aromatic hydrocarbons			Aromatics											
		C ₁ -C ₅ alkane	Ethylene	Propylene	Durene	1,2,3,5-TeMB	1,2,3,4-TeMB	1,3,5-TriMB	1,2,3-TriMB	4-ET	PX	MX	OX	T	B	Others
1/9	11.3	4.1	1.7	0.6	16.8	2.4	1.0	30.8	17.3	1.0	4.5	11.9	4.3	2.4	0.3	0.9
2/8	17.0	5.3	1.9	0.4	26.3	4.1	1.9	21.9	11.3	0.9	4.7	11.9	4.5	1.6	0.2	3.1
3/7	18.0	7.9	2.5	0.8	28.9	2.8	1.4	15.6	9.7	1.1	4.7	11.5	4.3	1.4	0.2	7.2
4/6	21.6	10.2	3.4	0.7	37.7	3.0	1.6	10.2	5.5	1.3	5.0	11.9	4.4	1.4	0.2	3.5
5/5	20.0	11.4	4.7	1.3	38.2	3.2	1.7	9.2	5.0	1.3	4.8	10.8	4.1	1.2	0.1	3.0

Catalyst: ZZO-Z5 (Zn/Zr molar ratio of 1/7, and Z5 SiO₂/Al₂O₃ ratio of 85). Reaction conditions: CO/H₂/N₂ = 30/60/10, T = 320 °C, P = 3.0

MPa, GHSV = 12000 mL g⁻¹ h⁻¹, and 1,2,4-TriMB vaporized at 110 °C. Conv.: 1,2,4-TriMB conversion; 4-ET: 4-ethyltoluene; PX: *para*-xylene;

MX: *meta*-xylene; OX: *ortho*-xylene; T: toluene; B: benzene; Others: other C₁₁₊ aromatics.

Table S2. Relative concentration of CuZnZr catalysts analyzed by XRF.

Sample	Relative concentration of metal (wt%)		
	Cu	Zn	Zr
4CuZnZr	4.4	8.9	86.7
5CuZnZr	5.0	7.0	88.0
6CuZnZr	5.8	4.4	89.8
7CuZnZr	6.6	4.0	89.4

Table S3. Pore structures of Z5, ZZO and CuZZO catalysts.

Catalyst	BET surface area	Pore volume
	(m ² /g)	(cm ³ /g)
Z5	310	0.1781
ZZO	20	0.0330
4CuZZO	13	0.0218
5CuZZO	14	0.0209
6CuZZO	15	0.0224
7CuZZO	15	0.0232

Table S4. Catalytic performance of methanol route and syngas route.

Methylation reagent	Catalyst	Conv. of 1,2,4-TriMB (%)	Selec. (%)		Durene/C ₁₀ (%)
			C ₁₀	Durene	
MeOH	Z5	18.8	35.0	22.3	76.7
CO + H ₂	5CuZZO-Z5	19.1	63.7	44.6	89.9

Reaction conditions: $T = 320$ °C, $P = 3.0$ MPa. Methanol as methylation reagent: H₂/N₂ = 60/40, molar ratio of 1,2,4-TriMB and MeOH = 2/1, and WHSV = 1.3 h⁻¹. Syngas as methylation reagent: CO/H₂/N₂ = 30/60/10, GHSV = 12000 mL g⁻¹ h⁻¹, and 1,2,4-TriMB vaped at 110 °C.

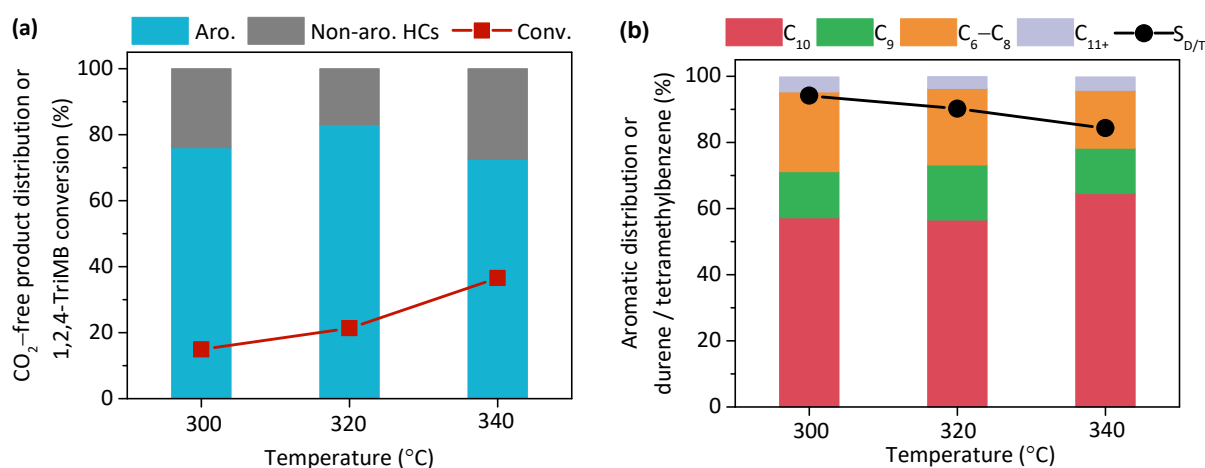


Fig. S1. Catalytic performance of 1,2,4-TriMB methylated with syngas in different temperatures. Distribution of (a) CO₂-free products and (b) aromatics. Catalyst: ZZO-Z5 (mass ratio of 4/6, Zn/Zr molar ratio of 1/7, and Z5 SiO₂/Al₂O₃ ratio of 130). Reaction conditions: CO/H₂/N₂ = 30/60/10, $P = 3.0$ MPa, GHSV = 12000 mL g⁻¹ h⁻¹, and 1,2,4-TriMB vaped at 110 °C.

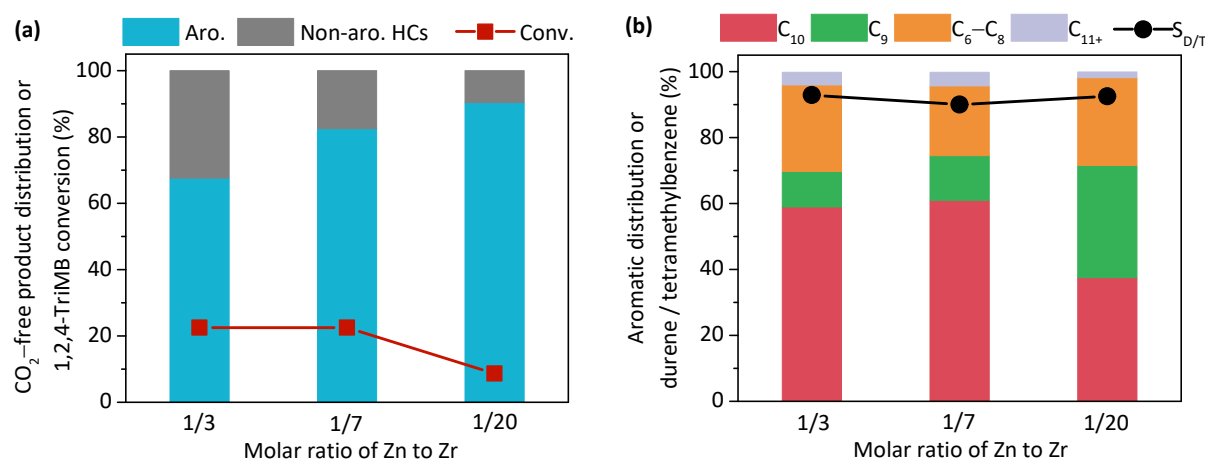


Fig. S2. Catalytic performance of 1,2,4-TriMB methylated with syngas in different Zn/Zr molar ratio. Distribution of (a) CO₂-free products and (b) aromatics. Catalyst: ZZO-Z5 (mass ratio of 4/6, Z5 SiO₂/Al₂O₃ ratio of 130). Reaction conditions: CO/H₂/N₂ = 30/60/10, $T = 320$ °C, $P = 3.0$ MPa, GHSV = 12000 mL g⁻¹ h⁻¹, and 1,2,4-TriMB vaped at 110 °C.

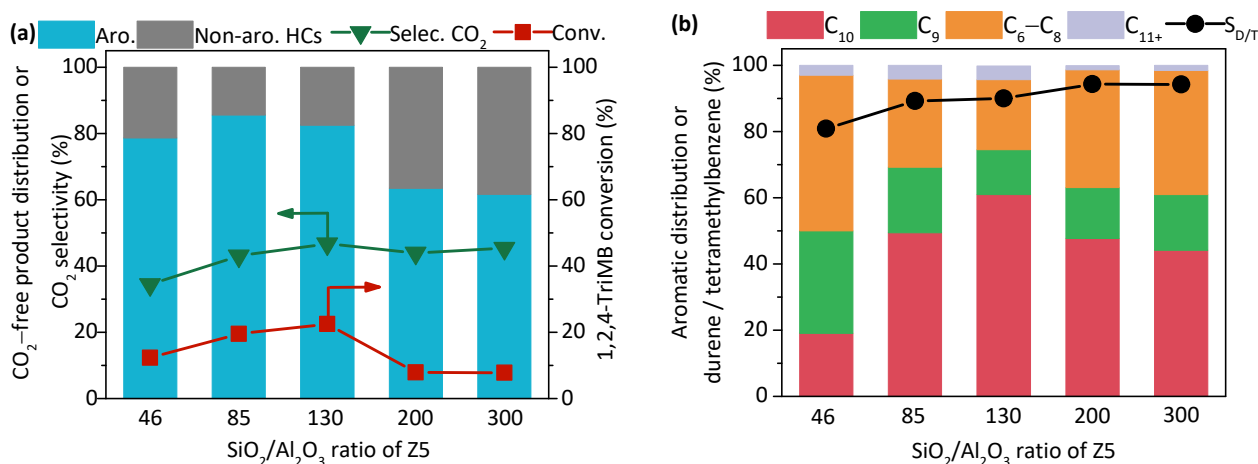


Fig. S3. Catalytic performance of 1,2,4-TriMB methylated with syngas in different Z5 SiO₂/Al₂O₃ ratio. Distribution of (a) CO₂-free products and (b) aromatics. Catalyst: ZZO-Z5 (mass ratio of 4/6, Zn/Zr molar ratio of 1/7). Reaction conditions: CO/H₂/N₂ = 30/60/10, $T = 320$ °C, $P = 3.0$ MPa, GHSV = 12000 mL g⁻¹ h⁻¹, and 1,2,4-TriMB vaped at 110 °C.

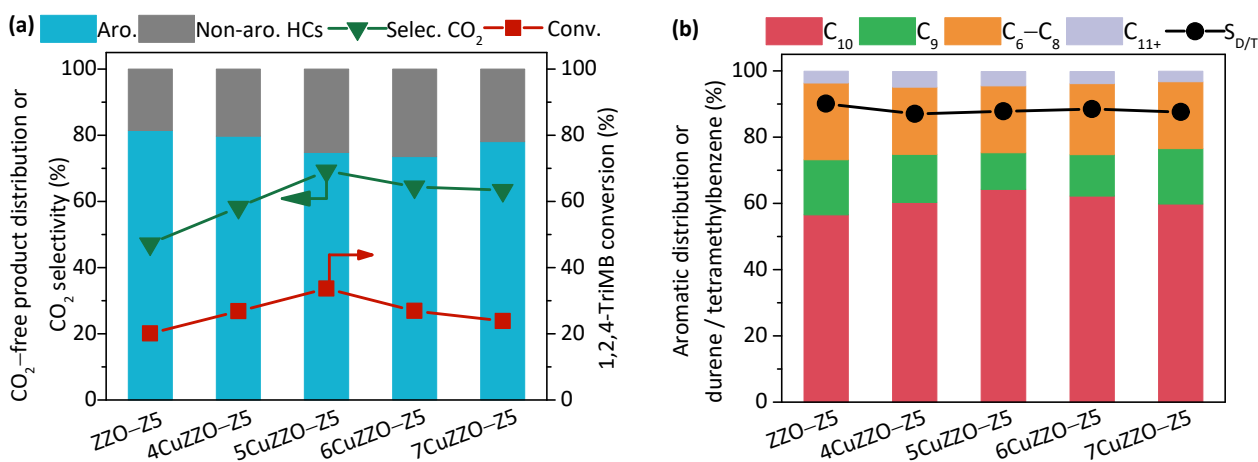


Fig. S4. Catalytic performance of 1,2,4-TriMB methylated with syngas in different Cu contents. Distribution of (a) CO₂-free products and (b) aromatics. Catalyst: Oxides-Z5. Reaction conditions: CO/H₂/N₂ = 30/60/10, $T = 320$ °C, $P = 3.0$ MPa, GHSV = 12000 mL g⁻¹ h⁻¹, and 1,2,4-TriMB vaped at 110 °C. Selec. CO₂: CO₂ selectivity.

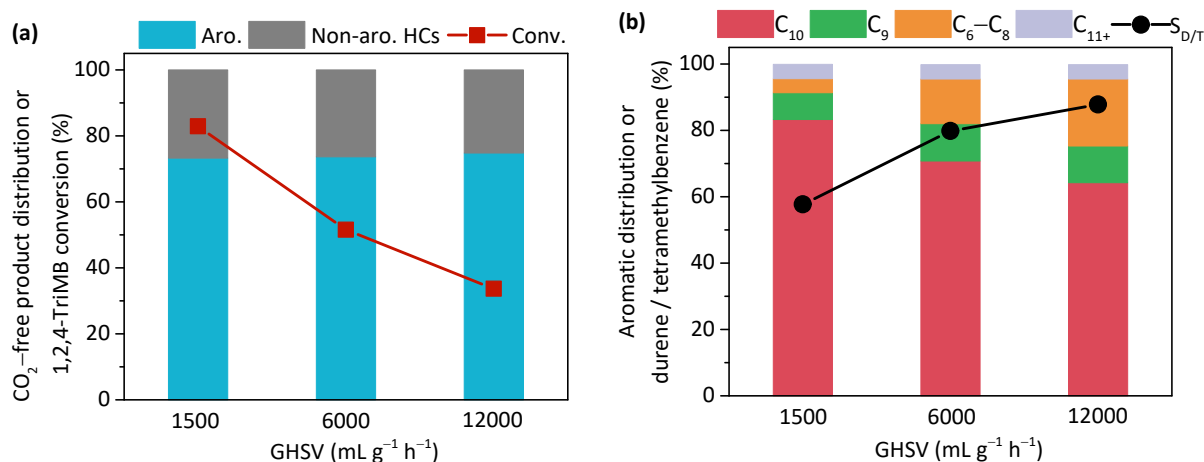


Fig. S5. Catalytic performance of 1,2,4-TriMB methylated with syngas in different GHSV. Distribution of (a) CO₂-free products and (b) aromatics. Catalyst: 5CuZZO-Z5 (mass ratio of 4/6, Z5 SiO₂/Al₂O₃ ratio of 130). Reaction conditions: CO/H₂/N₂ = 30/60/10, $T = 320$ °C, $P = 3.0$ MPa, and 1,2,4-TriMB vaped at 110 °C.

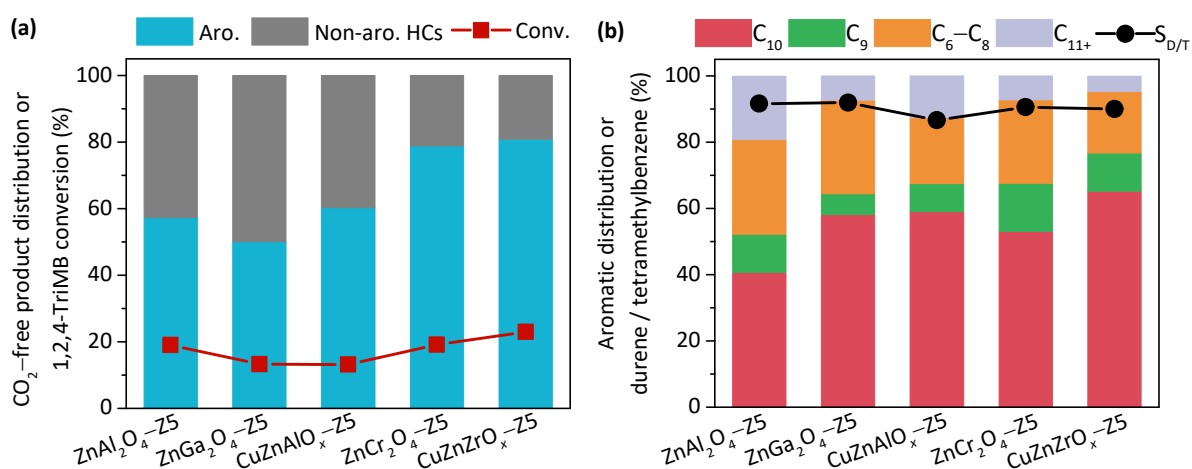


Fig. S6. Catalytic performance of 1,2,4-TriMB methylated with syngas in different catalysts. Distribution of (a) CO₂-free products and (b) aromatics. Catalyst: Oxides-Z5 (mass ratio of 4/6, and Z5 SiO₂/Al₂O₃ ratio of 130). Reaction conditions: CO/H₂/N₂ = 30/60/10, $T = 290$ °C, $P = 3.0$ MPa, GHSV = 12000 mL g⁻¹ h⁻¹, and 1,2,4-TriMB vaped at 110 °C.

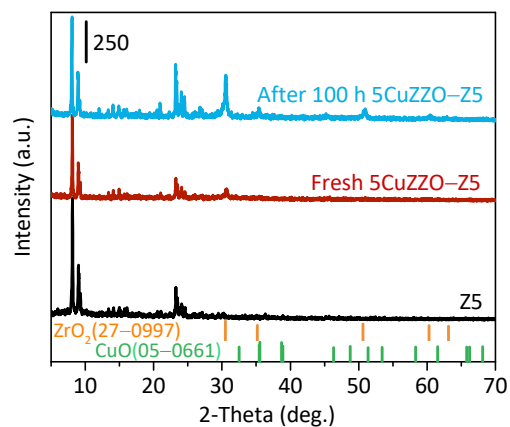


Fig. S7. XRD pattern of Z5 and 5CuZZO-Z5 which are fresh and after 100 h reaction, respectively.

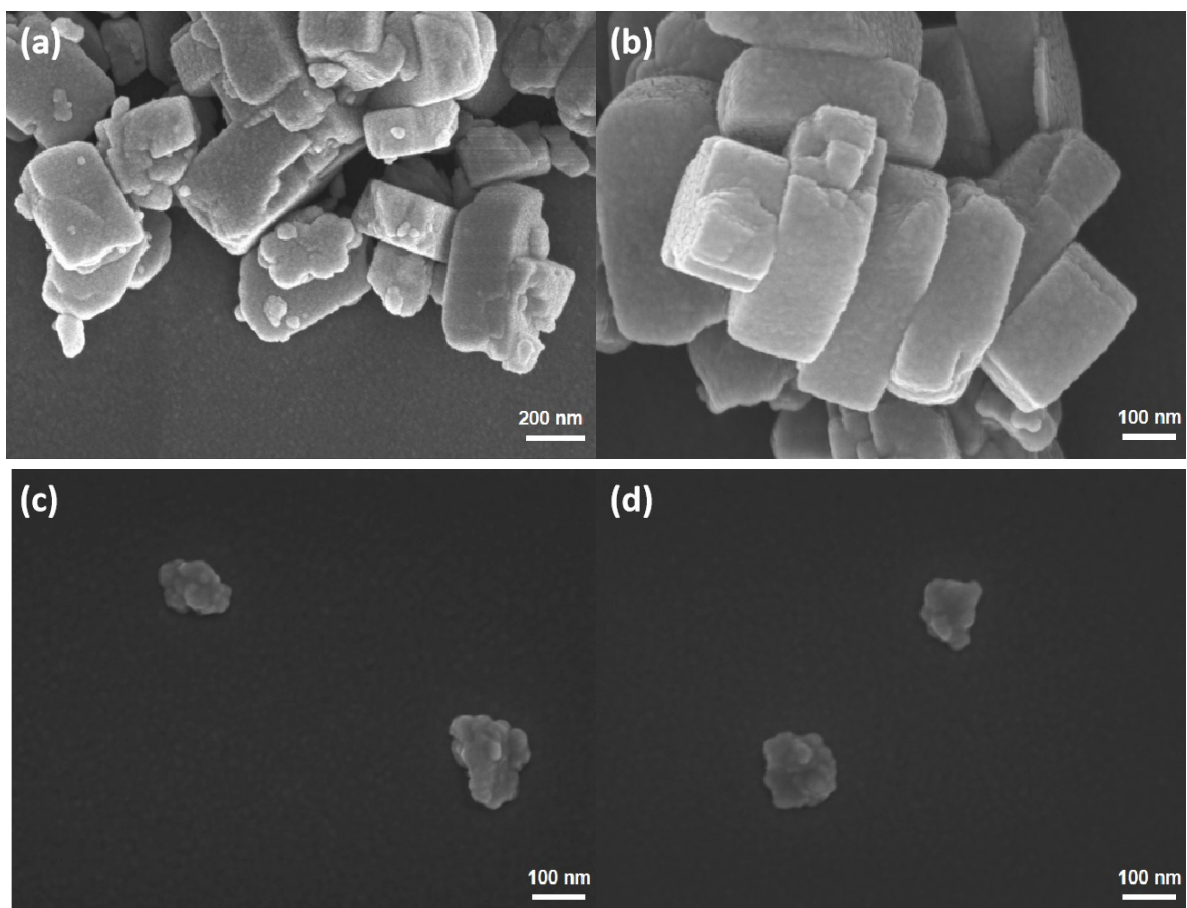


Fig. S8. SEM images of (a) ZZO-Z5, (b) Z5, (c) ZZO, and (d) 5CuZZO.

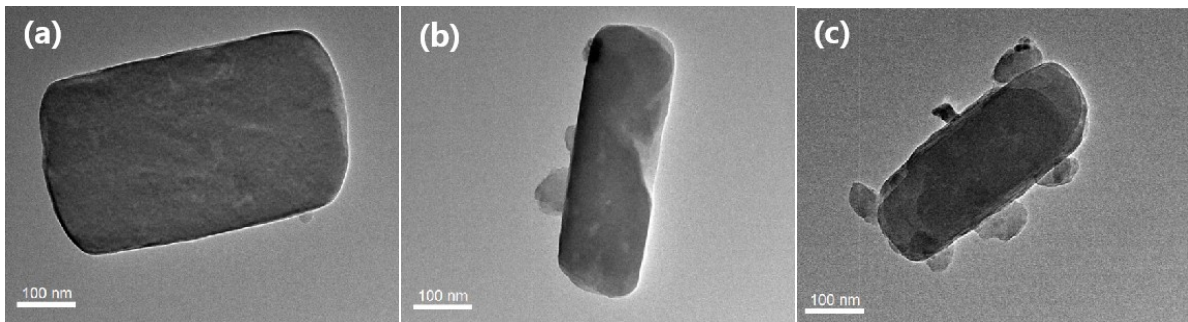


Fig. S9. TEM images of (a) Z5, (b) ZZO-Z5, and (c) 5CuZZO-Z5.

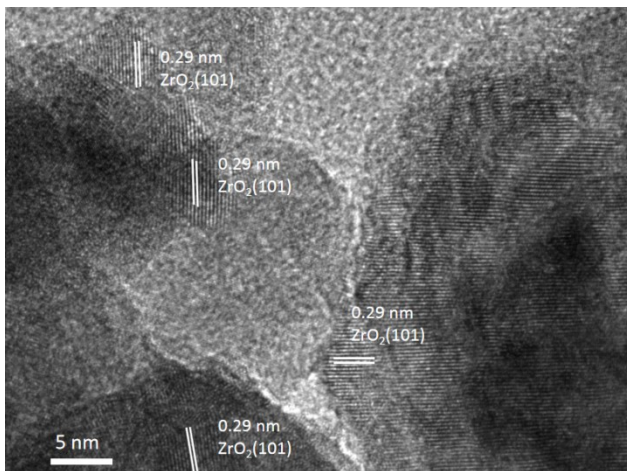


Fig. S10. HR-TEM image of ZZO-Z5.

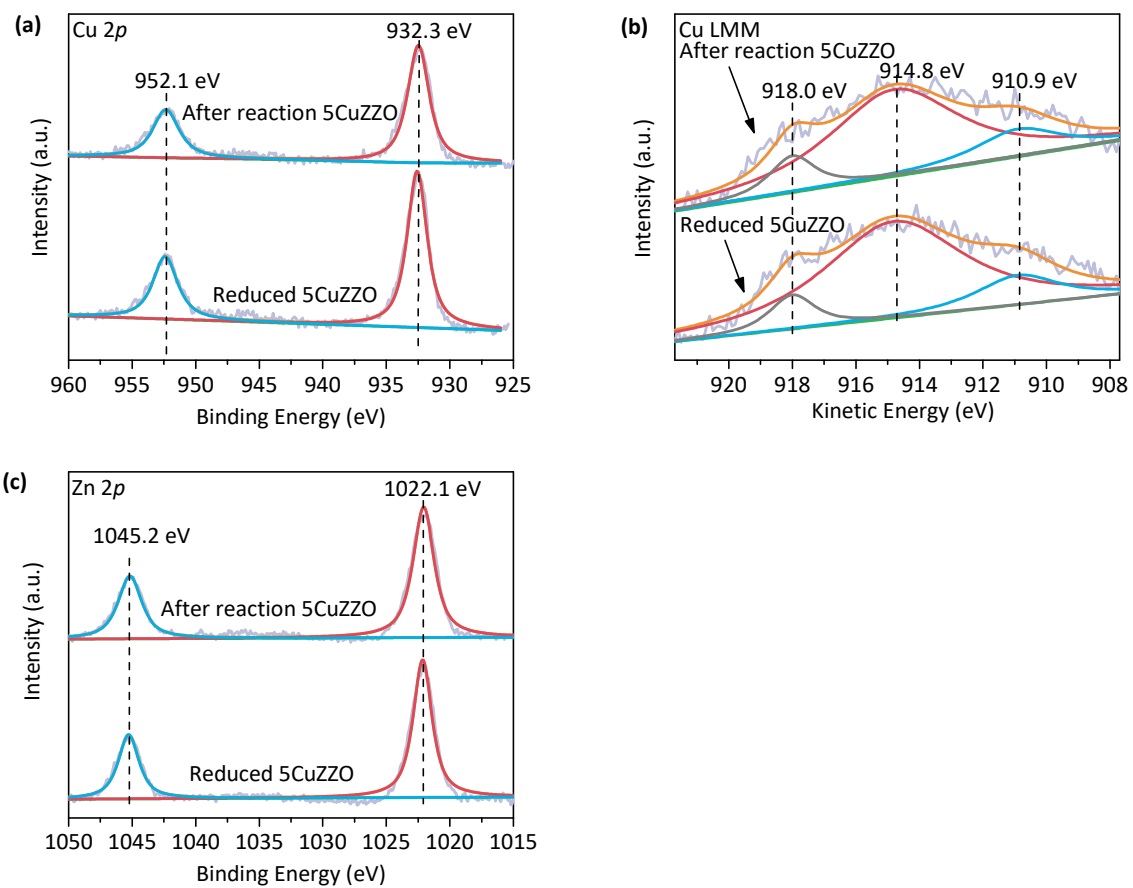


Fig. S11. In situ XPS–AES spectra of (a) Cu 2*p*, (b) Cu LMM, and (c) Zn 2*p* for after 15 h reaction and reduced 5CuZZO.