

Recent advances in bifunctional synthesis gas conversion to chemicals and fuels with a comparison to monofunctional processes

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1. DME

To determine the overall carbon atom based selectivity of different processes to convert synthesis gas to DME, we calculated the yield of DME (Equation 1, Equation 2, Equation 3) from published data and plotted this against the corresponding CO conversion (Equation 4). The resulting slope gives the selectivity to DME and can be averaged over a set of data (Equation 5).

$$Y(DME) = \frac{\dot{n}_{out}(DME)}{\dot{n}_{in}(CO_x)} * f(DME) \quad \text{Equation 1}$$



$$f(P1) = \frac{a}{c} \quad \text{Equation 3}$$

$$X(CO_x) = \frac{\dot{n}_{in}(CO_x) - \dot{n}_{out}(CO_x)}{\dot{n}_{in}(CO_x)} \quad \text{Equation 4}$$

$$S(DME) = \frac{Y(DME)}{X(CO_x)} \quad \text{Equation 5}$$

Where,

Y : yield [-]

\dot{n}_{out} : molar carbon flow at reactor outlet [mol_C/s]

\dot{n}_{in} : molar carbon flow at reactor inlet [mol_C/s]

f : ratio of stoichiometric coefficients from the reaction equation

$P1, P2$: reaction products

S : selectivity [-]

X : conversion [-]

We distinguished between bifunctional catalysts, bifunctional catalysts with *in-situ* water removal and a dual reactor process. For the bifunctional catalysts a methanol synthesis function is combined with a methanol dehydration function. Bifunctional catalysts with *in-situ* water removal additionally comprise a molecular sieve material that allows to remove water being formed during the reaction by adsorption. This can push the equilibrium of the reactants further to the side of DME and boost activity. The dual reactor approach shows the combination of methanol synthesis with consecutive methanol dehydration in separate processes. We used reported catalytic data of methanol synthesis catalysts and combined these with reported data of methanol dehydration catalysts. The calculation of the DME yields can be found in Table S1 (bifunctional catalysts), Table S2 (bifunctional catalysts with *in-situ* water removal) and Table S3 (dual reactor process).

Table S1: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to DME

catalyst	MeOH cat	Solid acid	Temperature	Pressure	CO conversion	CO ₂ selectivity	DME selectivity	MeOH selectivity	Hydrocarbon selectivity	DME yield	ref
			°C	bar(g)	%	% _c	% _c	% _c	% _c	% _c	
Zn@m-Al ₂ O ₃	CuZnAl	γ-Al ₂ O ₃	250	30	0.8	0.0	65.3	21.1	13.6	0.5	1
Cr/ZnO-SAPO46-M	CrZn	SAPO46	350	50	4.7	2.9	16.0	69.6	11.5	0.8	2
15.9%Nb/Al + CCMS	CuZnAl	Nb ₂ O ₅ -Al ₂ O ₃	265	50	6	27.2	66.0	6.1	0.7	4.0	3
Cr/ZnO-SAPO46-PhyC	CrZn	SAPO46	350	50	6.9	6.0	34.8	49.1	10.2	2.4	2
CZA-4	CuZn	γ-Al ₂ O ₃	250	50	7.1	29.9	67.0	1.1	2.0	4.8	4
5.9%Nb/Al + CCMS	CuZnAl	Nb ₂ O ₅ -Al ₂ O ₃	265	50	8	27.7	64.9	6.8	0.6	5.2	3
Pd/silica-SZ	Pd-SiO ₂	HZSM-5	250	50	9	1.7	69.0	4.8	26.5	6.2	5
CZA-Z-IP	CuZnAl	γ-Al ₂ O ₃	250	50	10	29.0	61.0	9.0	1.0	6.1	6
Pd/Ga(1:2)/γ-Al ₂ O ₃	Pd	γ-Al ₂ O ₃	250	50	10.9	33.6	52.4	1.9	12.1	5.7	7
CZA-2	CuZn	γ-Al ₂ O ₃	250	50	11.1	30.7	64.3	1.2	3.9	7.1	4
Cu@m-Al ₂ O ₃	CuZnAl	γ-Al ₂ O ₃	250	30	13.2	25.7	68.5	4.7	1.2	9.0	1
CZA-ZSM5	CuZnAl	HZSM-5	250	40	13.9	20.9	14.4	64.1	0.6	2.0	8
CZA-NaY	CuZnAl	NaY	250	40	14.6	15.2	12.5	71.7	0.6	1.8	8
Pd/Ga(1:2)/γ-Al ₂ O ₃	Pd	γ-Al ₂ O ₃	260	50	14.6	35.1	46.2	1.8	16.9	6.7	7
CuZn@m-Al ₂ O ₃	CuZnAl	γ-Al ₂ O ₃	250	30	15.5	24.5	70.3	4.3	0.9	10.9	1
CZA-Z-CF	CuZnAl	γ-Al ₂ O ₃	250	50	17	46.0	38.0	9.0	7.0	6.5	6
CuZn/m-Al ₂ O ₃	CuZnAl	γ-Al ₂ O ₃	250	30	17.4	15.9	70.2	11.8	2.1	12.2	1
Pd/Ga(1:2)/γ-Al ₂ O ₃	Pd	γ-Al ₂ O ₃	270	50	19.6	37.6	38.2	1.7	22.2	7.5	7
CZA-5	CuZn	γ-Al ₂ O ₃	250	50	19.9	30.2	68.3	0.9	0.7	13.6	4
CZA-MA	CuZnAl	γ-Al ₂ O ₃	275	50	22	30.3	52.5	17	0.2	11.5	9
CZA-Y	CuZnAl	Y	250	40	22.7	57.2	29.7	12.5	0.6	6.7	8
CZA-Y	CuZnAl	Y	250	40	22.9	59.8	26.8	12.8	0.6	6.1	10
CZA-ZSM5	CuZnAl	HZSM-5	250	40	23.3	26.2	27.9	45.0	0.9	6.5	10
CZA-1	CuZn	γ-Al ₂ O ₃	250	50	24.4	31.8	58.7	6.2	3.4	14.3	4
CZA@HZSM-5-SS	CuZnAl	HZSM-5	250	30	26.3	14.3	28.7	56.3	0.6	7.5	11
FCZZ25(N)-10Z	CuZnZr	HZSM-5	250	45	29.4	31.5	60.1	8.3	0.1	17.7	12
CZA/ZrFER(5)	CuZnAl	FER	250	40	29.8	31.6	34.0	34.0	0.4	10.1	13
CZA-FER	CuZnAl	FER	250	40	30.2	27.8	28.7	42.8	0.7	8.7	8
CZA/ZrFER(0)	CuZnAl	FER	250	40	30.4	27.9	28.7	42.8	0.6	8.7	13
CZA-Z-CS	CuZnAl	γ-Al ₂ O ₃	250	50	35	32.0	66.0	2.0	1.0	23.1	6
CZA/ZrFER(1)	CuZnAl	FER	250	40	35.3	36.7	40.8	22.1	0.4	14.4	13
T-4611+H-MOR 90	CuZnAl	H-MOR 90	250	50	37	43.9	25.2	1.3	29.6	9.3	14
CZAZr/HFER	CuZnAl	FER	250	50	38	33.0	65.0	2.0	0.0	24.7	15
0-CLZ-A	CuZrLa	γ-Al ₂ O ₃	260	40	38.7	42.4	54.6	2.8	0.2	21.1	16
13 wt-% Cu + HZSM-5 (140)	CuZn	HZSM-5	280	50	40	-	-	2.6	-	25.0	17
CZA/ZrFER(K)	CuZnAl	FER	250	40	40.8	33.4	37.5	27.7	1.4	15.3	13

Table S1: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to DME (continued)

catalyst	MeOH cat	Solid acid	Temperature	Pressure	CO conversion	CO ₂ selectivity	DME selectivity	MeOH selectivity	Hydrocarbon selectivity	DME yield	ref
			°C	bar(g)	%	% _c	% _c	% _c	% _c	% _c	
CZA/Al(10)-FER	CuZnAl	FER	250	35	43	22.2	74.1	2.8	1.0	31.9	18
g-Al ₂ O ₃	CuZnAl	γ-Al ₂ O ₃	260	40	44	25.0	70.5	3.8	0.8	31.0	19
CZA-Z-OX	CuZnAl	γ-Al ₂ O ₃	250	50	45	32.0	66.0	1.0	1.0	29.7	6
CuZnAl/SAPO11-M	CuZnAl	SAPO11	250	50	46.2	6.1	43.8	48.3	1.9	20.2	20
CZA/Al(0)-FER	CuZnAl	FER	250	35	46.6	24.1	70.9	2.9	2.1	33.0	18
C/Z-PC	CuZnAl	HZSM-5	250	30	47.6	31.1	66.3	3.4	0.2	31.6	21
CZA-Z	CuZnAl	γ-Al ₂ O ₃	250	50	48	30.0	69.0	1.0	0.0	33.1	6
6-CLZ-A	CuZrLa	γ-Al ₂ O ₃	260	40	48.2	33.5	63.7	2.6	0.2	30.7	16
CZA-FER	CuZnAl	FER	250	40	49	33.7	58.2	7.8	0.3	28.5	10
CZA/ZrFER(3)	CuZnAl	FER	250	40	49	33.7	58.2	7.8	0.3	28.5	13
25STA@CZA-MA	CuZnAl	γ-Al ₂ O ₃ + H ₄ [SiW ₁₂ O ₄₀]	275	50	49	31.6	59.8	8	0.4	29.3	9
NbOPO ₄	CuZnAl	NbOPO ₄	260	40	53	25.0	72.0	2.3	0.8	38.2	19
C/Z-P	CuZnAl	HZSM-5	250	30	54.5	31.3	65.3	2.3	1.1	35.6	21
18-CLZ-A	CuZrLa	γ-Al ₂ O ₃	260	40	54.6	30.7	67.3	2.0	0.0	36.7	16
12-CLZ-A	CuZrLa	γ-Al ₂ O ₃	260	40	56.7	29.3	69.0	1.7	0.0	39.1	16
C/Z-G	CuZnAl	HZSM-5	250	30	57.4	31.4	64	2.1	2.5	36.7	21
FCZZ25(N)-10Z	CuZnZr	HZSM-5	275	45	57.7	32.0	62.7	5.0	0.3	36.2	12
CuZnAl/SAPO11-PhyC	CuZnAl	SAPO11	250	50	58.5	9.1	82.1	8.4	0.5	48.0	20
CZA/ZrFER(NH ₃)	CuZnAl	FER	250	40	59.4	34.7	62.9	1.9	0.5	37.4	13
T-4611+γ-Al ₂ O ₃	CuZnAl	γ-Al ₂ O ₃	250	50	61	31.8	67.0	1.1	0.2	40.9	14
CZA/Al(2.5)-FER	CuZnAl	FER	250	35	61.8	25.6	71.4	2.5	0.5	44.1	18
Nb ₂ O ₅ -nH ₂ O	CuZnAl	Nb ₂ O ₅ -nH ₂ O	260	40	62	25.0	66.8	6.0	2.3	41.4	19
CZA/Al(5)-FER	CuZnAl	FER	250	35	62.1	26.8	69.4	3.0	0.7	43.1	18
CZA(A)	CuZnAl	γ-Al ₂ O ₃	250	50	65.8	17.0	55.6	26.9	0.5	36.6	22
T-4611+H-MFI 90	CuZnAl	H-MFI 90	250	50	66	49.0	32.7	3.1	15.2	21.6	14
T-4611+H-MFI 400	CuZnAl	H-MFI 400	250	50	68	31.5	66.8	1.5	0.2	45.4	14
FCZZ25(N)-10Z	CuZnZr	HZSM-5	300	45	68	30.6	63.8	5.1	0.5	43.4	12
g-Al ₂ O ₃	CuZnAl	γ-Al ₂ O ₃	280	40	69	27.0	70.5	3.0	1.5	48.6	19
NbOPO ₄	CuZnAl	NbOPO ₄	280	40	73	27.0	70.5	2.3	1.5	51.5	19
Nb ₂ O ₅ -nH ₂ O	CuZnAl	Nb ₂ O ₅ -nH ₂ O	280	40	75	27.0	69.0	2.3	3.8	51.8	19
CZA@HZSM-5-EtOH	CuZnAl	HZSM-5	250	30	76.5	26.7	70.8	2.5	0.1	54.2	11
CuO-ZnO-Al ₂ O ₃ /MgZ ₁	CuZnAl	HZSM-5	260	40	96.3	30.5	64.5	4.6	0.4	62.1	23

Table S2: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to DME using *in-situ* water removal

catalyst	MeOH cat	Solid acid	Temperature	Pressure	CO conversion	CO2 selectivity	DME selectivity	MeOH selectivity	Hydrocarbon selectivity	DME yield	ref
			°C	bar(g)	%	% _c	% _c	% _c	% _c		
CZA_comm	CuZnAl	γ-Al ₂ O ₃	275	25	55	4.0	95.0	-	-	52.3	24
mech mixture 1/1, 3mm		modelling			68.1 ¹		97.8			66.6	25
Cu/ZnO/Al ₂ O ₃ + zeolite (3Å)	CuZnAl	γ-Al ₂ O ₃	275	25	70	-	92.9	-	-	65.0	26
MeOH@DME 1/1, 3mm		modelling			72.6 ¹		97.5			70.8	25
MeOH@DME 2/1, 3mm		modelling			76.8 ¹		97.9			75.2	25
DME@MeOH 1/1, 3mm		modelling			77.5 ¹		97.2			75.3	25
hybrid 1/1, 3mm		modelling			78.4 ¹		97.4			76.4	25
mech mixture 1/1, 1.5mm		modelling			78.6 ¹		97.7			76.8	25
mech mixture 1/1, 1mm		modelling			81.4 ¹		97.9			79.7	25
Cu/ZnO/Al ₂ O ₃ + zeolite (3Å)	CuZnAl	γ-Al ₂ O ₃	250	24	90.1 ¹		99.2			89.4	27,28
Cu/ZnO/Al ₂ O ₃ + LTA (3Å)	CuZnAl	γ-Al ₂ O ₃	252	25	94.5 ¹		99.0			93.6	29

¹ CO_x conversion, experiments were conducted with mixture of CO, CO₂ and H₂

Table S3: combined reported catalytic performance of catalysts for the conversion of synthesis gas to DME via a dual reactor process by combining methanol synthesis and methanol dehydration.

	CO conversion %	CO ₂ selectivity % _c	methanol selectivity % _c	DME selectivity from methanol % _c	DME selectivity from synthesis gas % _c	yield % _c	ref
dual reactor process							
MeOH							
Cu/ZnO/Al ₂ O ₃	8.6		97.7			8.4	30
2Cu_MCF 10.7	10.7		97			10.4	31
Cu/ZnO/Al ₂ O ₃	29.9		99.6			29.8	30
Cu/ZnO/Al ₂ O ₃	34.4		99.8			34.3	30
Cu/ZnO/Al ₂ O ₃	40.3		98.7			39.8	30
Cu/ZnO/Al ₂ O ₃	47.0		98.9			46.5	30
MeOH + DME							
Al-HMS-10	8.6	0		100 (at 89% methanol conversion)	87.0	7.5	32
Al-HMS-10	10.7	0		100 (at 89% methanol conversion)	86.3	9.2	32
Al-HMS-10	29.9	0		100 (at 89% methanol conversion)	88.6	26.5	32
Al-HMS-10	34.4	0		100 (at 89% methanol conversion)	88.8	30.6	32
Al-HMS-10	40.3	0		100 (at 89% methanol conversion)	87.8	35.4	32
Al-HMS-10	47.0	0		100 (at 89% methanol conversion)	88.0	41.4	32

2. Olefins

The overall selectivity of the conversion of synthesis gas to C₂-C₄ olefins was analyzed by calculation of the yield to C₂-C₄ olefins (Equation 6) and dividing by the conversion to obtain the selectivity (Equation 7). The olefins analyzed own different carbon atom numbers, hence the yield was directly calculated using the amount of carbon atoms within the C₂-C₄ olefins formed ($\dot{n}_{out}(C_{olefins})$ in Equation 6).

Three different approaches were analyzed to convert synthesis gas into olefins, namely OX-ZEO, Fischer-Tropsch to olefins (FTO) and a dual reactor process. The OX-ZEO and FTO process both include recent studies with decreased water-gas-shift activity and are labeled with *low CO₂*. The dual reactor approach shows the combination of methanol synthesis with consecutive methanol-to-olefins (MTO) reaction in separate processes. We used reported catalytic data of methanol synthesis catalysts and combined these with reported data of MTO catalysts. The calculation of the C₂-C₄ olefin yields can be found in Table S4 (OX-ZEO), Table S5 (FTO) and Table S6 (dual reactor process).

$$Y(olefins) = \frac{\dot{n}_{out}(C_{olefins})}{\dot{n}_{in}(CO_x)} \quad \text{Equation 6}$$

$$S(olefins) = \frac{Y(olefins)}{X(CO_x)} \quad \text{Equation 7}$$

Where,

Y:yield

\dot{n}_{out} :molar flow at reactor outlet

\dot{n}_{in} :molar flow at reactor inlet

$C_{olefins}$:carbon atoms in olefin molecules

S:selectivity

X:conversion

Table S4: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to C₂-C₄ olefins via the OX-ZEO process

catalyst	CO conversion	CO ₂ selectivity	C ₂ -C ₄ olefins in hydrocarbons	hydrocarbons selectivity	C ₂ -C ₄ olefin selectivity	C ₂ -C ₄ olefin yield	ref
	%	% _C	% _C	% _C	% _C	% _C	
OX-ZEO							
ZrO ₂	4	42.0	79.0	58.0	45.8	1.8	33
ZnCr/SAPO-17, 1 Mpa	4.3	47.9	75.6	52.1	39.4	1.7	34
Mn/Ga ₂ O ₃	5.3	44.8	61.5	55.2	33.9	1.8	35
ZnO	6	42.0	26.5	58.0	15.4	0.9	33
ZnCrOx/MSAPO	6	45.0	68.0	55.0	37.4	2.2	36
MnxZry/SAPO34 Mn:Zr = 1 : 0	6.9	24.3	68.5	75.7	51.9	3.6	37
ZnAlOx/CHA Si/Al=307	8	40.0	86.0	60.0	51.6	4.1	38
MnxZry/SAPO34 Mn:Zr = 1 : 0,25	8.5	48.4	49.3	51.6	25.4	2.2	37
MG-(SM)	8.6	44.5	68.3	55.5	37.9	3.3	35
MnxZry/SAPO34 Mn:Zr = 1 : 0,5	8.8	46.0	50.2	54.0	27.1	2.4	37
ZnAlOx/CHA Si/Al=237	9	40.0	85.0	60.0	51.0	4.6	38
MnxZry/SAPO34 Mn:Zr = 1 : 4	9.3	47.2	52.2	52.8	27.6	2.6	37
ZnAlOx/CHA Si/Al=138	9.5	40.0	80.0	60.0	48.0	4.6	38
MnxZry/SAPO34 Mn:Zr = 1 : 1	9.7	43.9	43.5	56.1	24.4	2.4	37
ZnAlOx/CHA Si/Al=76	10	45.0	75.0	55.0	41.3	4.1	38
GaCeOx	10	42	79	58.0	45.8	4.6	39
MnxZry/SAPO34 Mn:Zr = 1 : 2	10.6	45.3	59.6	54.7	32.6	3.5	37
ZnCrOx/MSAPO	12	45.0	72.0	55.0	39.6	4.8	36
ZnAlOx/CHA Si/Al=20	12	47.0	56.0	53.0	29.7	3.6	38
ZnAlOx/CHA Si/Al=38	12	46.0	67.0	54.0	36.2	4.3	38
ZnCr/SAPO-17, 2 Mpa	12.6	47.9	87.3	52.1	45.5	5.7	34
ZnCrOx + H-SSZ-13 (27C)	12.6	51.3	60.9	48.7	29.7	3.7	40
InZr/SAPO34	13.1	40.0	79.9	60.0	47.9	6.3	41
ZnCrOx + SAPO-35(0.17)	13.9	46.9	74.2	53.1	39.4	5.5	42
ZnAl ₂ O ₄ /SAPO-35	15	44.0	56.0	56.0	31.4	4.7	43
SP17(48h)	15.6	47.8	88.7	52.2	46.3	7.2	44
ZnCrOx + H-SSZ-13 (23C)	16	50.2	66.1	49.8	32.9	5.3	40
InZr/SAPO34	16.2	40.0	73.7	60.0	44.2	7.2	41
ZnCr/SAPO-17, 370°C	16.4	42.5	91.4	57.5	52.6	8.6	34
ZnCrOx + SAPO-35(0.11)	16.5	47.4	75.1	52.6	39.5	6.5	42
Zn-ZrO ₂ (1:64)/H-SSZ-13-45H	17	42.0	76.7	58.0	44.5	7.6	33
ZnCrOx/MSAPO	17	45.0	73.0	55.0	40.2	6.8	36
ZnO-ZrO ₂ /SAPO-34 0,12mmol/g	17	43.0	76.0	57.0	43.3	7.4	45
ZnCrOx + SAPO-18(0.030)	17.2	49.9	75.1	50.1	37.6	6.5	42
SP17(72h)	17.2	46.7	86.2	53.3	45.9	7.9	44

Table S4: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to C₂-C₄ olefins via the OX-ZEO process (continued)

catalyst	CO conversion	CO ₂ selectivity	C ₂ -C ₄ olefins in hydrocarbons		hydrocarbons selectivity	C ₂ -C ₄ olefin selectivity	C ₂ -C ₄ olefin yield	ref
	%	% _c	% _c	% _c	% _c	% _c	% _c	
ZnCrOx + H-SSZ-13 (19C)	17.3	49.7		53.9	50.3	27.1	4.7	40
ZnCr/SAPO-17, 360°C	17.4	38.4		91.5	61.6	56.4	9.8	34
ZnCr/SAPO-17, 380°C	17.5	47.0		90.9	53.0	48.2	8.4	34
ZnCrOx + SAPO-18(0.054)	18.2	49.4		69.9	50.6	35.4	6.4	42
ZnCr/Low Si AIPO-18	19						8.4	46
SP17(120h)	19.3	48.5		81.8	51.5	42.1	8.1	44
SP17(96h)	19.4	46.4		87	53.6	46.6	9.0	44
ZnCrOx + H-SSZ-13 (19S)	19.7	48.6		68.1	51.4	35.0	6.9	40
ZnCrOx + SAPO-18(0.048)	19.9	49.2		68.6	50.8	34.8	6.9	42
ZnCrOx/MSAPO	20	45.0		80.0	55.0	44.0	8.8	36
ZnO-ZrO ₂ /SAPO-34 0,16mmol/g	20	40.0		77.0	60.0	46.2	9.2	45
ZnCrOx + H-SSZ-13 (26S)	20	48.9		71.6	51.1	36.6	7.3	40
ZnCrOx + H-SSZ-13 (12S)	20.7	49.0		55.1	51.0	28.1	5.8	40
ZnCrOx + H-SSZ-13 (23S)	20.9	48.0		70.8	52.0	36.8	7.7	40
ZnAl ₂ O ₄ /SAPO-18	21	44.0		69.0	56.0	38.6	8.1	43
Zn-ZrO ₂ (1:32)/H-SSZ-13-45H	22	42.0		74.4	58.0	43.2	9.5	33
Zn-ZrO ₂ (4:1)/H-SSZ-13-45H	22	42.0		35.1	58.0	20.4	4.5	33
ZnCrOx/MSAPO	22	45.0		71.0	55.0	39.1	8.6	36
ZnCr/SAPO-17, 390°C	22	48.6		90.0	51.4	46.3	10.2	34
GaMnOx	22	42		89	58.0	51.6	11.4	39
ZnAl ₂ O ₄ /SAPO-17	23	42.0		65.0	58.0	37.7	8.7	43
Zn-ZrO ₂ (1:16)/H-SSZ-13-45H	24	42.0		74.0	58.0	42.9	10.3	33
ZnO-ZrO ₂ /SAPO-34 0,22mmol/g	24	41.0		81.0	59.0	47.8	11.5	45
ZnAl ₂ O ₄ /SAPO-34	24	44.0		80.0	56.0	44.8	10.8	43
ZnCr/Low Si AIPO-18	25						11.3	46
ZnCr/Low Si AIPO-18	25						10.6	46
ZnCrOx-MOR#2-py	26	45.0		73.0	55.0	40.2	10.4	47
ZnCr/SAPO-17, 400°C	26.2	48.6		88.3	51.4	45.4	11.9	34
ZnCr/SAPO-17, 3 Mpa	26.2	48.6		88.3	51.4	45.4	11.9	34
Zn-ZrO ₂ (1:4)/H-SSZ-13-45H	27	42.0		65.5	58.0	38.0	10.3	33
ZnO-ZrO ₂ /SAPO-34 0,26mmol/g	27	41.0		75.0	59.0	44.3	11.9	45
InZr/SAPO34	27.7	40.0		73.6	60.0	44.2	12.2	41
Zn-ZrO ₂ (2:1)/H-SSZ-13-45H	28	42.0		54.2	58.0	31.4	8.8	33
ZnCrOx/MSAPO	28	45.0		71.0	55.0	39.1	10.9	36
ZnCr/SAPO-17, 410°C	28.5	48.4		85.3	51.6	44.0	12.5	34
SP34	28.5	45.2		87.1	54.8	47.7	13.6	44

Table S4: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to C₂-C₄ olefins via the OX-ZEO process (continued)

catalyst	CO conversion	CO ₂ selectivity	C ₂ -C ₄ olefins in hydrocarbons		hydrocarbons selectivity	C ₂ -C ₄ olefin selectivity	C ₂ -C ₄ olefin yield	ref
	%	% _c	% _c	% _c	% _c	% _c	% _c	
SP18	28.7	45		87	55.0	47.9	13.7	44
Zn-ZrO ₂ (1:1)/H-SSZ-13-45H	29	42.0		61.8	58.0	35.9	10.4	33
ZnCrO _x /MSAPO	30	45.0		73.0	55.0	40.2	12.0	36
ZnCr/SAPO-34	30						12.6	46
ZnO-ZrO ₂ /SAPO-34 0,27mmol/g	30	41.0		70.0	59.0	41.3	12.4	45
InZr/SAPO34	30.7	40.0		67.3	60.0	40.4	12.4	41
ZnCr/Low Si AlPO-18	31						13.3	46
ZA-CP	33.9	43.5		75	56.5	42.4	14.4	48
ZnCr/Low Si AlPO-18	34						14.3	46
ZnCr/Low Si AlPO-18	34						15.3	46
ZnCrO _x -SAPO-18 Si/Al = 0,011	35.5	41.4		82.0	58.6	48.1	17.1	49
ZnCr/SAPO-17, 4 Mpa	38.2	47.6		87.3	52.4	45.7	17.5	34
ZA-RP	39.2	43.3		73.3	56.7	41.6	16.3	48
ZnCr/SAPO-34	40						16.4	46
ZA-SP	40.2	44.6		74.1	55.4	41.1	16.5	48
ZnCr/Low Si AlPO-18	43						18.1	46
ZnCr/Low Si AlPO-18	43						18.9	46
GaZrO _x	44.5	42		89	58.0	51.6	23.0	39
ZnCrO _x -SAPO 450-900μm	47	41.0		72.0	59.0	42.5	20.0	50
ZnCrO _x -SAPO-18 Si/Al = 0,054	47.1	41.8		61.0	58.2	35.5	16.7	49
ZnCr/Low Si AlPO-18	49						20.6	46
ZnCr/Low Si AlPO-18	49						21.1	46
ZnCrO _x -SAPO-18 Si/Al = 0,045	49.5	40.9		69.0	59.1	40.8	20.2	49
ZnCrO _x -SAPO 150-74μm	58	40.0		72.0	60.0	43.2	25.1	50
ZnCr/SAPO-34	59						22.1	46
ZnCrO _x -SAPO 20-50μm	59	39.0		65.0	61.0	39.7	23.4	50
ZnCrO _x -SAPO 200-300μm	60	39.0		76.0	61.0	46.4	27.8	50
ZnCrO _x -GeAPO-18 _{0,027}	85	32		83	68	56.5	48	51
low CO₂ OX-ZEO:								
Zn _{0.3} Ce ₂ -yZryO ₄	5	4.0		60	96.0	57.6	2.9	52
Zn _{0.3} Ce ₂ -yZryO ₄	6.5	5.5		77	94.5	72.8	4.7	52
Zn _{0.3} Ce ₂ -yZryO ₄	6.5	8.5		78	91.5	71.4	4.6	52
Zn _{0.3} Ce ₂ -yZryO ₄	7	11.0		76	89.0	67.6	4.7	52
Zn _{0.3} Ce ₂ -yZryO ₄	7	12.0		73	88.0	64.2	4.5	52
Zn _{0.3} Ce ₂ -yZryO ₄	7	10.0		77	90.0	69.3	4.9	52
Zn _{0.3} Ce ₂ -yZryO ₄	7	11.0		78	89.0	69.4	4.9	52

Table S4: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to C₂-C₄ olefins via the OX-ZEO process (continued)

catalyst	CO conversion	CO ₂ selectivity	C ₂ -C ₄ olefins in hydrocarbons	hydrocarbons selectivity	C ₂ -C ₄ olefin selectivity	C ₂ -C ₄ olefin yield	ref
	%	% _c	% _c	% _c	% _c	% _c	
Zn _{0.3} Ce ₂ -γZr _y O ₄	7	12.0	75	88.0	66.0	4.6	52
Zn _{0.3} Ce ₂ -γZr _y O ₄	7.5	13.0	75	87.0	65.3	4.9	52
Zn _{0.3} Ce ₂ -γZr _y O ₄	7.5	12.0	75	88.0	66.0	5.0	52
Zn _{0.3} Ce ₂ -γZr _y O ₄	8	15.0	75	85.0	63.8	5.1	52
Zn _{0.3} Ce ₂ -γZr _y O ₄	8	12.5	72	87.5	63.0	5.0	52
Zn _{0.3} Ce ₂ -γZr _y O ₄	9	22.0	76	78.0	59.3	5.3	52
Zn _{0.3} Ce ₂ -γZr _y O ₄	10	23.0	72	77.0	55.4	5.5	52
Zn-Cr@SAPO capsule catalyst	10.4	36.0	63.8	64.0	40.8	4.2	53
Zn _{0.3} Ce ₂ -γZr _y O ₄	12	26.0	59	74.0	43.7	5.2	52

Table S5: reported catalytic performance of FTO catalysts for the direct conversion of synthesis gas to C₂-C₄ olefins

catalyst	CO conversion	CO ₂ selectivity	C ₂ -C ₄ olefins in hydrocarbons	hydrocarbon selectivity	C ₂ -C ₄ olefin selectivity	C ₂ -C ₄ olefin yield	ref
	%	% _c	% _c	% _c	% _c	% _c	
FTO							
CoMn carbide nano prisms	6.3	48.3	45.1	51.7	23.3	1.5	54
Fe/SiO ₂	10.1	29.0	29.6	71.0	21.0	2.1	55
CoMn carbide nano prisms	11.5	48.0	50.0	52.0	26.0	3.0	54
CoMn carbide nano prisms	14.3	48.4	44.3	51.6	22.9	3.3	54
Co ₁ Mn ₃ -Na ₂ S	18	3.0	30.0	97.0	29.1	5.2	56
Co ₁ Mn ₃ -Na ₂ S ₂ O ₃	22	3.0	25.0	97.0	24.3	5.3	56
CoMn carbide nano prisms	23.6	48.0	41.2	52.0	21.4	5.1	54
Co ₃ Mn ₁ -Na ₂ S	25	13.0	20.0	87.0	17.4	4.4	56
N5 @340°C	27.4	47.8	43.0	52.2	22.4	6.2	57
CoMn carbide nano prisms	28.6	46.6	31.9	53.4	17.0	4.9	54
Co ₃ Mn ₁	31	2.0	17.0	98.0	16.7	5.2	56
CoMn carbide nano prisms	31.8	47.3	60.8	52.7	32.0	10.2	54
6Fe	32.7	21.2	17.5	78.8	13.8	4.5	58
4Fe-Zn	34.1	33.1	13.3	66.9	8.9	3.0	58
N1 @340°C	38.3	48.0	52.1	52.0	27.1	10.4	57
5Fe-1.2Na	48.7	21.9	20.3	78.1	15.9	7.7	58
FeBi/CNT	50.7	46.0	36.1	54.0	19.5	9.9	55
2Fe.Zn0.2Na (SC-I)3	52.3	41.9	50.5	58.1	29.3	15.3	59
FePb/CNT	56.8	48.0	35.8	52.0	18.6	10.6	55
Fe/CNT	57.3	40.0	32.4	60.0	19.4	11.1	55
2Fe.Zn0.2Na (AH-I)	60.2	39.1	47.7	60.9	29.0	17.5	59
1Fe-Zn-3.4Na	63	22.5	19.9	77.5	15.4	9.7	58
5AFeP	69	45.0	51.0	55.0	28.1	19.4	60
2Fe-Zn-0.81Na	77.2	23.8	22.7	76.2	17.3	13.4	58
FeBi/CNT	78.3	47.0	35.2	53.0	18.7	14.6	55
2Fe.Zn0.2Na (SC-I)2	79.3	40.6	50.3	59.4	29.9	23.7	59
2Fe.Zn0.1Na (AH-I)	81.1	39.25	42.8	60.8	26.0	21.1	59
3Fe-Zn-0.36Na	82.7	25.9	22.9	74.1	16.9	14.0	58
10IMP	86	47.0	52.0	53.0	27.6	23.7	61
N5 @370°C	87.8	44.7	34.4	55.3	19.0	16.7	57
N1 @370°C	90	46.3	37.3	53.7	20.0	18.0	57
FePb/CNT	96	50.0	28.4	50.0	14.2	13.6	55
2Fe.Zn0.2Na (SC-I)1	97.4	34.4	50	65.6	32.8	31.9	59
low CO₂ FTO:							
FeZn@16.9-SiO ₂ -c	52.2	8.5	44.5	91.5	40.7	21.2	62

Table S5: reported catalytic performance of FTO catalysts for the direct conversion of synthesis gas to C₂-C₄ olefins (continued)

catalyst	CO conversion	CO ₂ selectivity	C ₂ -C ₄ olefins in hydrocarbons	hydrocarbon selectivity	C ₂ -C ₄ olefin selectivity	C ₂ -C ₄ olefin yield	ref
	%	% _c	% _c	% _c	% _c	% _c	
Fe@SAPO-34	55.4	17.1	52.6	82.9	43.6	24.2	63
FeZn@7.3-SiO ₂ -c	63.1	8.8	47.3	91.2	43.1	27.2	62
FeZn@4.1-SiO ₂ -c	65.3	7.2	52.6	92.8	48.8	31.9	62
FeZn@2.4-SiO ₂ -c	77.8	11.9	50.7	88.1	44.7	34.8	62
FeZn@1.3-SiO ₂ -c	82.3	17.2	50.4	82.8	41.7	34.3	62

Table S6: combined reported catalytic performance of catalysts for the conversion of synthesis gas to C₂-C₄ olefins via a dual reactor process

catalyst	CO conversion	CO ₂ selectivity	methanol selectivity	C ₂ -C ₄ olefin selectivity from methanol	C ₂ -C ₄ olefin selectivity from synthesis gas	yield	ref
	%	% _c	% _c	% _c	% _c	% _c	
dual reactor process							
MeOH							
Cu/ZnO/Al ₂ O ₃	8.6		97.7			8.4	30
2Cu_MCF 10.7	10.7		97.0			10.4	31
Cu/ZnO/Al ₂ O ₃	29.9		99.6			29.8	30
Cu/ZnO/Al ₂ O ₃	34.4		99.8			34.3	30
Cu/ZnO/Al ₂ O ₃	40.3		98.7			39.8	30
Cu/ZnO/Al ₂ O ₃	47.0		98.9			46.5	30
MeOH + MTO							
SSZ-13	8.6	0.0		94.1	91.9	7.9	64
meso-Z	8.6	0.0		95.5	93.3	8.0	64
meso-Z-22-4-4	8.6	0.0		93.5	91.3	7.9	64
meso-Z-22-4-4-sil	8.6	0.0		94.2	92.0	7.9	64
SSZ-13	10.7	0.0		94.1	91.3	9.8	64
meso-Z	10.7	0.0		95.5	92.6	9.9	64
meso-Z-22-4-4	10.7	0.0		93.5	90.7	9.7	64
meso-Z-22-4-4-sil	10.7	0.0		94.2	91.4	9.8	64
SSZ-13	29.9	0.0		94.1	93.7	28.0	64
meso-Z	29.9	0.0		95.5	95.1	28.4	64
meso-Z-22-4-4	29.9	0.0		93.5	93.1	27.8	64
meso-Z-22-4-4-sil	29.9	0.0		94.2	93.8	28.1	64
SSZ-13	34.4	0.0		94.1	93.9	32.3	64
meso-Z	34.4	0.0		95.5	95.3	32.8	64
meso-Z-22-4-4	34.4	0.0		93.5	93.3	32.1	64
meso-Z-22-4-4-sil	34.4	0.0		94.2	94.0	32.3	64
SSZ-13	40.3	0.0		94.1	92.9	37.4	64
meso-Z	40.3	0.0		95.5	94.3	38.0	64
meso-Z-22-4-4	40.3	0.0		93.5	92.3	37.2	64
meso-Z-22-4-4-sil	40.3	0.0		94.2	93.0	37.5	64
SSZ-13	47.0	0.0		94.1	93.1	43.7	64
meso-Z	47.0	0.0		95.5	94.4	44.4	64
meso-Z-22-4-4	47.0	0.0		93.5	92.5	43.5	64
meso-Z-22-4-4-sil	47.0	0.0		94.2	93.2	43.8	64

3. Aromatics

The overall selectivity of the conversion of synthesis gas to aromatics was analyzed analog to the selectivity of C₂-C₄ olefins (Equation 8 and Equation 9).

$$Y(\text{aromatics}) = \frac{n_{\text{out}}(C_{\text{aromatics}})}{n_{\text{in}}(CO_x)} \quad \text{Equation 8}$$

$$S(\text{aromatics}) = \frac{Y(\text{aromatics})}{X(CO_x)} \quad \text{Equation 9}$$

Where,

Y:yield

\dot{n}_{out} :molar flow at reactor outlet

\dot{n}_{in} :molar flow at reactor inlet

$C_{\text{aromatics}}$:carbon atoms in aromatic molecules

S:selectivity

X:conversion

The following processes were analyzed: OX-ZEO, combination of FTO catalysts with zeolites and a dual reactor process. The OX-XEO process also includes recent studies with decreased water-gas-shift activity and are labeled with *low* CO₂. The dual reactor approach shows the combination of methanol synthesis with consecutive methanol-to-aromatics (MTA) reaction in separate processes. Additionally, the resulting yields of a combination of methanol synthesis and MTA process that follows dehydrogenation is added. The calculation of the aromatic yields can be found in Table S7 (OX-ZEO), Table S8 (FTO + zeolite) and Table S9 (dual reactor process).

Table S7: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to aromatics via the OX-ZEO process

catalyst	CO conversion	CO ₂ selectivity	aromatics in hydrocarbons	hydrocarbon selectivity	aromatics selectivity	aromatics yield	ref
	%	% _c	% _c	% _c	% _c	% _c	
OX-ZEO							
ZrO ₂	3	34.0	49.0	66.0	32.3	1.0	65
Ce _{0.2} Zr _{0.8} O ₂ /H-ZSM5-40-350	4	28.0	86.0	72.0	61.9	2.5	65
80Ce-ZrO ₂	4.8	34.0	69.0	66.0	45.5	2.2	65
CeO ₂	4.8	34.0	59.0	66.0	38.9	1.9	65
20Ce-ZrO ₂	5.1	34.0	75.0	66.0	49.5	2.5	65
Ce _{0.2} Zr _{0.8} O ₂ /H-ZSM5-40-380	5.5	33.0	83.0	67.0	55.6	3.1	65
40Ce-ZrO ₂	5.8	34.0	74.0	66.0	48.8	2.8	65
50% ZnCrO _x + 50% H-ZSM-5	6.4	49.0	63.9	51.0	32.6	2.1	66
Ce _{0.2} Zr _{0.8} O ₂ /H-ZSM5-40-400	7.5	33.0	77.0	67.0	51.6	3.9	65
20Ce-ZrO ₂	8	34.0	83.0	66.0	54.8	4.4	65
40Ce-ZrO ₂	8	34.0	72.0	66.0	47.5	3.8	65
ZnAlO _x /H-ZSM-5H	8.5	44	79	56.0	44.2	3.8	67
80Ce-ZrO ₂	9	34.0	69.0	66.0	45.5	4.1	65
Ce _{0.2} Zr _{0.8} O ₂ /H-ZSM5-40-450	10	35.0	56.0	65.0	36.4	3.6	65
CeO ₂	11	34.0	58.0	66.0	38.3	4.2	65
50% ZnCrO _x + 50% H-ZSM-5	11.2	49.0	70.4	51.0	35.9	4.0	66
MgZrO _x /HZSM5-350°C	12.5	17	68.7	83.0	57.0	7.1	68
t-ZrO ₂ /HZSM-5-mix	14.2	33.5	65.0	66.5	43.2	6.1	69
50% ZnCrO _x + 50% H-ZSM-5	14.7	49.0	69.8	51.0	35.6	5.2	66
ZnCr ₂ O ₄ -600&H-ZSM-5	14.7	48.0	70.2	52.0	36.5	5.4	70
50% ZnCrO _x + 50% H-ZSM-5	15.4	49.0	67.0	51.0	34.2	5.3	66
MgZrO _x /HZSM5-400°C	15.5	18	81.7	82.0	67.0	10.4	68
ZnCrO ZSM-5 powder mixing	16.1	43.0	74.0	57.0	42.2	6.8	71
ZnCr ₂ O ₄ /Sbx-H-ZSM-5	17	47.5	83	52.5	43.6	7.4	72
ZnCrO x -ZSM-5-2.8	18.3	49.0	69.0	51.0	35.2	6.4	73
MgZrO _x /HZSM5-450°C	20.5	21	60.2	79.0	47.5	9.7	68
Zn-ZrO ₂ /H-ZSM-5	21	42.0	81.0	58.0	47.0	9.9	74
ZO.8C/s-Z5-150	21	36	56.5	64.0	36.2	7.6	75
ZrO ₂ -H&H-ZSM-5	21.6	44.3	52.4	55.7	29.2	6.3	76
Mo-ZrO ₂ /H-ZSM-5	22	42.0	74.0	58.0	42.9	9.4	77
Ce _{0.2} Zr _{0.8} O ₂ /H-ZSM5-40	22.4	34.1	56.3	65.9	37.1	8.3	65
ZnCr ₂ O ₄ -500&H-ZSM-5	23	47.8	73.3	52.2	38.3	8.8	70
ZnCr ₂ O ₄ -400&H-ZSM-5	23.6	46.9	76.0	53.1	40.4	9.5	70
m-ZrO ₂ /HZSM-5-mix	24	36.4	67.4	63.6	42.9	10.3	69
ZO.8C/c-Z5-150	25	35	70	65.0	45.5	11.4	75

Table S7: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to aromatics via the OX-ZEO process (continued)

catalyst	CO conversion	CO ₂ selectivity	aromatics in hydrocarbons	hydrocarbon selectivity	aromatics selectivity	aromatics yield	ref
	%	% _c	% _c	% _c	% _c	% _c	
Ce0.2Zr0.8O2/H-ZSM5-40	27.8	35.1	57.0	64.9	37.0	10.3	65
ZO.8C/n-Z5-150	28	36.5	62	63.5	39.4	11.0	75
ZO.8C/i-Z5-150	28	36.5	64	63.5	40.6	11.4	75
2.89%Fe-Zn/Cr+ZSM-5	36	45.5	82.5	54.5	45.0	16.2	78
4.48%Fe-Zn/Cr+ZSM-5	45	46.5	81	53.5	43.3	19.5	78
Cr/Zn-Zn/Z5@S1 hybrid	55			100.0	35.7	19.6	79
low CO₂ OX-ZEO							
ZnO-ZrO2/H-ZSM-5	11	0.0	72.0	100.0	72.0	7.9	80
ZnO-ZrO2/H-ZSM-5	15	5.0	71.0	95.0	67.5	10.1	80
Cr2O3/Mg-ZSM-5@SiO2	17.4	0.0	64.9	100.0	64.9	11.3	81
Cr2O3/La-ZSM-5@SiO2	17.5	0.0	72.2	100.0	72.2	12.6	81
Cr2O3/H-ZSM-5@SiO2-56.1%	17.8	0.0	68.2	100.0	68.2	12.2	81
Cr2O3/H-ZSM-5@SiO2-13.8%	19.5	0.0	68.0	100.0	68.0	13.3	81
Cr2O3/H-ZSM-5@SiO2-39.0%	19.7	0.0	69.3	100.0	69.3	13.7	81
Cr2O3/H-ZSM-5@SiO2	19.7	0.0	69.3	100.0	69.3	13.7	81
Cr2O3/Zn-ZSM-5@SiO2	22.8	0.0	71.4	100.0	71.4	16.3	81
Cr2O3/Ga-ZSM-5@SiO2	24.6	0.0	76.4	100.0	76.4	18.8	81

Table S8: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to aromatics by combining FTO catalysts and zeolites

catalyst	CO conversion	CO ₂ selectivity	aromatics in hydrocarbons	hydrocarbon selectivity	aromatics selectivity	aromatics yield	ref
	%	% _c	% _c	% _c	% _c	% _c	
Fe+Z							
FeMn-HZSM-5	6.7	26.3	36.5	73.7	26.9	1.8	82
CMA Z-300	17.5	29.9	38.8	70.1	27.2	4.8	83
FeMn-HZSM-5	19.9	35.1	36.5	64.9	23.7	4.7	82
FeMn-HZSM-5	23.1	22.1	39.4	77.9	30.7	7.1	82
CMA Z-300	23.7	34.0	43.3	66.0	28.6	6.8	83
FeMn-HZSM-5	24.9	34.6	24.2	65.4	15.8	3.9	82
α-Fe ₂ O ₃ -0.75Na/HZSM-5	25.3	41.5	36.2	58.5	21.2	5.4	84
FeNiOx(5:1)-0.41Na/HZSM-5	32.3	47.4	44.8	52.6	23.6	7.6	84
CMA Z-300	34.9	39.6	55.5	60.4	33.5	11.7	83
CMA Z-300	35.8	38.5	31.0	61.5	19.1	6.8	83
CMA Z-300	36.4	37.5	57.0	62.5	35.6	13.0	83
FeMn-HZSM-5	39.9	47.6	43.4	52.4	22.7	9.1	82
FeMnOx(5:1)-0.4Na/HZSM-5	42.1	45.4	28.3	54.6	15.5	6.5	84
FeMn-HZSM-5	44.6	33.7	37.9	66.3	25.1	11.2	82
FeNiOx(5:1)-0.87Na/HZSM-5	46.3	46.6	36.2	53.4	19.3	9.0	84
FeMn-HZSM-5	46.6	42.0	33.9	58.0	19.7	9.2	82
FeNiOx(5:1)-0.87Na/HZSM-5	47.2	46.6	23.4	53.4	12.5	5.9	84
FeMn@MZ5	51.9	36.6	47.1	63.4	29.9	15.5	85
Fe ₁₀ Mn ₁ KSi-Hol HZSM-5 (27)	53.4	49.4	33.8	50.6	17.1	9.1	86
Fe ₁ Mn _{0.5} @MZ5-(89)	57	38.0	59.0	62.0	36.6	20.9	85
FeMn-HZSM-5	60.4	42.8	34.1	57.2	19.5	11.8	82
FeMn-HZSM-5	60.4	42.8	34.1	57.2	19.5	11.8	82
CMA Z-300	68.9	41.6	59.1	58.4	34.5	23.8	83
FeMn-HZSM-5	69.9	45.5	32.4	54.5	17.7	12.3	82
FeMnK/SiO ₂ +HZSM-5 powder mix.	74	47.0	29.0	53.0	15.4	11.4	87
CMA/Hol-Z5-N@S1	75	41	61	59.0	36.0	27.0	88
FeMnK/SiO ₂ +HZSM-5 dual bed	77	48.0	23.0	52.0	12.0	9.2	87
FeMn-HZSM-5	79.1	43.7	38.0	56.3	21.4	16.9	82
FeMn-HZSM-5	81.1	40.9	40.7	59.1	24.1	19.5	82
Fe ₁₀ Mn ₀ KSi-Hol HZSM-5 (27)	82.5	47.5	33.5	52.5	17.6	14.5	86
3Fe:1Cu:0.5Co/HZ, calc 700°C	83	32.0	37.0	68.0	25.2	20.9	89
Fe ₁₀ Mn ₅ KSi-Hol HZSM-5 (27)	83.8	46.8	37.7	53.2	20.0	16.8	86
FeMnK/SiO ₂ +HZSM-5 gran. mix.	84	47.0	26.0	53.0	13.8	11.6	87
FeMnOx(5:1)-0.4Na/HZSM-5	84.1	45.4	15.7	54.6	8.6	7.2	84
Fe ₁₀ Mn ₁₀ KSi-Hol HZSM-5 (27)	85.9	47.1	38.2	52.9	20.2	17.3	86

Table S8: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to aromatics by combining FTO catalysts and zeolites (continued)

catalyst	CO conversion	CO ₂ selectivity	aromatics in hydrocarbons	hydrocarbon selectivity	aromatics selectivity	aromatics yield	ref
	%	% _c	% _c	% _c	% _c	% _c	
FeMn-HZSM-5	86.7	41.2	34.2	58.8	20.1	17.4	82
FeMn-HZSM-5	86.8	46.9	24.0	53.1	12.7	11.1	82
3Fe:1Cu:0.5Co/HZ, 3500 h-1	88	34.0	28.0	66.0	18.5	16.3	89
FeZnNa@0.6-HZSM-5-a	88.8	27.5	50.6	72.5	36.7	32.6	90
FeZnNa@0.6-HZSM-5	89.2	26.9	40.5	73.1	29.6	26.4	90
3Fe:1Cu:0.5Co/HZ, calc 350°C	90	26.0	40.0	74.0	29.6	26.6	89
3Fe:2Cu/HZ	92.5	32.0	38.0	68.0	25.8	23.9	89
3Fe:1Cu:0.5Co/HZ, 2 Mpa	92.5	16.0	30.0	84.0	25.2	23.3	89
3Fe:2Cu:0.5Co/HZ	93	30.0	39.0	70.0	27.3	25.4	89
3Fe:1Cu:0.5Co/HZ, calc 400°C	93	25.0	44.0	75.0	33.0	30.7	89
3Fe:1Cu:0.5Co/HZ, calc 600°C	93	25.0	45.0	75.0	33.8	31.4	89
3Fe:1Cu:0.5Co/HZ, 2500 h-1	93	26.0	43.0	74.0	31.8	29.6	89
FeMnOx(5:1)-0.4Na/HZSM-5	93.7	45.3	26.0	54.7	14.2	13.3	84
3Fe:1Cu:0.5Co/HZ, 320°C	94	23.0	40.0	77.0	30.8	29.0	89
3Fe:1Cu:0.5Co/HZ, 1000 h-1	94	17.0	40.0	83.0	33.2	31.2	89
3Fe:1Cu:0.5Co/HZ, calc 450°C	95	26.0	46.0	74.0	34.0	32.3	89
3Fe:1Cu:0.5Co/HZ, H ₂ /CO=1	95	29.0	43.0	71.0	30.5	29.0	89
3Fe:1Cu:0.5Co/HZ, 3 Mpa	95	18.0	43.0	82.0	35.3	33.5	89
Fe/HZ	96	36.0	31.0	64.0	19.8	19.0	89
3Fe:1Cu:0.5Co/HZ, 330°C	96	22.0	45.0	78.0	35.1	33.7	89
KF80M	96.4	36.9	34.1	63.1	21.5	20.7	91
3Fe:1Cu:0.5Co/HZ	97	23.0	53.0	77.0	40.8	39.6	89
KF60M	97	32.8	39.8	67.2	26.7	25.9	91
3Fe:0.5Co/HZ	97.5	27.0	41.0	73.0	29.9	29.2	89
3Fe:1Cu/HZ	97.5	29.0	40.0	71.0	28.4	27.7	89
3Fe:1Cu:0.5Co/HZ, H ₂ /CO=2	97.5	18.0	44.0	82.0	36.1	35.2	89
3Fe:1Cu:0.5Co/HZ, H ₂ /CO=3	97.5	16.0	30.0	84.0	25.2	24.6	89
KF40M	97.6	32.1	36.2	67.9	24.6	24.0	91
KF20M	97.7	31.4	34.4	68.6	23.6	23.1	91
3Fe:1Co/HZ	98	25.0	38.0	75.0	28.5	27.9	89
3Fe:1Cu:1Co/HZ	98	24.0	45.0	76.0	34.2	33.5	89
3Fe:1Cu:0.5Co/HZ, 360°C	98	26.0	40.0	74.0	29.6	29.0	89
3Fe:1Cu:0.5Co/HZ, 5 Mpa	98	31.0	37.0	69.0	25.5	25.0	89
3Fe:1Cu:0.5Co/HZ, 350°C	98.5	23.0	45.0	77.0	34.7	34.1	89
0.2Cu-Fe/Z5	99	41	37.5	59.0	22.1	21.9	92
0.7Cu-Fe/Z5	99	41	39	59.0	23.0	22.8	92

Table S8: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to aromatics by combining FTO catalysts and zeolites (continued)

catalyst	CO conversion	CO₂ selectivity	aromatics in hydrocarbons	hydrocarbon selectivity	aromatics selectivity	aromatics yield	ref
	%	%_c	%_c	%_c	%_c	%_c	
1.5Cu-Fe/Z5	99	39	43	61.0	26.2	26.0	92

Table S9: combined reported catalytic performance of catalysts for the conversion of synthesis gas to aromatics via a dual reactor process

catalyst	CO conversion	CO₂ selectivity	methanol selectivity	aromatics selectivity from methanol	aromatics selectivity from synthesis gas	yield	ref
	%	%_C	%_C	%_C	%_C	%_C	
dual reactor process							
MeOH							
Cu/ZnO/Al ₂ O ₃	8.6			97.7		8.4	30
2Cu_MCF 10.7	10.7			97.0		10.4	31
Cu/ZnO/Al ₂ O ₃	29.9			99.6		29.8	30
Cu/ZnO/Al ₂ O ₃	34.4			99.8		34.3	30
Cu/ZnO/Al ₂ O ₃	40.3			98.7		39.8	30
Cu/ZnO/Al ₂ O ₃	47.0			98.9		46.5	30
MeOH + MTA							
H-ZSM-5	8.6	0.0	33.0	33.0	32.2	2.8	93
8% Ga/ZSM-5	8.6	0.0	50.0	50.0	48.9	4.2	94
Gd-ZSM-5	8.6	0.0	35.0	35.0	34.2	2.9	95
Zn-ZSM-5	8.6	0.0	46.0	46.0	44.9	3.9	96
Zn-ZSM-5	8.6	0.0	41.0	41.0	40.1	3.4	96
H-ZSM-5	10.7	0.0	33.0	33.0	32.0	3.4	93
8% Ga/ZSM-5	10.7		50.0	50.0	48.5	5.2	94
Gd-ZSM-5	10.7	0.0	35.0	35.0	34.0	3.6	95
Zn-ZSM-5	10.7	0.0	46.0	46.0	44.6	4.8	96
Zn-ZSM-5	10.7	0.0	41.0	41.0	39.8	4.3	96
H-ZSM-5	29.9	0.0	33.0	33.0	32.9	9.8	93
8% Ga/ZSM-5	29.9	0.0	50.0	50.0	49.8	14.9	94
Gd-ZSM-5	29.9	0.0	35.0	35.0	34.9	10.4	95
Zn-ZSM-5	29.9	0.0	46.0	46.0	45.8	13.7	96
Zn-ZSM-5	29.9	0.0	41.0	41.0	40.8	12.2	96
H-ZSM-5	34.4	0.0	33.0	33.0	32.9	11.3	93
8% Ga/ZSM-5	34.4	0.0	50.0	50.0	49.9	17.2	94
Gd-ZSM-5	34.4	0.0	35.0	35.0	34.9	12.0	95
Zn-ZSM-5	34.4	0.0	46.0	46.0	45.9	15.8	96
Zn-ZSM-5	34.4	0.0	41.0	41.0	40.9	14.1	96
H-ZSM-5	40.3	0.0	33.0	33.0	32.6	13.1	93
8% Ga/ZSM-5	40.3	0.0	50.0	50.0	49.4	19.9	94
Gd-ZSM-5	40.3	0.0	35.0	35.0	34.5	13.9	95
Zn-ZSM-5	40.3	0.0	46.0	46.0	45.4	18.3	96
Zn-ZSM-5	40.3	0.0	41.0	41.0	40.5	16.3	96
H-ZSM-5	47.0	0.0	33.0	33.0	32.6	15.3	93

Table S9: combined reported catalytic performance of catalysts for the conversion of synthesis gas to aromatics via a dual reactor process (continued)

catalyst	CO conversion	CO ₂ selectivity	methanol selectivity	aromatics selectivity from methanol	aromatics selectivity from synthesis gas	yield	ref
	%	% _c	% _c	% _c	% _c	% _c	
8% Ga/ZSM-5	47.0	0.0	50.0	50.0	49.5	23.2	94
Gd-ZSM-5	47.0	0.0	35.0	35.0	34.6	16.3	95
Zn-ZSM-5	47.0	0.0	46.0	46.0	45.5	21.4	96
Zn-ZSM-5	47.0	0.0	41.0	41.0	40.5	19.1	96
MTA via dehydrogenation							
Zn/ZSM-5	8.6		95.8	95.8	93.6	8.1	97
Zn/ZSM-5	10.7		95.8	95.8	92.9	9.9	97
Zn/ZSM-5	29.9		95.8	95.8	95.4	28.5	97
Zn/ZSM-5	34.4		95.8	95.8	95.6	32.9	97
Zn/ZSM-5	40.3		95.8	95.8	94.6	38.1	97
Zn/ZSM-5	47.0		95.8	95.8	94.8	44.5	97

4. Gasoline

We analyzed recent publications of bifunctional catalysis to convert synthesis gas directly to gasoline. Beside the overall selectivity of the bifunctional process, we also focused on the resulting octane number of the C₅-C₁₁ products.

4.1. Octane number

The octane number of the C₅-C₁₁ products was estimated by using the blending research octane number (BRON) of the single components. The BRON can describe the effect of a single component being blended into a base gasoline fuel, whereas the pure research octane number (RON) of a component is measured as pure compound⁹⁸. The BRON of the C₅-C₁₁ paraffins, iso-paraffins, olefins, iso-olefins and aromatics were either found in literature⁹⁸⁻¹⁰⁰ or estimated by extrapolation.

The average C₅-C₁₁ paraffins BRON can be found in Table S10 and Figure S1. The individual BRON of all isomers were averaged for every carbon number with the same number of branches. Analog, the average BRON for olefins were determined (Table S11 and Figure S2). However, the olefins were not further divided by the position of the double bond, despite the effect of the double bond position on the BRON (Figure S3). The BRON of C₆-C₁₁ aromatics was averaged over the corresponding carbon numbers (Table S12, Figure S4 and Figure S5).

Table S10: average blending research octane numbers of C₅-C₁₁ paraffins divided into number of branches.

	number of branches					
	0	1	2	3	4	5
C ₅	62	99	100			
C ₆	19	85	93			
C ₇	0	54	84	113		
C ₈	-19	31	69	101	120	
C ₉	-30	20 ¹	56 ¹	92	121	
C ₁₀	-41	2	34	70 ¹	111	
C ₁₁	-48 ¹	-12 ¹	18 ¹	55 ¹	98 ¹	130 ¹

¹: extrapolated

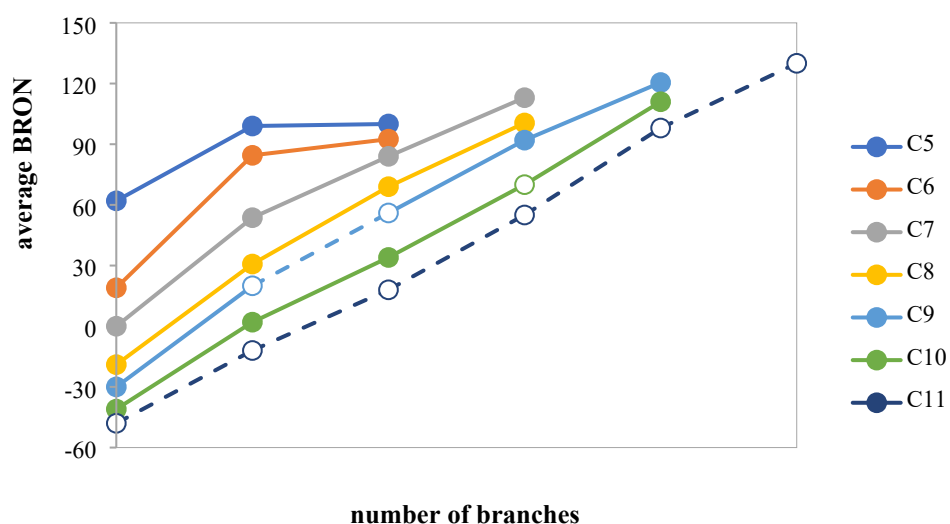


Figure S1: average blending research octane number of C₅-C₁₁ paraffins as function of number of branching.

Table S11: average blending research octane numbers of C₅-C₁₁ olefins divided into number of branches.

	number of branches					
	0	1	2	3	4	5
C ₅	112	125	127			
C ₆	100	112	120			
C ₇	75	86	98	110 ¹		
C ₈	61	72 ¹	85 ¹	100 ¹	115 ¹	
C ₉	48	60 ¹	72 ¹	87 ¹	102 ¹	
C ₁₀	35	47 ¹	59 ¹	75 ¹	90 ¹	
C ₁₁	20 ¹	32 ¹	46 ¹	63 ¹	78 ¹	90 ¹

¹: extrapolated

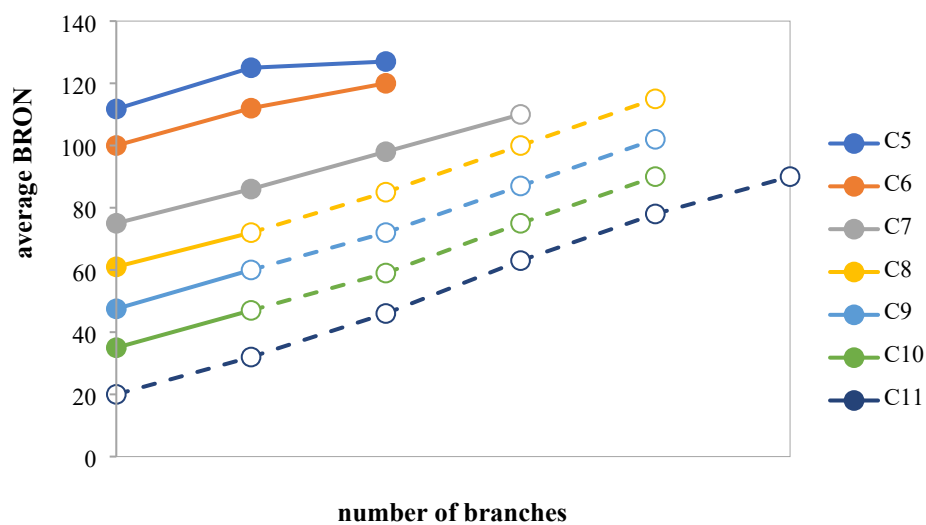


Figure S2: average blending research octane number of C₅-C₁₁ olefins as function of number of branching.

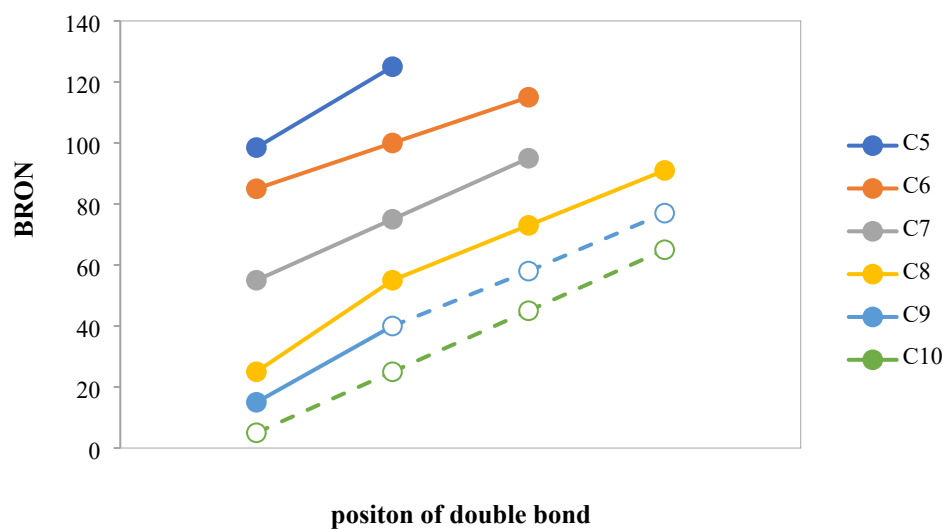


Figure S3: blending research octane number of linear C₅-C₁₀ olefins as function of double bond position.

Table S12: average blending research octane numbers of C₆-C₁₁ aromatics divided into number of side chains.

	side chains					average
	0	1	2	3	4	
C ₆	108					108
C ₇		120				120
C ₈		120.9	131.5			126
C ₉		124.1	127 ¹	131 ¹		127
C ₁₀		116.7	121.8	126.9	133	125
C ₁₁		101	112.7	120 ¹	125 ¹	117

¹: extrapolated

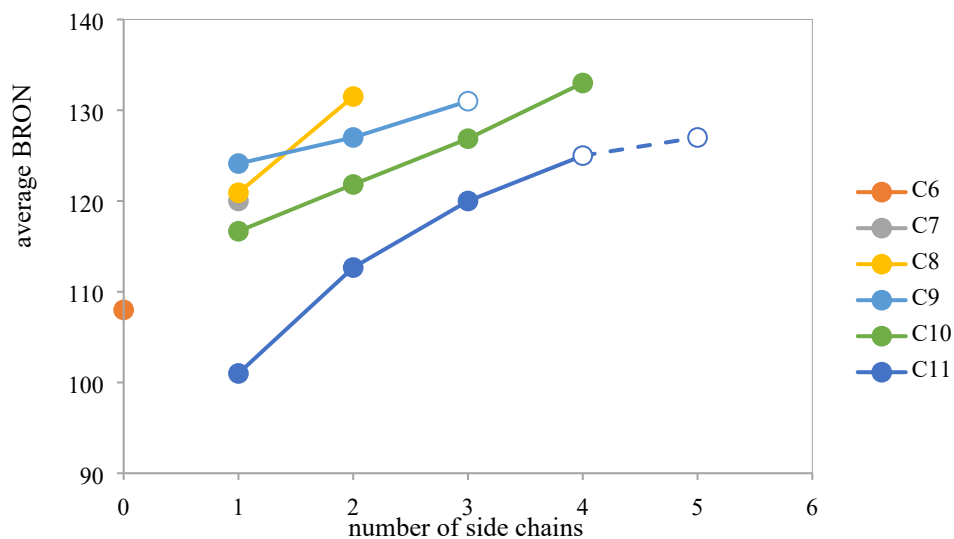


Figure S4: average blending research octane number of C₆-C₁₁ aromatics as function of number of side chains.

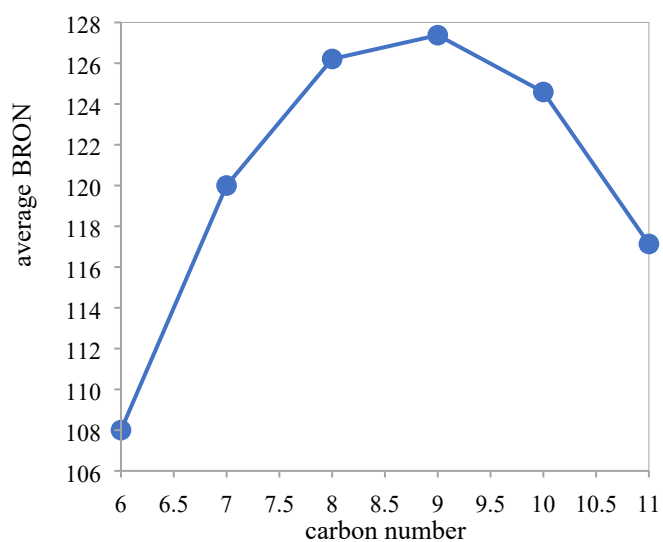


Figure S5: average blending research octane number of aromatics as function of carbon number.

4.2. Analysis of published literature

The overall selectivity of the conversion of synthesis gas to gasoline was analyzed analog to the selectivity of C₂-C₄ olefins (Equation 10 and Equation 11). Here, paraffins, olefins (both including isomers) and aromatics in the range of C₅-C₁₁ were considered.

$$Y(\text{gasoline}) = \frac{n_{out}(C_{\text{gasoline}})}{n_{in}(CO_x)} \quad \text{Equation 10}$$

$$S(\text{gasoline}) = \frac{Y(\text{gasoline})}{X(CO_x)} \quad \text{Equation 11}$$

Where,

Y: yield

n_{out}: molar flow at reactor outlet

n_{in}: molar flow at reactor inlet

C_{gasoline}: carbon atoms in the C₅ – C₁₁ fraction

S: selectivity

X: conversion

To estimate the octane number of the C₅-C₁₁ products the reported selectivities of C₅-C₁₁ paraffins, iso-paraffins, olefins, iso-olefins and aromatics were normalized. Isomers (if not reported in detail) were further divided by the number of branches according to the thermodynamic equilibrium at the corresponding reaction temperature. If the fraction of isomers was not reported for paraffins or olefins, the linear components were considered as well (Table S13). The individual concentrations of paraffins, iso-paraffins, olefins, iso-olefins and aromatics were multiplied with the corresponding BON (Table S10 - Table S12) and added up, resulting in the overall octane number of the C₅-C₁₁ products. If the concentration of olefins exceeded the allowed amount of 18%, we reduced the concentration of olefins in favor of additional paraffins. Also, when *iso*-paraffins and olefins were reported as a single group we divided the corresponding concentration to olefins and *iso*-paraffins accordingly.

We analyzed recent publications with the following approaches to convert synthesis gas to gasoline: combination of Co-based FT catalysts with zeolite, whereas we distinguished between 12-membered ring (Table S14) and 10-membered ring zeolites (Table S15) and non-micro-porous solid acids (NMPA, Table S16). The combination of iron-based FT catalysts and zeolites (Table S17), the OX-ZEO process (Table S18) were analyzed. Additionally, dual bed configurations with dedicated temperatures for the individual catalyst beds were investigated (Table S19). Finally, the dual reactor approach shows the combination of methanol synthesis with consecutive methanol-to-gasoline (MTG) reaction in separate processes was added as a comparison (Table 20).

These calculations of the octane number of the C₅-C₁₁ products are theoretical and based on several assumptions, estimations, and simplifications. To determine the real RON, the mixture of condensed products must be analyzed using validated methods, such as ASTM D2699, GB/T 5487. However, this estimation can give a good indication of the real RON of the corresponding products.

Table S14: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to gasoline by combining Co-based FT catalysts and 12-membered ring zeolites

catalyst	zeolite	temperature	pressure	CO conversion	CO ₂ selectivity	hydrocarbon distribution			C ₅ -C ₁₁				ref
						CH ₄	C ₅ -C ₁₁	C ₅ -C ₁₁ yield	lin paraffins	iso-paraffins	olefins	octane number	
		°C	bar(g)	%	% _c	% _c	% _c	% _c	% _c	% _c	% _c		
Co/USY-S	USY	260	10	50	0	28	39.4	19.7	29.6	41.5	28.9	64.7	101
									34.1	47.9	18	60.0	
									41.6	58.4	0	52.3	
Co/Y-Ce	Y	250	20	34	2	11	73.5	24.5	28.6	71.4	0	29.3	102
									28.6	53.4	18	34.4	
									28.6	0	71.4	49.6	
Co/Y-La	Y	250	20	40	2	9.5	54.5	21.4	26.6	73.4	0	19.6	102
									26.6	55.4	18	25.2	
									26.6	0	73.4	42.3	
Co/Y-P	Y	260	10	50.2	1.1	21.9	59.4	29.5	27	44	29	44.2	103
									31.2	50.8	18	35.6	
									38	62	0	21.4	
Co/Y-A	Y	260	10	66.2	1.5	10.8	69.5	45.3	28.5	64.1	7.4	48.2	103
									29.7	66.8	3.5	46.7	
									30.8	69.2	0	43.1	
Co/Y-B	Y	260	10	69.7	2.9	11.9	65.3	44.2	31	56.9	12.1	49.8	103
									33.1	60.9	6	47.4	
									35.2	64.8	0	41.8	
Co/Y-AB0.25	Y	260	10	66.3	1.9	14.7	67.3	43.8	26.9	46.4	26.7	47.1	103
									30.1	51.9	18	40.4	
									36.7	63.3	0	30.6	
Co/Y-AB1	Y	260	10	75.7	3.5	11.4	66.8	48.8	24.9	51.3	23.8	44.9	103
									26.8	55.2	18	37.6	
									32.7	67.3	0	28.0	
Co/Y-AB4	Y	260	10	75.9	1.8	8.4	71.5	53.3	15	61.2	23.8	49.7	103
									16.1	65.9	18	42.7	
									19.7	80.3	0	34.1	
Co/Y-AB6	Y	260	10	66.5	2	14.5	64.3	41.9	28.3	54.5	17.1	44.1	103
									31.2	60.2	8.6	40.0	
									34.2	65.8	0	31.6	
Co/MOR	MOR	250	20	39.7	0.6	9.2	18.1	7.1	61	29.3	9.7	22.6	104
									64.2	30.9	4.9	19.1	
									67.5	32.5	0	15.6	
Co/BEA	BEA	250	20	17.5	0.7	10.5	18.7	3.2	56	37.5	6.5	27.4	104

Table S14: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to gasoline by combining Co-based FT catalysts and 12-membered ring zeolites (continued)

catalyst	zeolite	temperature	pressure	CO conversion	CO ₂ selectivity	hydrocarbon distribution			C ₅ -C ₁₁				ref
						CH ₄	C ₅ -C ₁₁	C ₅ -C ₁₁ yield	lin paraffins	iso-paraffins	olefins	octane number	
		°C	bar(g)	%	% _c	% _c	% _c	% _c	% _c	% _c	% _c		
								57.9	38.8	3.3	25.1		
								59.9	40.1	0	22.7		

Table S15: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to gasoline by combining Co-based FT catalysts and 10-membered ring zeolites

catalyst	zeolite	temperature	pressure	CO conversion	CO2 selectivity	hydrocarbon distribution			C5-C11				ref
						CH4	C5-C11	C5-C11 yield	lin paraffins	iso-paraffins	olefins	octane number	
						% _c	% _c	% _c	% _c	% _c	% _c	% _c	
		°C	bar(g)	%	% _c								
Z/Co/SiO2	ZSM5	260	10	83	4	21	39.7	31.7	70.6	29.4	0	28.8	105
									70.6	11.4	18	33.5	
									70.6	0	29.4	36.5	
Co/SiO2+ZSM5	ZSM5	260	10	82	15	13.5	40.4	28.2	55.3	44.7	0	30.3	105
									55.3	26.7	18	35.1	
									55.3	0	44.7	42.2	
Z/Co/SiO2-crushed	ZSM5	260	10.0	81	7	19.5	42.1	31.7	66.1	33.9	0	31.5	105
									66.1	15.9	18	36.2	
									66.1	0	33.9	40.4	
Z/Co/SiO2-no TEOS	ZSM5	260	10	90	12	21.5	37.8	30.0	70.1	29.9	0	28.7	105
									70.1	11.9	18	33.5	
									70.1	0	29.9	36.6	
Z/Co/SiO2	ZSM5	260	10.0	34	9	11.5	53.6	16.6	61.4	38.6	0	18.1	105
									61.4	20.6	18	22.9	
									61.4	0	38.6	28.5	
Co/ZSM5	ZSM5	240	15	31	1	19	43.6	13.4	65.7	34.3	0	17.4	105
									65.7	16.3	18	22.3	
									65.7	0	34.3	26.6	
Co/meso-ZSM5	ZSM5	240	15.0	80	3	19	46.6	36.2	47.3	52.7	0	28.1	105
									47.3	34.7	18	33.1	
									47.3	0	52.7	43.0	
ZSM-5/Co-Al2O3/M	ZSM5	230	12	78.7		10.9	89.0	70.0	25.7	50.9	23.3	38.2	106
									<i>in liquid products</i>	<i>in liquid products</i>	27.5	54.5	
ZSM-5/Co-Al2O3/M	ZSM5	250	12	78.9		17.2	91.4	72.1	26.1	53	20.8	36.5	106
									<i>in liquid products</i>	<i>in liquid products</i>	27.1	54.9	
ZSM-5/Co-Al2O3/M	ZSM5	230	6	81.6		17.3	92.1	75.2	24.6	49.3	26.1	40.5	106
									<i>in liquid products</i>	<i>in liquid products</i>	27.3	54.7	
ZSM-5/Co-Al2O3/M	ZSM5	230	20	63.2		10.2	72.9	46.1	28.8	46.2	25.1	28.5	106
									<i>in liquid products</i>	<i>in liquid products</i>	31.5	50.5	
Co/MZ	meso ZSM5	260	10	25.9	0	17.6	65.5	17.0	38.4	61.6	0	12.2	107

Table S15: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to gasoline by combining Co-based FT catalysts and 10-membered ring zeolites (continued)

catalyst	zeolite	temperature °C	pressure bar(g)	CO conversion %	CO2 selectivity % _c	hydrocarbon distribution			C5-C11				ref
						CH4 % _c	C5-C11 % _c	C5-C11 yield % _c	lin paraffins % _c	iso-paraffins % _c	olefins % _c	octane number	
Co/Z	ZSM5	250	20	22	0.99	29.9	44.3	9.7	26.8	55.2	18	48.0	108
									32.7	67.3	0	36.8	
									22.2	77.8	0	53.7	
Co/M-4Z	ZSM5	250	20	6.9	1.08	26.5	44.8	3.1	22.2	59.8	18	58.4	108
									22.2	0	77.8	74.1	
									20.7	79.3	0	67.8	
Co/M-Z	ZSM5	250	20	22.2	0.96	18.7	54.0	11.9	20.7	61.3	18	72.4	108
									20.7	0	79.3	87.9	
									37.1	62.9	0	35.4	
4Co/M-Z	ZSM5	250	20	40.2	0.63	15.6	40.1	16.0	37.1	44.9	18	40.5	108
									37.1	0	62.9	53.2	
									56.5	43.5	0	16.8	
Co-4.5/Z5	ZSM5	240	20	18	0	28.3	41.9	7.5	56.5	25.5	18	22.1	109
									56.5	0	43.5	29.7	
									52.5	18.1	29.4	40.9	
Co-9.9/Z5	ZSM5	240	20	59	0	21.9	44.4	26.2	61	21	18	31.8	109
									74.4	25.6	0	17.3	
									69.9	15	15	19.2	
Co-14/Z5	ZSM5	240	20	58	0	20.9	45.1	26.1	76.1	16.4	7.5	14.5	109
									82.3	17.7	0	9.8	
									72.9	11.3	15.8	8.4	
Co-18/Z5	ZSM5	240	20	50	0	21	40.3	20.1	79.8	12.4	7.9	3.4	109
									86.6	13.4	0	-1.6	
									73.2	11.8	15	9.8	
Co/ZSM-5	ZSM5	250	20	26.8	0.5	11.7	23.9	6.4	79.7	12.8	7.5	4.8	104
									86.2	13.8	0	-0.2	
									20	56.7	23.2	50.2	
Co-SiO ₂ /ZSM-5/Al ₂ O ₃	ZSM5	250	10	75.2	2.2	15.6	39.9	29.3	21.4	60.6	18	47.6	110
									26.1	73.9	0	38.6	
									18.3	22.5	59.2	51.7	
									36.8	45.2	18	27.7	
									44.9	55.1	0	17.3	

Table S16: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to gasoline by combining Co-based FT catalysts and non-microporous solid acids

catalyst	zeolite	temperature	pressure	CO conversion	CO ₂ selectivity	hydrocarbon distribution			C ₅ -C ₁₁				ref
						CH ₄	C ₅ -C ₁₁	C ₅ -C ₁₁ yield	lin paraffins	iso-paraffins	olefins	octane number	
		°C	bar(g)	%	% _c	% _c	% _c	% _c	% _c	% _c	% _c		
Co/SBA15	SBA15	260	10	81.7	2.4	7.1	54.2	43.3	64.9	7.9	27.2	22.2	107
									73.1	8.9	18	13.1	
									89.2	10.8	0	-4.6	
Co/Al-SBA15	SBA15	260	10	64.2	0.9	10.7	62.8	40.0	37.9	21.7	40.5	50.1	107
									52.2	29.8	18	31.9	
									63.6	36.4	0	17.3	

Table S17: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to gasoline by combining Fe-based FT catalysts and zeolites

catalyst	zeolite	temperature	pressure	CO conversion	CO ₂ selectivity	hydrocarbon distribution			C ₅ -C ₁₁					ref
						CH ₄	C ₅ -C ₁₁	C ₅ -C ₁₁ yield	lin paraffins	iso-paraffins	olefins	aromatics	octane number	
						% _c	% _c	% _c	% _c	% _c	% _c	% _c	% _c	
CMA/Hol-Z5-N@S1	H-ZSM-5	280	20	57.3	40.6	2.8	23.9	8.1	8.0	15.0	1.7	75.3	110.0	88
									21.0	39.4	4.5	35.0	86.9	
									32.3	60.7	7.0	0	66.9	
FeK/9mmZ	H-ZSM-5	300	20.0	15.1	50.0	11.0	50.7	3.8	13.4	66.9	0	19.6	78.9	111
									13.4	48.9	18	19.6	83.4	
									13.4	0	66.9	19.6	95.7	
FeK/13mmZ	H-ZSM-5	300	20.0	21.4	50.0	10	52.8	5.7	15.8	57.5	0	26.7	82.0	111
									15.8	39.5	18	26.7	86.4	
									15.8	0	57.5	26.7	96.3	
FeK/17mmZ	H-ZSM-5	300	20.0	20.8	50.0	9	55.1	5.7	16.9	48.8	0	34.3	86.3	111
									16.9	30.8	18	34.3	90.7	
									16.9	0	48.8	34.3	98.3	
Fe-Z-30-5	H-ZSM-5	300	20.0	25.6	45 <i>estimation</i>	27.3	12.9	1.8	3.3	26.3	3.3	67	96.4	112
									6.6	51.9	6.5	35	67.9	
									10.1	79.8	10.1	0	36.7	
Fe-Z-50-5	H-ZSM-5	300	20.0	30.9	45 <i>estimation</i>	28	10.2	1.7	2.9	22.8	3.5	70.8	99.1	112
									6.4	50.8	7.8	35	66.6	
									9.9	78.2	11.9	0	34.9	
Fe-Z-80-5	H-ZSM-5	300	20.0	69.4	45 <i>estimation</i>	23.8	32.0	12.2	4.1	30.3	7.8	57.9	90.5	112
									6.3	46.7	12	35	72.0	
									9.6	71.9	18.5	0	43.9	
Fe-Z-80-10	H-ZSM-5	300	20.0	35	45 <i>estimation</i>	21.3	36.2	7.0	3.4	26.1	13.4	57	90.7	112
									5.1	39.5	20.3	35	73.1	
									7.9	60.8	31.3	0	45.0	
Fe-Z-80-15	H-ZSM-5	300	20.0	56.3	45 <i>estimation</i>	18.7	43.1	13.3	3	23.7	19.6	53.7	89.8	112
									4.3	33.2	27.5	35	75.3	
									6.6	51.1	42.3	0	48.3	
Fe-Z-100-5	H-ZSM-5	300	20.0	65.3	45 <i>estimation</i>	25	24.9	8.9	4.5	33.2	18.9	43.4	82.5	112
									5.2	38.1	21.7	35	76.2	
									7.9	58.6	33.4	0	50.4	
Fe-Z-300-5	H-ZSM-5	300	20.0	73.3	45 <i>estimation</i>	27.7	15.6	6.3	3.7	27.8	34.5	34	79.2	112
									3.7	44.3	18	34	74.5	
									3.7	62.3	0	34	69.4	
Fe/SiO ₂ -M	H-ZSM-5	280	10	60	29.9	7	49.3	20.7	14.5	26.2	59.3	0	88.3	113
									29.1	52.9	18	0	64.5	
									35.5	64.5	0	0	54.2	
Fe/SiO ₂ -S-Z	H-ZSM-5	280	10	54.8	33.8	14.9	51.2	18.6	21.3	48	30.7	0	73.8	113
									25.2	56.8	18	0	68.4	
									30.8	69.2	0	0	60.8	
FeNa@Si-c+HZSM-5	H-ZSM-5	260	20	49.8	14.3	7	62.5	26.7	18.3	46.3	10.8	24.6	68.2	114

Table S18: reported catalytic performance of bifunctional OX-ZEO catalysts for the direct conversion of synthesis gas to gasoline.

catalyst	zeolite	temperature °C	pressure bar(g)	CO conversion %	CO ₂ selectivity % _c	hydrocarbon distribution					C ₅ -C ₁₁			ref
						CH ₄ % _c	C ₅ -C ₁₁ % _c	C ₅ -C ₁₁ yield % _c	lin paraffins % _c	iso-paraffins % _c	olefins % _c	aromatics % _c	octane number	
Zn ₂ Mn ₁ O _x /SAPO-11 = 2/1	SAPO-11	360	40	20.3	50	2.3	76.7	7.8	3.6	52.3	27.8	16.3	89.4	115
ZnAl ₂ O ₄ /SAPO-11	SAPO-11	350	30	36	44	2.4	70.0	14.1	5.5	77.2	17.3	0	73.1	43
ZnAl ₂ O ₄ /SAPO-31	SAPO-31	350	30	22	40	1.3	66.8	8.8	5	78.1	16.9	0	72.7	43

Table S19: reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to gasoline operated in dual bed mode with dedicated temperatures.

catalyst	zeolite	temperature	pressure	CO conversion	CO ₂ selectivity	hydrocarbon distribution			C ₅ -C ₁₁				ref	
						CH ₄ % _c	C ₅ -C ₁₁ % _c	C ₅ -C ₁₁ yield % _c	lin paraffins % _c	iso-paraffins % _c	olefins % _c	aromatics % _c		octane number
		°C	bar(g)	%	% _c	% _c	% _c	% _c	% _c	% _c	% _c	% _c		
CZA + Al₂O₃¹ nano-H-ZSM-5²	nano-H-ZSM-5	260 ¹ /320 ²	30	88	32	3	77.8	46.6	2.7	51.1	2.4	43.8	100.3	116
									3.1	59.1	2.7	35	96.4	
									4.8	91	4.2	0	80.8	
CMA Z-300	H-ZSM-5	270 ¹ /320 ²	10	38	37.5	2.1	69.5	16.5	4.2	21.2	3.1	71.5	108.1	83
									9.7	48.3	7	35	87.5	
									14.9	74.3	10.8	0	67.6	

¹: upstream bed, ²: downstream bed

Table S20: combined reported catalytic performance of catalysts for the conversion of synthesis gas to gasoline combining methanol synthesis and MTG in individual processes.

catalyst	conversion %	CO ₂ selectivity % _c	methanol selectivity % _c	gasoline selectivity from methanol % _c	gasoline selectivity from synthesis gas % _c	yield % _c	ref
MeOH							
Cu/ZnO/Al ₂ O ₃	8.6	0	97.7			8.4	30
2Cu_MCF 10.7	10.7	0	97			10.4	31
Cu/ZnO/Al ₂ O ₃	29.9	0	99.6			29.8	30
Cu/ZnO/Al ₂ O ₃	34.4	0	99.8			34.3	30
Cu/ZnO/Al ₂ O ₃	40.3	0	98.7			39.8	30
Cu/ZnO/Al ₂ O ₃	47	0	98.9			46.5	30
MTG							
CUO/NH ₄ -ZSM-5(%3)	99.6	0		100		99.6	117
CUO/NH ₄ -ZSM-5(%5)	99.7	0		100		99.7	117
CUO/NH ₄ -ZSM-5(%7)	99.9	0		100		99.9	117
CUO/NH ₄ -ZSM-5(%9)	99	0		100		99	117
Zn/HZ5/0.3AT	100	0		99.4		99.4	117
HZ5/0.3AT	100	0		99.3		99.3	117
HZ5/0.1AT	100	0		99.2		99.2	117
dual reactor process							
Cu/ZnO/Al ₂ O ₃	8.6	0			97	8.4	30,117
2Cu_MCF 10.7	10.7	0			96	10.3	31,117
Cu/ZnO/Al ₂ O ₃	29.9	0			99	29.6	30,117
Cu/ZnO/Al ₂ O ₃	34.4	0			99	34.1	30,117
Cu/ZnO/Al ₂ O ₃	40.3	0			98	39.6	30,117
Cu/ZnO/Al ₂ O ₃	47	0			98	46.2	30,117

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