Supplementary Information

Efficient Syngas Conversion into Light Aromatics over Ceria-Zirconia and Cu-ZSM-5 Bifunctional Catalyst

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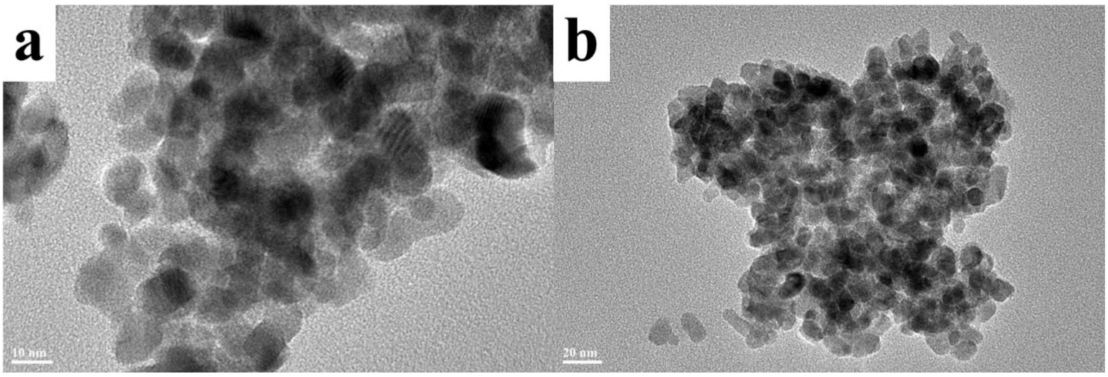

Fig. S1. TEM images of CZS ($Ce_{0.2}Zr_{0.8}O_x$).

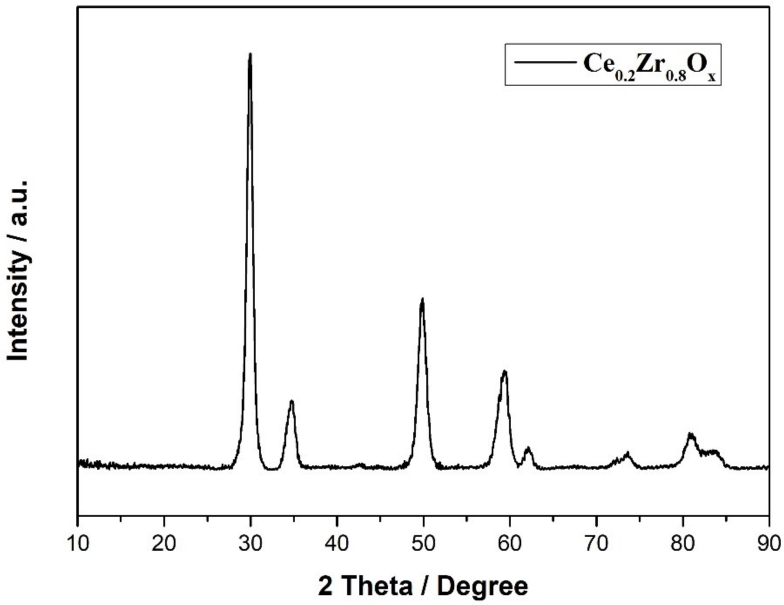

Fig. S2. XRD pattern of CZS ($Ce_{0.2}Zr_{0.8}O_x$).

Table S1. Textural properties of ceria-zirconia solid solutions.

Sample	S_{BET}[a] (m^2/g)	V_{pore}[a] (cm^3/g)	d_{pore}[a] (nm)	Crystal parameters[b] (nm)		
				a	b	c
$Ce_{0.2}Zr_{0.8}O_2$	79.2	0.37	18.8	0.3634	-	0.5238

[a] The BET surface area, pore volume and average pore size were determined by N_2 physisorption. [b] Lattice parameters were obtained from XRD studies.

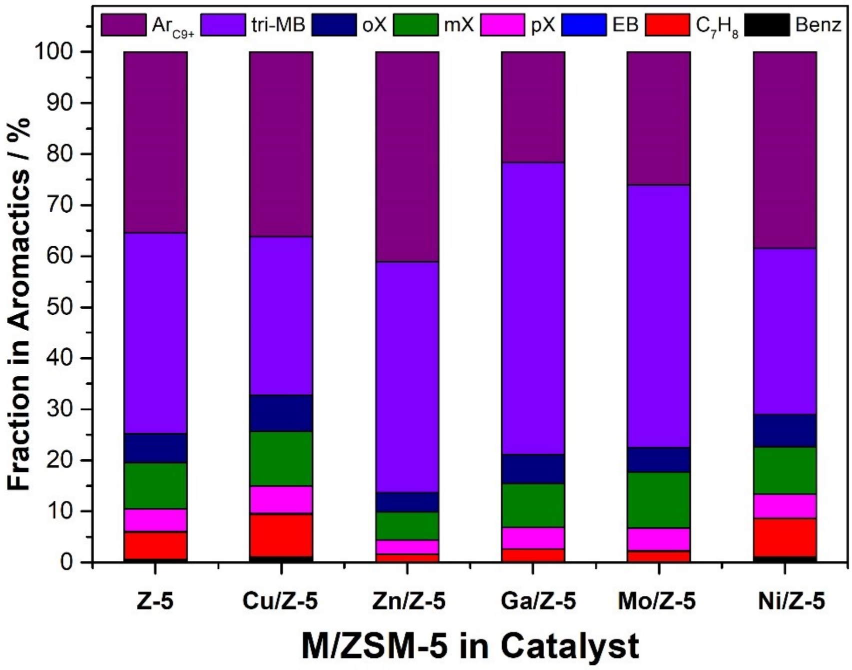

Fig. S3. The effect of metal on ZSM-5 catalyst on the aromatics distributions. Reaction conditions: catalyst = CZS + Zeolite (weight ratio = 1), 450 ^{o}C, TOS=20 h, 3.6 MPa, GHSV = 600 ml_{syngas} / $g_{cat.}$·h.

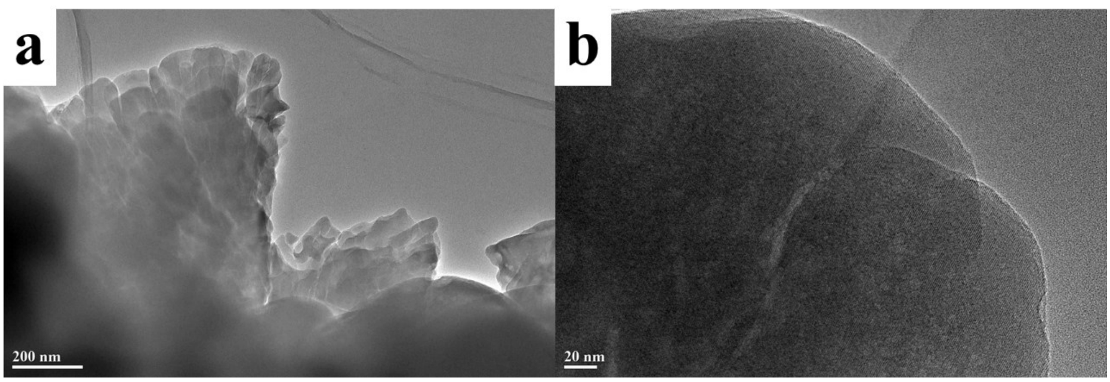

Fig. S4. TEM images of ZSM-5 (Si/Al = 120).

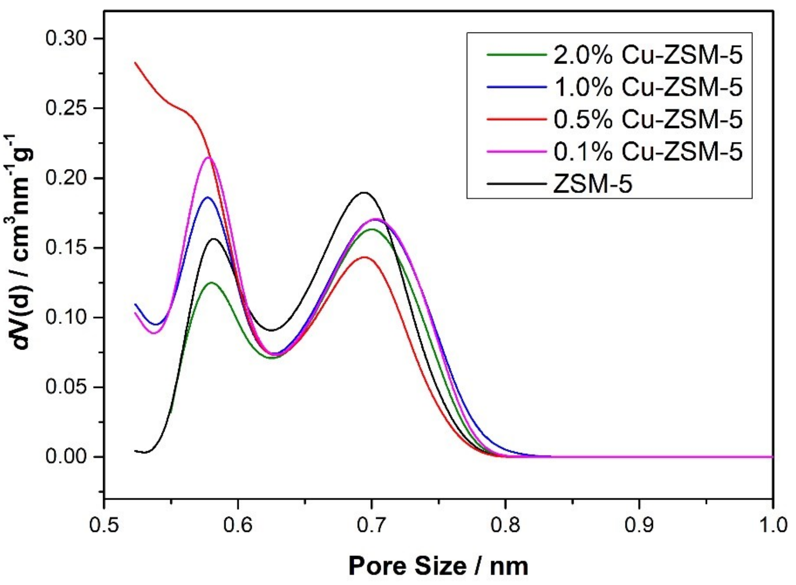

Fig. S5. The micropore size distributions of ZSM-5 samples calculated with N_2-DFT model

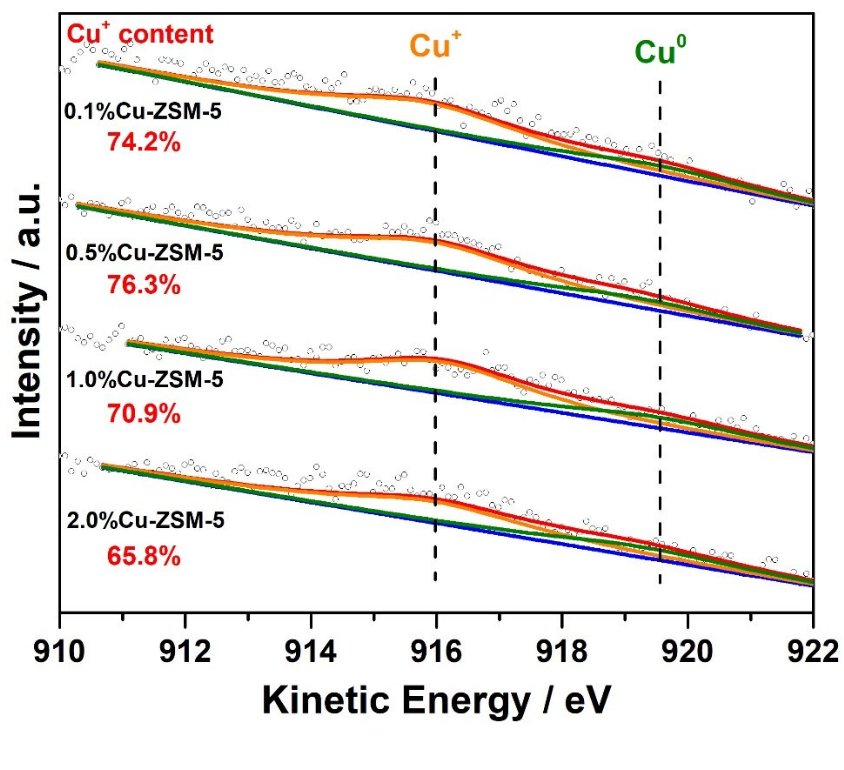

Fig. S6. Cu LMM X-ray excited Auger electron spectra of the reduced Cu-ZSM-5 catalysts with different copper contents. Cu^+ content was calculated based on peak area ($X_{Cu^+} = Cu^+ / (Cu^+ + Cu^0)$).

Table S2. H_2/Cu consumption ratios derived from TPR spectra.

Sample	Cu loading (μmol/g)	H_2 consumption (μmol/g)	H_2/Cu
0.1%Cu-ZSM-5	15.7	4.36	0.28
0.5%Cu-ZSM-5	78.5	35.81	0.46
1.0%Cu-ZSM-5	157.5	68.47	0.43
2.0%Cu-ZSM-5	314.9	148.04	0.47

Table S3. The acidity of ZSM-5 and Cu-ZMS-5 analyzed by ^{31}P MAS NMR.

Sample	Acidity / (μmol/g)	
	Brønsted acid	Lewis acid
ZSM-5	105	-
0.5%Cu-ZSM-5	64	91
0.5%Cu-ZSM-5-re	81	57

Table S4. The catalytic performance of control catalysts.[a]

Samples	CO conv. / %	CO_2 select. / %	Selectivity in Hydrocarbons / %					
			CH_4	$C_{2-4}^{=}$	C_{2-4}^{o}	C_{5+}	Ar	Others
SiO_2 + 0.5%Cu-Z5[b]	0.5	50.3	25.7	5.5	65.0	2.6	/	/
CZS + SiO_2[b]	12.8	36.2	9.6	47.2	25.4	17.6	/	0.2

[a] Reaction conditions: catalyst = oxide + zeolite (weight ratio = 1), 450 °C, 3.6 MPa, TOS = 10 h, GHSV = 600 ml_{syngas} / $g_{cat.}$·h. [b] SiO_2 (quartz sand) used as a control. ($C_{2-4}^{=}$, C_{2-4}^{o}, C_{5+}, and Ar denote C_2-C_4 olefins, C_2-C_4 paraffins, C_{5+} hydrocarbons exclusive of aromatics, and aromatics, respectively).

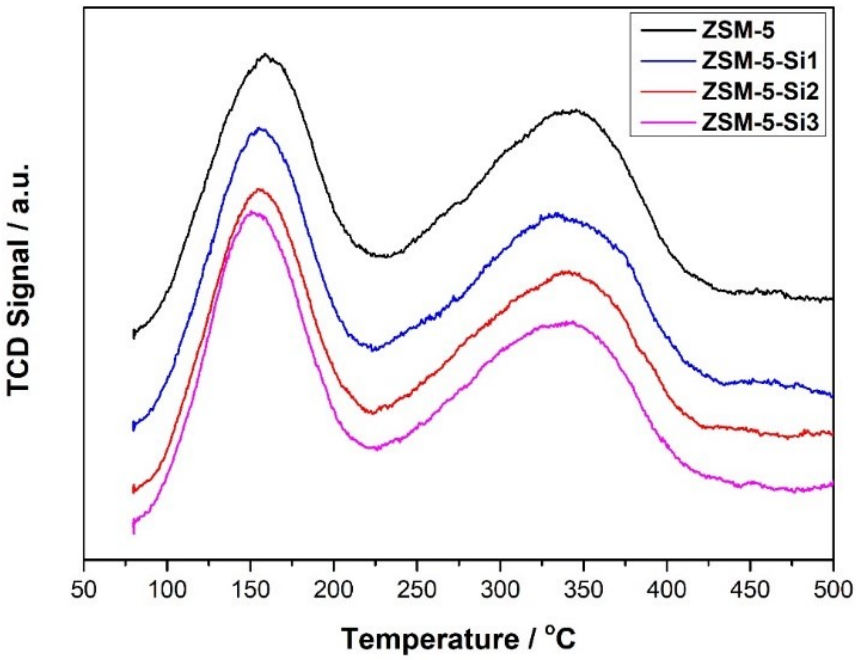

Fig. S7. NH_3-TPD profiles of passivated ZSM-5 samples

Table S5. The surface acidity of ZSM-5 samples derived from NH_3-TPD.

Sample	T_1 / °C	Weak acidity / (μmol·g^{-1})	T_2 / °C	Strong acidity / (μmol·g^{-1})
Z5	157.0	106.2	333.0	144.7
Z5-Si1	155.0	103.5	334.2	125.0
Z5-Si2	155.5	104.3	340.7	114.1
Z5-Si3	150.4	106.5	338.3	108.7

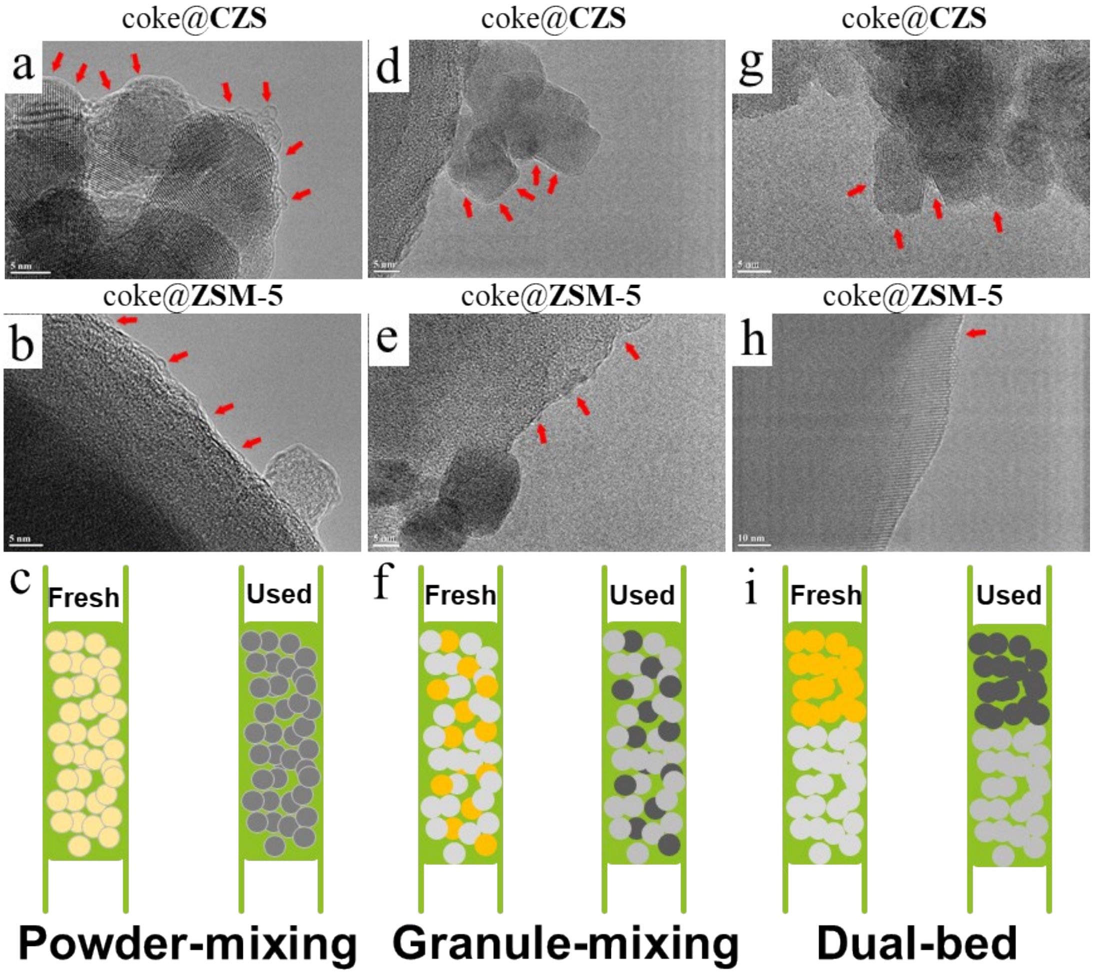

Fig. S8. The TEM images of coke on catalysts with different proximity. a-c) poder-mixing, d-f) granule-mixing and g-i) dual-bed. Reaction conditions: catalyst = CZS + ZSM-5 (weight ratio = 1), 450 °C, 3.6 MPa, TOS = 20 h, GHSV = 600 ml_{syngas} / $g_{cat.}$·h.

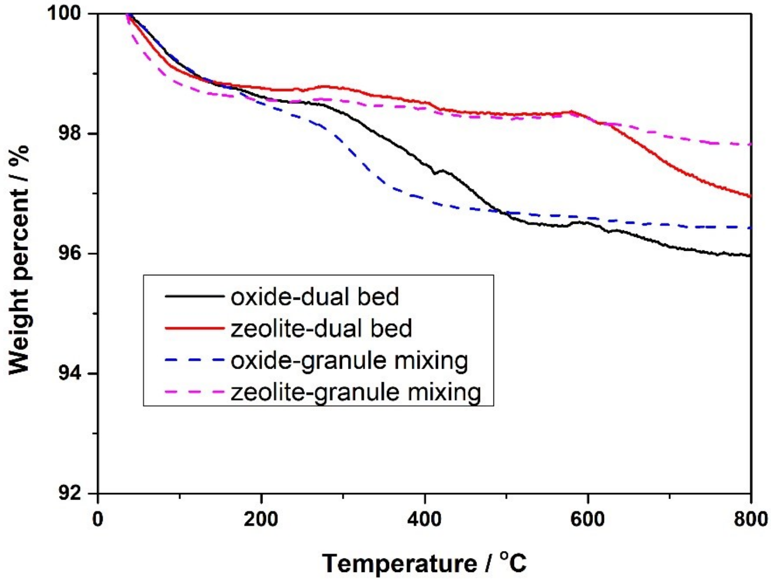

Fig. S9. The TGA curves of the used bifunctional catalyst. Reaction conditions: catalyst = CZS + ZSM-5 (weight ratio = 1), 450 ^{o}C, 3.6 MPa, TOS = 20 h, GHSV = 600 ml_{syngas} / $g_{cat.}$·h.