High CO conversion in syngas to aromatics by addition of ZnMnZr oxides as methanol synthesis components

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Table S1 XRF results of materials.

Sample	Molar composition	
6Mn4Zr	Mn (mol%)	Zr (mol%)
	59.35	40.65
H-ZSM-5(60)	Si/Al (in mole)	
	58.52	
SAPO-34(0.1)	Si/Al (in mole)	
	0.12	

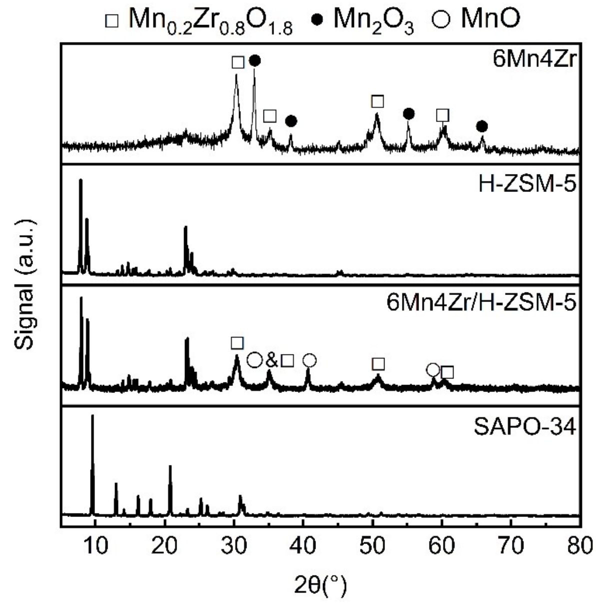

Figure S1. XRD patterns of 6Mn4Zr, H-ZSM-5, 6Mn4Zr/H-ZSM-5(S) and SAPO-34

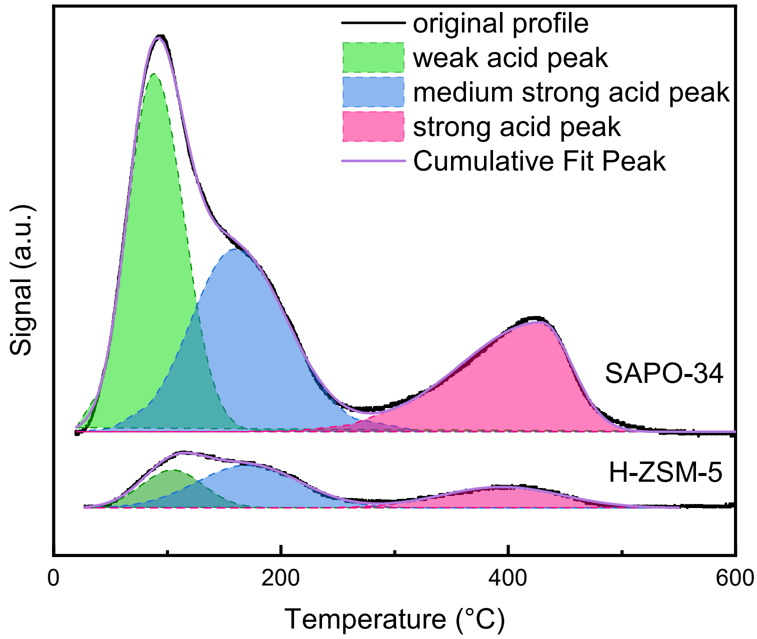

Figure S2. NH_3-TPD profile of zeolites.

Table S2 Quantification of acid sites in Figure S2

Zeolites	Acid sites distribution			Total acid sites
	Weak acid sites	Medium strong acid sites	Strong acid sites	μmol/g
H-ZSM-5	19.07%	52.09%	28.84%	73.45
SAPO-34	43.01%	31.56%	25.43%	720.41

Table S3 Crystallinity and crystal size (nm) (calculated by Scherrer equation) of oxides.

Sample	Crystallinity (%)	Crystal Size (nm)
2Mn8Zr	19.5	12.3
0.2Zn2Mn8Zr	16.3	16.5
0.4Zn2Mn8Zr	15.4	15.0
1Zn2Mn8Zr	13.1	18.0
2Zn2Mn8Zr	12.0	17.7
2Mn8Zr*	21.2	13.2
0.2Zn2Mn8Zr*	17.2	16.8
0.4Zn2Mn8Zr*	16.1	15.9
1Zn2Mn8Zr*	13.5	18.2
2Zn2Mn8Zr*	12.1	17.9

Table S4 Quantification oxides O 1s orbit with different composition

Oxides	Lattice O (O_L)	Vacancy O(O_V)	Chemi-sorbed O(O_C)
2Mn8Zr	58.34%	28.12%	13.54%
0.2Zn2Mn8Zr	58.92%	29.07%	12.01%
0.4Zn2Mn8Zr	57.20%	30.91%	11.89%
1Zn2Mn8Zr	55.41%	32.45%	12.13%
2Zn2Mn8Zr	54.96%	34.62%	10.41%

Table S5 Quantification oxides Mn 2p orbit with different composition

Oxides	Mn^{2+}	Mn^{3+}
2Mn8Zr	59.30%	40.70%
0.2Zn2Mn8Zr	57.81	42.19
0.4Zn2Mn8Zr	50.31	49.69
1Zn2Mn8Zr	48.58	51.42
2Zn2Mn8Zr	39.31	60.69

Table S6. Detailed organic products distribution of bifunctional catalyst and multi-functional catalyst

Catalyst	Methanol & DME	Methane	Ethylene	Ethane	Propylene	Propane	Butane	Butene (including 1,3-butadiene)	C_5-C_6	C_7	C_8^+	Aromatics
2Zn2Mn8Zr/H-ZSM-5	0.37%	11.52%	1.40%	24.48%	0.50%	10.67%	20.27%	0.06%	29.95%	0.44%	0.00%	0.34%
2Zn2Mn8Zr|H-ZSM-5	0.17%	7.31%	1.27%	5.28%	1.01%	24.44%	26.33%	0.94%	24.90%	0.70%	0.11%	7.55%
2Zn2Mn8Zr|(6Mn4Zr/H-ZSM-5)(1:1:1)	0.33%	7.43%	1.51%	9.84%	0.86%	9.72%	24.50%	0.80%	42.40%	0.80%	0.35%	1.46%

Table S7 Coke deposition over bifunctional catalyst in figure 4.

Catalyst	Mass ratio at 200°C	Mass ratio at 800°C	Mass loss of coke
2Zn2Mn8Zr|H-ZSM-5	98.09%	96.79%	1.30%
2Zn2Mn8Zr/H-ZSM-5	98.32%	97.06%	1.26%
6Mn4Zr/H-ZSM-5	98.19%	95.52%	2.66%
2Zn2Mn8Zr/SAPO-34	95.04%	91.41%	3.63%

Table S8 Reaction condition and results of orthogonal experiment

Entry	Reaction Temperature	Reaction Pressure	Mass ratio of 6Mn4Zr to H-ZSM-5	Mass ratio of 0.1Zn1Mn4Zr to bifunctional catalyst	CO conversion	CO_2 selectivity	Methanol & DME	Methane	C_2-C_4 paraffin	C_2-C_4 olefin	C_5^+	Aromatics	Carbon Balance
1	400	3	1:1	1:8	25.90%	39.89%	0.08%	2.20%	14.37%	2.29%	8.97%	72.09%	99.55%
2	400	2	2:1	1:4	20.73%	38.86%	0.07%	2.50%	25.77%	4.82%	19.01%	47.55%	98.42%
3	400	5	1:2	1:2	40.86%	38.68%	0.12%	2.30%	32.75%	2.83%	38.33%	23.37%	100.87%
4	400	4	4:1	1:1	39.59%	38.79%	0.29%	1.87%	29.41%	5.11%	41.64%	21.24%	97.15%
5	375	3	2:1	1:2	17.21%	36.90%	0.24%	3.47%	25.41%	4.26%	28.47%	37.50%	101.63%
6	375	2	1:1	1:1	16.94%	37.77%	0.31%	1.84%	26.90%	5.91%	44.10%	20.95%	99.91%
7	375	5	4:1	1:8	20.94%	40.02%	0.33%	1.66%	8.07%	4.98%	13.26%	71.56%	96.07%
8	375	4	1:2	1:4	21.24%	38.82%	0.16%	1.42%	14.46%	3.29%	20.36%	60.20%	102.29%
9	350	3	1:2	1:1	11.92%	37.50%	0.24%	1.22%	20.33%	5.71%	43.68%	28.81%	97.54%
10	350	2	4:1	1:2	8.70%	39.04%	0.52%	1.18%	10.61%	11.62%	27.19%	48.49%	100.76%
11	350	5	1:1	1:4	13.50%	37.10%	0.14%	1.04%	11.22%	1.47%	13.43%	72.69%	98.03%
12	350	4	2:1	1:8	8.32%	34.21%	0.13%	1.22%	8.25%	1.81%	9.10%	79.50%	101.98%
13	425	3	4:1	1:4	35.11%	39.40%	0.14%	3.07%	32.47%	6.38%	28.09%	29.36%	96.36%
14	425	2	1:2	1:8	23.23%	39.73%	0.08%	3.37%	32.35%	6.76%	22.60%	34.46%	99.68%
15	425	5	2:1	1:1	51.06%	37.53%	0.16%	5.71%	48.32%	1.80%	38.43%	5.58%	97.22%
16	425	4	1:1	1:2	50.15%	38.52%	0.05%	4.93%	52.10%	2.14%	25.82%	14.95%	100.50%

Table S9 Range analysis of orthogonal experiment

Factor	Value	CO conversion	CO_2 selectivity	Organic products distribution							Determinant factor
				Methanol & DME	Methane	C_2-C_4 paraffin	C_2-C_4 olefin	C_5^+	Aromatics	Paraffins	
Reaction Temperature (°C)	350	10.61%	36.96%	0.26%	1.17%	12.60%	5.15%	23.35%	57.37%	37.12%	3.83
	375	19.08%	38.38%	0.26%	2.10%	18.71%	4.61%	26.55%	47.55%	47.36%	4.78
	400	31.77%	39.06%	0.14%	2.22%	25.58%	3.76%	26.99%	41.06%	54.79%	5.90
	425	39.89%	38.80%	0.11%	4.27%	41.31%	4.27%	28.74%	21.09%	74.32%	2.16
Reaction Pressure (MPa)	2	17.40%	38.85%	0.25%	2.22%	23.91%	7.28%	28.23%	37.86%	54.36%	3.01
	3	22.54%	38.42%	0.18%	2.49%	23.15%	4.66%	27.30%	41.94%	52.94%	4.45
	4	29.83%	37.59%	0.16%	2.36%	26.06%	3.09%	24.23%	43.97%	52.65%	6.21
	5	31.59%	38.33%	0.19%	2.68%	25.09%	2.77%	25.86%	43.30%	53.63%	6.34
Mass ratio of 6Mn4Zr to H-ZSM-5	1:2	24.31%	38.68%	0.15%	2.08%	24.97%	4.65%	31.24%	36.71%	58.29%	3.72
	1:1	26.62%	38.32%	0.15%	2.50%	26.15%	2.95%	23.08%	45.17%	51.73%	5.80
	2:1	24.33%	36.88%	0.15%	3.23%	26.94%	3.17%	23.75%	42.53%	53.92%	4.77
	4:1	26.09%	39.31%	0.32%	1.95%	20.14%	7.02%	27.55%	42.66%	49.64%	5.61
Mass ratio of 0.1Zn1Mn4Zr to bifunctional catalyst	1:1	29.88%	37.90%	0.25%	2.66%	31.24%	4.63%	41.96%	19.15%	75.86%	1.38
	1:2	29.23%	38.29%	0.23%	2.97%	30.22%	5.21%	29.95%	31.08%	63.14%	3.35
	1:4	22.65%	38.55%	0.13%	2.01%	20.98%	3.99%	20.22%	52.45%	43.21%	6.75
	1:8	19.60%	38.46%	0.16%	2.11%	15.76%	3.96%	13.48%	64.40%	31.35%	8.67

Analysis of influence of each factor on reaction results in range analysis:

As shown in table S9, factor 1 and factor 4 exhibited significant impact on reaction results. Raising reaction temperature could promote the activation of H_2 over both 0.2Zn2Mn8Zr and 6Mn4Zr. It provided more methanol from 0.2Zn2Mn8Zr, which could act as H carrier and enhance over-hydrogenation; moreover, the C-C coupling over 6Mn4Zr could be interrupted because of the enhanced H_2 supplementary[1], and remarkably increase the selectivity of C_2-C_4 paraffin. While increasing the addition of

0.2Zn2Mn8Zr, it mainly affects the generation of methanol, while the C-C coupling ability over 6Mn4Zr could be maintained. Thus, at higher addition of 0.2Zn2Mn8Zr, it generates more C_5^+ rather than aromatics. Increasing reaction pressure from 2 MPa to 3 MPa could promote the generation of aromatics at the expense of C_2-C_4 olefin, which could be benefited from the improvement in C-C coupling over 6Mn4Zr that related to adsorption of CO. However, as the selectivity of C_2-C_4 olefin at 3 MPa was already consumed to 4.66% which is a quite low value, further increasing reaction pressure showed little influence on product selectivity. The mass ratio of 6Mn4Zr to H-ZSM-5 shows little influence of CO conversion, as CO was mainly activated over 0.2Zn2Mn8Zr. Both lacking of 6Mn4Zr or H-ZSM-5 would result in mismatch between the two-stage C-C coupling, and increase the selectivity of C_5^+.

Table S10 Carbon balance data of reaction results in main text

Table 2

Catalyst	Carbon balance
2Zn2Mn8Zr	99.15%
1Zn2Mn8Zr	101.57%
0.4Zn2Mn8Zr	97.58%
0.2Zn2Mn8Zr	103.88%
2Mn8Zr	97.02%

Table 3

Catalyst	Carbon balance
6Mn4Zr/H-ZSM-5*	98.05%
2Zn2Mn8Zr/H-ZSM-5	100.72%
2Zn2Mn8Zr|H-ZSM-5	99.55%
2Zn2Mn8Zr/SAPO-34	99.66%

Table 4

ZnMnZr composition	Carbon balance
2Zn2Mn8Zr[a]	97.55%
2Zn2Mn8Zr[b]	99.93%
2Zn2Mn8Zr[c]	103.18%
1Zn2Mn8Zr[b]	100.42%
0.4Zn2Mn8Zr[b]	99.72%
0.2Zn2Mn8Zr[b]	99.99%

Table 5

Mass ratioa	Carbon balance
1:(1:1)	99.99%
1:(2:2)	100.42%
1:(4:4)	99.55%

Table 6

Space velocity (mL·gcat-1·h-1)	Carbon balance
3000	99.55%
2400	101.44%
1800	98.37%
1200	99.24%
600	100.14%

Table S11 Comparation of catalyst performance of OX-ZEO catalyst in STA

Catalyst	Pressure	Reaction temperature	Space velocity	CO conversion	Aromatics selectivity	References
	MPa	°C	mL/(g_{cat}·h)	%	%	
Zn-ZrO_2/HZSM-5(1:2)	3(2:1)	400	500	21	81	[2]
$ZnCrO_x$/HZSM-5(1:1)	4(1:1)	350	1500	16	73.9	[3]
$Ce_{0.2}Zr_{0.8}O_2$/HZSM-5(1:1)	2(1:1)	380	600	8.1	83.1	[4]
$ZnCrO_x$/ZSM-5(1:1)	4(1:1)	350	1500	18.3	69.0	[5]
ZnCrOx/HZSM-5(1:1)	4(2:1)	400	1200	16.1	74	[6]
$MoZrO_2$/HZSM-5(1:2)	4(2:1)	400	3000	22	76	[7]
ZnO-MnO&H-ZSM-5(3:1)	3(1:1)	340	750	14.8	80.1	[8]
MnO/HZSM-5(2:1)	2(2:1)	350	333	21	83	[9]
Cr_2O_3/ZSM-5(1:1)	4(1:1)	395	2000	17.9	80.8	[10]
MnCr/ZSM-5(1:3)	4(1:1)	430	2250	13	70.9	[11]
ZrO_2/HZSM-5(1:1)	3.8(1:1)	400	500	24	67.4	[12]
$CeZrO_x$/Cu-ZSM-5(1:1)	3.6(1:1)	450	500	40.8	72.1	[13]
1CeZrOx-2ZnZrOx/Z5@Si(1.25:1)	3.6(2:1)	420	500	38	74.7	[14]
Fe-$ZnCr_2O_4$/HZSM-5(3:1)	3(1:1)	380	1500	57.5	74	[15]
ZnZrOx/HZSM-5(1:1)	3(2:1)	390	1000	10	74	[16]
$Zn_{0.8}CrO$/HZSM-5(1:1)	4(1:1)	350	3000	29.8	69.9	[17]
0.15Zn&$ZnCr_2O_4$/ZSM-5(1:1)	4(1:1)	350	3000	23.5	74.2	[18]
1/200Cu-CeZrOx/ZSM-5@Si(1.25:1)	3.6(2:1)	420	500	44.5	80.2	[19]
6Mn4Zr/H-ZSM-5(1:1)	3(2:1)	400	3000	15.11	84.33	[1]
0.2Zn2Mn8Zr|6Mn4Zr/H-ZSM-5(1:4:4)	3(2:1)	400	3000	25.9	72.09	This work

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