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).

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

$$a\, CO_x + b\, H_2 \rightarrow c\, P1 + d\, P2 \qquad \text{Equation 2}$$

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

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

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

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	CO2 selectivity	DME selectivity	MeOH selectivity	Hydrocarbon selectivity	DME yield	ref
			°C	bar(g)	%	$\%_C$	$\%_C$	$\%_C$	$\%_C$	$\%_C$	
Zn@m-Al2O3	CuZnAl	γ-Al2O3	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	Nb2O5-Al2O3	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-Al2O3	250	50	7.1	29.9	67.0	1.1	2.0	4.8	4
5.9%Nb/Al + CCMS	CuZnAl	Nb2O5-Al2O3	265	50	8	27.7	64.9	6.8	0.6	5.2	3
Pd/silica-SZ	Pd-SiO2	HZSM-5	250	50	9	1.7	69.0	4.8	26.5	6.2	5
CZA-Z-IP	CuZnAl	γ-Al2O3	250	50	10	29.0	61.0	9.0	1.0	6.1	6
Pd/Ga(1:2)/γ-Al2O3	Pd	γ-Al2O3	250	50	10.9	33.6	52.4	1.9	12.1	5.7	7
CZA-2	CuZn	γ-Al2O3	250	50	11.1	30.7	64.3	1.2	3.9	7.1	4
Cu@m-Al2O3	CuZnAl	γ-Al2O3	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-Al2O3	Pd	γ-Al2O3	260	50	14.6	35.1	46.2	1.8	16.9	6.7	7
CuZn@m-Al2O3	CuZnAl	γ-Al2O3	250	30	15.5	24.5	70.3	4.3	0.9	10.9	1
CZA-Z-CF	CuZnAl	γ-Al2O3	250	50	17	46.0	38.0	9.0	7.0	6.5	6
CuZn/m-Al2O3	CuZnAl	γ-Al2O3	250	30	17.4	15.9	70.2	11.8	2.1	12.2	1
Pd/Ga(1:2)/γ-Al2O3	Pd	γ-Al2O3	270	50	19.6	37.6	38.2	1.7	22.2	7.5	7
CZA-5	CuZn	γ-Al2O3	250	50	19.9	30.2	68.3	0.9	0.7	13.6	4
CZA-MA	CuZnAl	γ-Al2O3	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-Al2O3	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-Al2O3	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-Al2O3	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

catalyst	MeOH cat	Solid acid	Temperature °C	Pressure bar(g)	CO conversion %	CO2 selectivity $\%_C$	DME selectivity $\%_C$	MeOH selectivity $\%_C$	Hydrocarbon selectivity $\%_C$	DME yield $\%_C$	ref
CZA/Al(10)-FER	CuZnAl	FER	250	35	43	22.2	74.1	2.8	1.0	31.9	18
g-Al2O3	CuZnAl	γ-Al2O3	260	40	44	25.0	70.5	3.8	0.8	31.0	19
CZA-Z-OX	CuZnAl	γ-Al2O3	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-Al2O3	250	50	48	30.0	69.0	1.0	0.0	33.1	6
6-CLZ-A	CuZrLa	γ-Al2O3	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-Al2O3 + $H_4[SiW_{12}O_{40}]$	275	50	49	31.6	59.8	8	0.4	29.3	9
NbOPO4	CuZnAl	NbOPO4	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-Al2O3	260	40	54.6	30.7	67.3	2.0	0.0	36.7	16
12-CLZ-A	CuZrLa	γ-Al2O3	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(NH3)	CuZnAl	FER	250	40	59.4	34.7	62.9	1.9	0.5	37.4	13
T-4611+γ-Al2O3	CuZnAl	γ-Al2O3	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
Nb2O5·nH2O	CuZnAl	Nb2O5·nH2O	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-Al2O3	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-Al2O3	CuZnAl	γ-Al2O3	280	40	69	27.0	70.5	3.0	1.5	48.6	19
NbOPO4	CuZnAl	NbOPO4	280	40	73	27.0	70.5	2.3	1.5	51.5	19
Nb2O5·nH2O	CuZnAl	Nb2O5·nH2O	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–Al2O3/MgZ1	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)	%	$\%_C$	$\%_C$	$\%_C$	$\%_C$	$\%_C$	
CZA_comm	CuZnAl	γ-Al2O3	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/Al2O3 + zeolite (3Å)	CuZnAl	γ-Al2O3	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
hydrid 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/Al2O3 + zeolite (3Å)	CuZnAl	γ-Al2O3	250	24	90.1[1]		99.2			89.4	27,28
Cu/ZnO/Al2O3 + LTA (3Å)	CuZnAl	γ-Al2O3	252	25	94.5[1]		99.0			93.6	29

[1] CO_x conversion, experiments were conducted with mixture of CO, CO_2 and H_2

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/Al2O3	8.6		97.7			8.4	30
2Cu_MCF 10.7	10.7		97			10.4	31
Cu/ZnO/Al2O3	29.9		99.6			29.8	30
Cu/ZnO/Al2O3	34.4		99.8			34.3	30
Cu/ZnO/Al2O3	40.3		98.7			39.8	30
Cu/ZnO/Al2O3	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 C_2-C_4 olefins was analyzed by calculation of the yield to C_2-C_4 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 C_2-C_4 olefins formed ($n_{out}(C_{olefins})$ 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-XEO and FTO process both include recent studies with decreased water-gas-shift activity and are labeled with *low CO_2*. 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 C_2-C_4 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 C_2-C_4 olefins via the OX-ZEO process

catalyst	CO conversion %	CO2 selectivity $\%_C$	C_2-C_4 olefins in hydrocarbons $\%_C$	hydrocarbons selectivity $\%_C$	C_2-C_4 olefin selectivity $\%_C$	C_2-C_4 olefin yield $\%_C$	ref
OX-ZEO							
ZrO2	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/Ga2O3	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
ZnAl2O4/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-ZrO2 (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-ZrO2/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 C_2-C_4 olefins via the OX-ZEO process

catalyst	CO conversion %	CO2 selectivity %C	C_2-C_4 olefins in hydrocarbons %C	hydrocarbons selectivity %C	C_2-C_4 olefin selectivity %C	C_2-C_4 olefin yield %C	ref
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 AlPO-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-ZrO2/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
ZnAl2O4/SAPO-18	21	44.0	69.0	56.0	38.6	8.1	43
Zn-ZrO2 (1:32)/H-SSZ-13-45H	22	42.0	74.4	58.0	43.2	9.5	33
Zn-ZrO2 (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
ZnAl2O4/SAPO-17	23	42.0	65.0	58.0	37.7	8.7	43
Zn-ZrO2 (1:16)/H-SSZ-13-45H	24	42.0	74.0	58.0	42.9	10.3	33
ZnO-ZrO2/SAPO-34 0,22mmol/g	24	41.0	81.0	59.0	47.8	11.5	45
ZnAl2O4/SAPO-34	24	44.0	80.0	56.0	44.8	10.8	43
ZnCr/Low Si AlPO-18	25					11.3	46
ZnCr/Low Si AlPO-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-ZrO2 (1:4)/H-SSZ-13-45H	27	42.0	65.5	58.0	38.0	10.3	33
ZnO-ZrO2/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-ZrO2 (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 C_2-C_4 olefins via the OX-ZEO process

catalyst	CO conversion %	CO2 selectivity $\%_C$	C_2-C_4 olefins in hydrocarbons $\%_C$	hydrocarbons selectivity $\%_C$	C_2-C_4 olefin selectivity $\%_C$	C_2-C_4 olefin yield $\%_C$	ref
SP18	28.7	45	87	55.0	47.9	13.7	44
Zn-ZrO2 (1:1)/H-SSZ-13-45H	29	42.0	61.8	58.0	35.9	10.4	33
ZnCrOx/MSAPO	30	45.0	73.0	55.0	40.2	12.0	36
ZnCr/SAPO-34	30					12.6	46
ZnO-ZrO2/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
ZnCrOx-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
GaZrOx	44.5	42	89	58.0	51.6	23.0	39
ZnCrOx-SAPO 450-900µm	47	41.0	72.0	59.0	42.5	20.0	50
ZnCrOx-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
ZnCrOx-SAPO-18 Si/Al = 0,045	49.5	40.9	69.0	59.1	40.8	20.2	49
ZnCrOx-SAPO 150-74µm	58	40.0	72.0	60.0	43.2	25.1	50
ZnCr/SAPO-34	59					22.1	46
ZnCrOx-SAPO 20-50µm	59	39.0	65.0	61.0	39.7	23.4	50
ZnCrOx-SAPO 200-300µm	60	39.0	76.0	61.0	46.4	27.8	50
ZnCrOx-GeAPO-$18_{0.027}$	85	32	83	68	56.5	48	51
low CO2 OX-ZEO:							
Zn0.3Ce2-yZryO4	5	4.0	60	96.0	57.6	2.9	52
Zn0.3Ce2-yZryO4	6.5	5.5	77	94.5	72.8	4.7	52
Zn0.3Ce2-yZryO4	6.5	8.5	78	91.5	71.4	4.6	52
Zn0.3Ce2-yZryO4	7	11.0	76	89.0	67.6	4.7	52
Zn0.3Ce2-yZryO4	7	12.0	73	88.0	64.2	4.5	52
Zn0.3Ce2-yZryO4	7	10.0	77	90.0	69.3	4.9	52
Zn0.3Ce2-yZryO4	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 C_2-C_4 olefins via the OX-ZEO process

catalyst	CO conversion %	CO2 selectivity $\%_C$	C_2-C_4 olefins in hydrocarbons $\%_C$	hydrocarbons selectivity $\%_C$	C_2-C_4 olefin selectivity $\%_C$	C_2-C_4 olefin yield $\%_C$	ref
Zn0.3Ce2-yZryO4	7	12.0	75	88.0	66.0	4.6	52
Zn0.3Ce2-yZryO4	7.5	13.0	75	87.0	65.3	4.9	52
Zn0.3Ce2-yZryO4	7.5	12.0	75	88.0	66.0	5.0	52
Zn0.3Ce2-yZryO4	8	15.0	75	85.0	63.8	5.1	52
Zn0.3Ce2-yZryO4	8	12.5	72	87.5	63.0	5.0	52
Zn0.3Ce2-yZryO4	9	22.0	76	78.0	59.3	5.3	52
Zn0.3Ce2-yZryO4	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
Zn0.3Ce2-yZryO4	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 C_2-C_4 olefins

catalyst	CO conversion %	CO_2 selectivity $\%_C$	C_2-C_4 olefins in hydrocarbons $\%_C$	hydrocarbon selectivity $\%_C$	C_2-C_4 olefin selectivity $\%_C$	C_2-C_4 olefin yield $\%_C$	ref
FTO							
CoMn carbide nano prisms	6.3	48.3	45.1	51.7	23.3	1.5	54
Fe/SiO2	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
Co1Mn3–Na2S	18	3.0	30.0	97.0	29.1	5.2	56
Co1Mn3–Na2S2O3	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
Co3Mn1–Na2S	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
Co3Mn1	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-SiO2-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 C_2-C_4 olefins

catalyst	CO conversion %	CO_2 selectivity $\%_C$	C_2-C_4 olefins in hydrocarbons $\%_C$	hydrocarbon selectivity $\%_C$	C_2-C_4 olefin selectivity $\%_C$	C_2-C_4 olefin yield $\%_C$	ref
Fe@SAPO-34	55.4	17.1	52.6	82.9	43.6	24.2	63
FeZn@7.3-SiO2-c	63.1	8.8	47.3	91.2	43.1	27.2	62
FeZn@4.1-SiO2-c	65.3	7.2	52.6	92.8	48.8	31.9	62
FeZn@2.4-SiO2-c	77.8	11.9	50.7	88.1	44.7	34.8	62
FeZn@1.3-SiO2-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 C_2-C_4 olefins via a dual reactor process

catalyst	CO conversion %	CO_2 selectivity $\%_C$	methanol selectivity $\%_C$	C_2-C_4 olefin selectivity from methanol $\%_C$	C_2-C_4 olefin selectivity from synthesis gas $\%_C$	yield $\%_C$	ref
dual reactor process							
MeOH							
Cu/ZnO/Al2O3	8.6		97.7			8.4	30
2Cu_MCF 10.7	10.7		97.0			10.4	31
Cu/ZnO/Al2O3	29.9		99.6			29.8	30
Cu/ZnO/Al2O3	34.4		99.8			34.3	30
Cu/ZnO/Al2O3	40.3		98.7			39.8	30
Cu/ZnO/Al2O3	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 C_2-C_4 olefins (Equation 8 and Equation 9).

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

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

Where,

Y: $yield$

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

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

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

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* CO_2. 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 $\%_C$	aromatics in hydrocarbons $\%_C$	hydrocarbon selectivity $\%_C$	aromatics selectivity $\%_C$	aromatics yield $\%_C$	ref
OX-ZEO							
ZrO2	3	34.0	49.0	66.0	32.3	1.0	65
Ce0.2Zr0.8O2/H-ZSM5-40-350	4	28.0	86.0	72.0	61.9	2.5	65
80Ce-ZrO2	4.8	34.0	69.0	66.0	45.5	2.2	65
CeO2	4.8	34.0	59.0	66.0	38.9	1.9	65
20Ce-ZrO2	5.1	34.0	75.0	66.0	49.5	2.5	65
Ce0.2Zr0.8O2/H-ZSM5-40-380	5.5	33.0	83.0	67.0	55.6	3.1	65
40Ce-ZrO2	5.8	34.0	74.0	66.0	48.8	2.8	65
50% ZnCrOx + 50% H-ZSM-5	6.4	49.0	63.9	51.0	32.6	2.1	66
Ce0.2Zr0.8O2/H-ZSM5-40-400	7.5	33.0	77.0	67.0	51.6	3.9	65
20Ce-ZrO2	8	34.0	83.0	66.0	54.8	4.4	65
40Ce-ZrO2	8	34.0	72.0	66.0	47.5	3.8	65
ZnAlOx/H-ZSM-5H	8.5	44	79	56.0	44.2	3.8	67
80Ce-ZrO2	9	34.0	69.0	66.0	45.5	4.1	65
Ce0.2Zr0.8O2/H-ZSM5-40-450	10	35.0	56.0	65.0	36.4	3.6	65
CeO2	11	34.0	58.0	66.0	38.3	4.2	65
50% ZnCrOx + 50% H-ZSM-5	11.2	49.0	70.4	51.0	35.9	4.0	66
MgZrOx/HZSM5-350°C	12.5	17	68.7	83.0	57.0	7.1	68
t-ZrO2/HZSM-5-mix	14.2	33.5	65.0	66.5	43.2	6.1	69
50% ZnCrOx + 50% H-ZSM-5	14.7	49.0	69.8	51.0	35.6	5.2	66
ZnCr2O4-600&H-ZSM-5	14.7	48.0	70.2	52.0	36.5	5.4	70
50% ZnCrOx + 50% H-ZSM-5	15.4	49.0	67.0	51.0	34.2	5.3	66
MgZrOx/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
ZnCr2O4/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
MgZrOx/HZSM5-450°C	20.5	21	60.2	79.0	47.5	9.7	68
Zn-ZrO2/H-ZSM-5	21	42.0	81.0	58.0	47.0	9.9	74
Z0.8C/s-Z5-150	21	36	56.5	64.0	36.2	7.6	75
ZrO2-H&H-ZSM-5	21.6	44.3	52.4	55.7	29.2	6.3	76
Mo-ZrO2/H-ZSM-5	22	42.0	74.0	58.0	42.9	9.4	77
Ce0.2Zr0.8O2/H-ZSM5-40	22.4	34.1	56.3	65.9	37.1	8.3	65
ZnCr2O4-500&H-ZSM-5	23	47.8	73.3	52.2	38.3	8.8	70
ZnCr2O4-400&H-ZSM-5	23.6	46.9	76.0	53.1	40.4	9.5	70
m-ZrO2/HZSM-5-mix	24	36.4	67.4	63.6	42.9	10.3	69
Z0.8C/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

catalyst	CO conversion %	CO_2 selectivity $\%_C$	aromatics in hydrocarbons $\%_C$	hydrocarbon selectivity $\%_C$	aromatics selectivity $\%_C$	aromatics yield $\%_C$	ref
Ce0.2Zr0.8O2/H-ZSM5-40	27.8	35.1	57.0	64.9	37.0	10.3	65
Z0.8C/n-Z5-150	28	36.5	62	63.5	39.4	11.0	75
Z0.8C/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 $\%_C$	aromatics in hydrocarbons $\%_C$	hydrocarbon selectivity $\%_C$	aromatics selectivity $\%_C$	aromatics yield $\%_C$	ref
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-Fe2O3-0.75Na/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
Fe10Mn1KSi-Hol HZSM-5 (27)	53.4	49.4	33.8	50.6	17.1	9.1	86
Fe1Mn0.5@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/SiO2+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/SiO2+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
Fe10Mn0KSi-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
Fe10Mn5KSi-Hol HZSM-5 (27)	83.8	46.8	37.7	53.2	20.0	16.8	86
FeMnK/SiO2+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
Fe10Mn10KSi-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

catalyst	CO conversion %	CO_2 selectivity %$_C$	aromatics in hydrocarbons %$_C$	hydrocarbon selectivity %$_C$	aromatics selectivity %$_C$	aromatics yield %$_C$	ref
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, H2/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, H2/CO=2	97.5	18.0	44.0	82.0	36.1	35.2	89
3Fe:1Cu:0.5Co/HZ, H2/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

catalyst	CO conversion %	CO_2 selectivity $\%_C$	aromatics in hydrocarbons $\%_C$	hydrocarbon selectivity $\%_C$	aromatics selectivity $\%_C$	aromatics yield $\%_C$	ref
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	CO_2 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/Al2O3	8.6			97.7		8.4	30
2Cu_MCF 10.7	10.7			97.0		10.4	31
Cu/ZnO/Al2O3	29.9			99.6		29.8	30
Cu/ZnO/Al2O3	34.4			99.8		34.3	30
Cu/ZnO/Al2O3	40.3			98.7		39.8	30
Cu/ZnO/Al2O3	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

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 C_5-C_{11} products.

4.1. Octane number

The octane number of the C_5-C_{11} 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 compound [98]. The BRON of the C_5-C_{11} paraffins, iso-paraffins, olefins, iso-olefins and aromatics were either found in literature [98–100] or estimated by extrapolation.

The average C_5-C_{11} 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 C_5-C_{11} 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

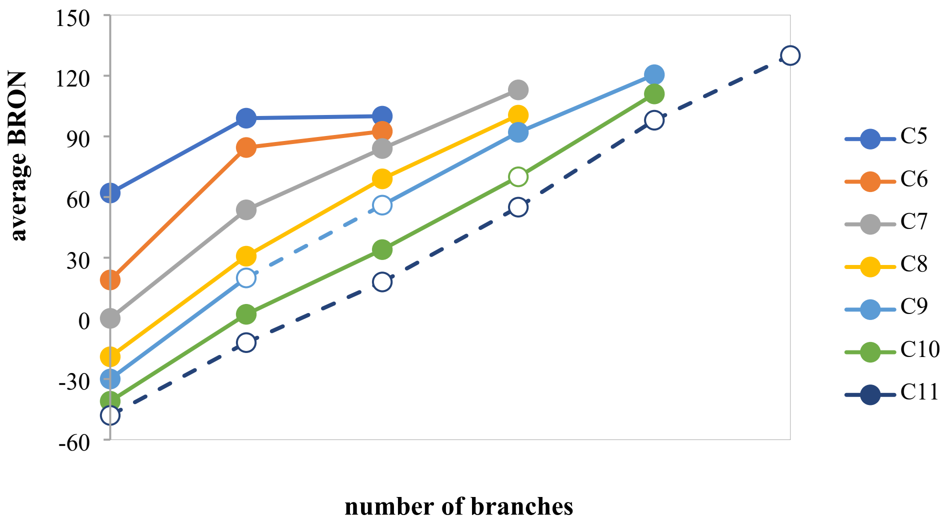

Figure S1: average blending research octane number of C_5-C_{11} paraffins as function of number of branching.

Table S11: average blending research octane numbers of C_5-C_{11} 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

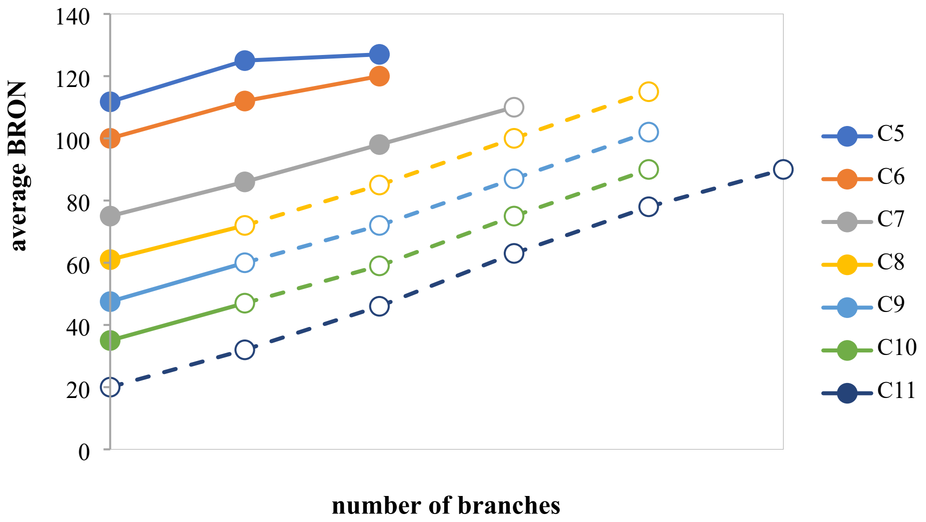

Figure S2: average blending research octane number of C_5-C_{11} olefins as function of number of branching.

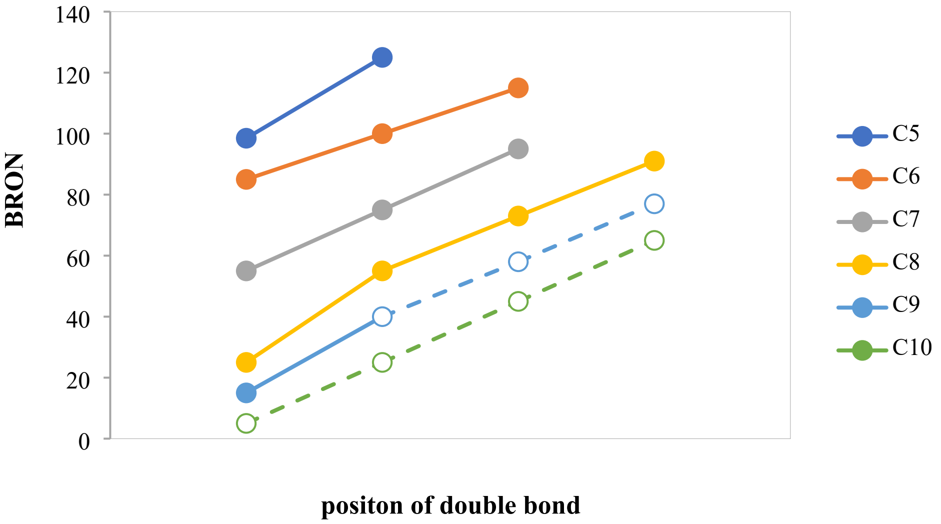

Figure S3: blending research octane number of linear C_5-C_{10} olefins as function of double bond position.

Table S12: average blending research octane numbers of C_6-C_{11} aromatics divided into number of side chains.

	side chains						
	0	1	2	3	4	5	average
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]	127[1]	117

[1]: extrapolated

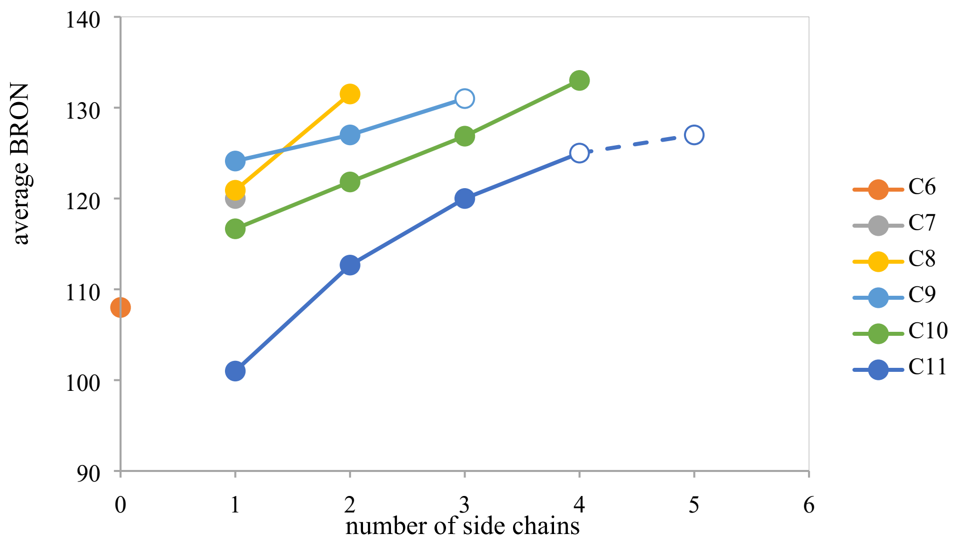

Figure S4: average blending research octane number of C_6-C_{11} aromatics as function of number of side chains.

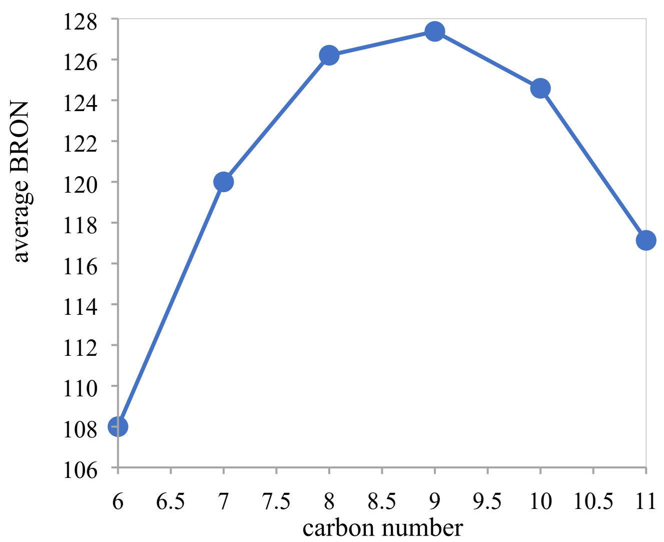

Figure S5: average blending research octane number of aromatics as function of carbon number.

4.2. Analysis of published literature

The overall selectivity of the conversion of synthesis gas to gasoline was analyzed analog to the selectivity of C_2-C_4 olefins (Equation 10 and Equation 11). Here, paraffins, olefins (both including isomers) and aromatics in the range of C_5-C_{11} were considered.

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

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

Where,

Y: $yield$

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

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

$C_{gasoline}$: $carbon\ atoms\ in\ the\ C_5 - C_{11}\ fraction$

S: $selectivity$

X: $conversion$

To estimate the octane number of the C_5-C_{11} products the reported selectivities of C_5-C_{11} 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 C_5-C_{11} 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 C_5-C_{11} 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 S13: thermodynamic distribution of C_5-C_{11} *n*- and *iso*-paraffins between 200°C and 300°C. Calculated with Outotec HSC 4 at 20 bar pressure.

	temperature																				
	200°C	**205°C**	**210°C**	**215°C**	**220°C**	**225°C**	**230°C**	**235°C**	**240°C**	**245°C**	**250°C**	**255°C**	**260°C**	**265°C**	**270°C**	**275°C**	**280°C**	**285°C**	**290°C**	**295°C**	**300°C**
C5 lin	20.0%	20.5%	21.0%	21.4%	21.9%	22.4%	22.8%	23.3%	23.7%	24.1%	24.6%	25.0%	25.4%	25.8%	26.2%	26.6%	27.0%	27.4%	27.8%	28.1%	28.5%
C5 mono	53.3%	53.6%	53.9%	54.2%	54.5%	54.7%	54.9%	55.1%	55.3%	55.5%	55.6%	55.8%	55.9%	56.0%	56.0%	56.1%	56.2%	56.2%	56.3%	56.3%	56.3%
C5 di	26.7%	25.9%	25.1%	24.3%	23.6%	22.9%	22.2%	21.6%	21.0%	20.4%	19.8%	19.3%	18.7%	18.2%	17.7%	17.3%	16.8%	16.4%	16.0%	15.6%	15.2%
C6 lin	11.0%	11.3%	11.6%	11.9%	12.2%	12.5%	12.8%	13.1%	13.4%	13.7%	13.9%	14.2%	14.5%	14.8%	15.0%	15.3%	15.5%	15.8%	16.1%	16.3%	16.6%
C6 mono	46.5%	47.0%	47.4%	47.9%	48.3%	48.7%	49.1%	49.4%	49.8%	50.1%	50.5%	50.8%	51.1%	51.4%	51.7%	51.9%	52.2%	52.4%	52.7%	52.9%	53.1%
C6 di	42.5%	41.8%	41.0%	40.2%	39.5%	38.8%	38.1%	37.5%	36.8%	36.2%	35.6%	35.0%	34.4%	33.9%	33.3%	32.8%	32.3%	31.8%	31.3%	30.8%	30.3%
C7 lin	10.6%	10.9%	11.1%	11.3%	11.5%	11.8%	12.0%	12.2%	12.4%	12.6%	12.8%	13.0%	13.2%	13.4%	13.6%	13.8%	13.9%	14.1%	14.3%	14.5%	14.7%
C7 mono	46.8%	47.2%	47.6%	47.9%	48.2%	48.6%	48.9%	49.2%	49.4%	49.7%	50.0%	50.2%	50.4%	50.7%	50.9%	51.1%	51.3%	51.5%	51.7%	51.8%	52.0%
C7 di	38.5%	37.9%	37.5%	37.0%	36.5%	36.1%	35.6%	35.2%	34.8%	34.4%	34.0%	33.6%	33.2%	32.9%	32.5%	32.2%	31.9%	31.6%	31.3%	30.9%	30.7%
C7 tri	4.1%	4.0%	3.9%	3.8%	3.7%	3.6%	3.6%	3.5%	3.4%	3.3%	3.3%	3.2%	3.1%	3.1%	3.0%	2.9%	2.9%	2.8%	2.8%	2.7%	2.7%
C8 lin	7.7%	7.8%	7.9%	8.1%	8.2%	8.4%	8.5%	8.6%	8.8%	8.9%	9.0%	9.2%	9.3%	9.4%	9.6%	9.7%	9.8%	9.9%	10.0%	10.2%	10.3%
C8 mono	42.4%	42.7%	43.0%	43.3%	43.5%	43.8%	44.1%	44.3%	44.6%	44.8%	45.0%	45.2%	45.4%	45.6%	45.8%	46.0%	46.2%	46.4%	46.6%	46.7%	46.9%
C8 di	45.9%	45.5%	45.1%	44.7%	44.3%	44.0%	43.6%	43.3%	42.9%	42.6%	42.3%	42.0%	41.7%	41.4%	41.1%	40.8%	40.5%	40.3%	40.0%	39.8%	39.5%
C8 tri	4.0%	4.0%	3.9%	3.9%	3.8%	3.8%	3.8%	3.7%	3.7%	3.6%	3.6%	3.6%	3.5%	3.5%	3.5%	3.4%	3.4%	3.4%	3.3%	3.3%	3.3%
C8 quad	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
C9 lin	8.9%	9.0%	9.2%	9.3%	9.5%	9.6%	9.8%	9.9%	10.1%	10.2%	10.4%	10.5%	10.6%	10.8%	10.9%	11.1%	11.2%	11.3%	11.4%	11.6%	11.7%
C9 mono	66.5%	66.6%	66.8%	66.9%	67.0%	67.1%	67.3%	67.4%	67.5%	67.6%	67.6%	67.7%	67.8%	67.9%	67.9%	68.0%	68.0%	68.1%	68.1%	68.2%	68.2%
C9 di	21.1%	20.8%	20.5%	20.2%	20.0%	19.7%	19.5%	19.2%	19.0%	18.8%	18.6%	18.4%	18.2%	18.0%	17.8%	17.6%	17.5%	17.3%	17.1%	17.0%	16.8%
C9 tri	3.5%	3.5%	3.5%	3.5%	3.4%	3.4%	3.4%	3.4%	3.4%	3.3%	3.3%	3.3%	3.3%	3.3%	3.3%	3.3%	3.2%	3.2%	3.2%	3.2%	3.2%
C9 quad	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%
C10 lin	7.4%	7.6%	7.7%	7.9%	8.1%	8.2%	8.4%	8.5%	8.7%	8.8%	9.0%	9.1%	9.3%	9.4%	9.6%	9.7%	9.9%	10.0%	10.1%	10.3%	10.4%
C10 mono	50.5%	50.9%	51.2%	51.5%	51.8%	52.1%	52.4%	52.7%	53.0%	53.2%	53.5%	53.7%	53.9%	54.2%	54.4%	54.6%	54.8%	55.0%	55.2%	55.3%	55.5%
C10 di	38.1%	37.6%	37.1%	36.6%	36.1%	35.7%	35.2%	34.8%	34.4%	34.0%	33.6%	33.2%	32.8%	32.5%	32.1%	31.8%	31.4%	31.1%	30.8%	30.5%	30.1%
C10 tri	3.8%	3.8%	3.8%	3.7%	3.7%	3.7%	3.7%	3.7%	3.7%	3.7%	3.7%	3.7%	3.7%	3.7%	3.7%	3.7%	3.7%	3.7%	3.7%	3.7%	3.7%
C10 quad	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.2%	0.3%	0.3%	0.3%	0.3%
C11 lin	9.3%	9.5%	9.7%	9.9%	10.0%	10.2%	10.4%	10.5%	10.7%	10.8%	11.0%	11.1%	11.3%	11.4%	11.6%	11.7%	11.9%	12.0%	12.1%	12.3%	12.4%
C11 mono	58.9%	59.2%	59.5%	59.7%	60.0%	60.2%	60.5%	60.7%	60.9%	61.1%	61.3%	61.4%	61.6%	61.8%	61.9%	62.1%	62.2%	62.4%	62.5%	62.6%	62.7%
C11 di	29.2%	28.8%	28.3%	27.9%	27.5%	27.1%	26.7%	26.4%	26.0%	25.7%	25.3%	25.0%	24.7%	24.4%	24.1%	23.8%	23.6%	23.3%	23.1%	22.8%	22.6%
C11 tri	2.5%	2.4%	2.4%	2.4%	2.4%	2.4%	2.4%	2.4%	2.4%	2.3%	2.3%	2.3%	2.3%	2.3%	2.3%	2.3%	2.3%	2.3%	2.2%	2.2%	2.2%
C11 quad	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%

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	
									34.1	47.9	18	60.0	101
									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	
									28.6	53.4	18	34.4	102
									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	
									26.6	55.4	18	25.2	102
									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	
									31.2	50.8	18	35.6	103
									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	
									29.7	66.8	3.5	46.7	103
									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	
									33.1	60.9	6	47.4	103
									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	
									30.1	51.9	18	40.4	103
									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	
									26.8	55.2	18	37.6	103
									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	
									16.1	65.9	18	42.7	103
									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	
									31.2	60.2	8.6	40.0	103
									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	
									64.2	30.9	4.9	19.1	104
									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

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	bar(g)	%	$\%_C$	$\%_C$	$\%_C$	$\%_C$	$\%_C$	$\%_C$	$\%_C$		
Z/Co/SiO2	ZSM5	260	10	83	4	21	39.7	31.7	70.6	29.4	0	28.8	
									70.6	11.4	18	33.5	105
									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	
									55.3	26.7	18	35.1	105
									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	
									66.1	15.9	18	36.2	105
									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	
									70.1	11.9	18	33.5	105
									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	
									61.4	20.6	18	22.9	105
									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	
									65.7	16.3	18	22.3	105
									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	
									47.3	34.7	18	33.1	105
									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	
							in liquid products	*in liquid products*	27.5	54.5	18	34.8	106
									33.6	66.4	0	23.7	
ZSM-5/Co-Al2O3/M	ZSM5	250	12	78.9		17.2	*91.4*	*72.1*	26.1	53	20.8	36.5	
							in liquid products	*in liquid products*	27.1	54.9	18	34.7	106
									33	67	0	23.1	
ZSM-5/Co-Al2O3/M	ZSM5	230	6	81.6		17.3	*92.1*	*75.2*	24.6	49.3	26.1	40.5	
							in liquid products	*in liquid products*	27.3	54.7	18	35.3	106
									33.3	66.7	0	23.7	
ZSM-5/Co-Al2O3/M	ZSM5	230	20	63.2		10.2	*72.9*	*46.1*	28.8	46.2	25.1	28.5	
							in liquid products	*in liquid products*	31.5	50.5	18	23.9	106
									38.4	61.6	0	12.2	
Co/MZ	meso ZSM5	260	10	25.9	0	17.6	65.5	17.0	23.6	48.6	27.7	54.1	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

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	bar(g)	%	%$_C$	%$_C$	%$_C$	%$_C$	%$_C$	%$_C$	%$_C$		
									26.8	55.2	18	48.0	
									32.7	67.3	0	36.8	
Co/Z	ZSM5	250	20	22	0.99	29.9	44.3	9.7	22.2	77.8	0	53.7	
									22.2	59.8	18	58.4	108
									22.2	0	77.8	74.1	
Co/M-4Z	ZSM5	250	20	6.9	1.08	26.5	44.8	3.1	20.7	79.3	0	67.8	
									20.7	61.3	18	72.4	108
									20.7	0	79.3	87.9	
Co/M-Z	ZSM5	250	20	22.2	0.96	18.7	54.0	11.9	37.1	62.9	0	35.4	
									37.1	44.9	18	40.5	108
									37.1	0	62.9	53.2	
4Co/M-Z	ZSM5	250	20	40.2	0.63	15.6	40.1	16.0	56.5	43.5	0	16.8	
									56.5	25.5	18	22.1	108
									56.5	0	43.5	29.7	
Co-4.5/Z5	ZSM5	240	20	18	0	28.3	41.9	7.5	52.5	18.1	29.4	40.9	
									61	21	18	31.8	109
									74.4	25.6	0	17.3	
Co-9.9/Z5	ZSM5	240	20	59	0	21.9	44.4	26.2	69.9	15	15	19.2	
									76.1	16.4	7.5	14.5	109
									82.3	17.7	0	9.8	
Co-14/Z5	ZSM5	240	20	58	0	20.9	45.1	26.1	72.9	11.3	15.8	8.4	
									79.8	12.4	7.9	3.4	109
									86.6	13.4	0	-1.6	
Co-18/Z5	ZSM5	240	20	50	0	21	40.3	20.1	73.2	11.8	15	9.8	
									79.7	12.8	7.5	4.8	109
									86.2	13.8	0	-0.2	
Co/ZSM-5	ZSM5	250	20	26.8	0.5	11.7	23.9	6.4	20	56.7	23.2	50.2	
									21.4	60.6	18	47.6	104
									26.1	73.9	0	38.6	
Co-SiO2/ZSM-5/Al2O3	ZSM5	250	10	75.2	2.2	15.6	39.9	29.3	18.3	22.5	59.2	51.7	
									36.8	45.2	18	27.7	110
									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-micro porous 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	
									73.1	8.9	18	13.1	107
									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	
									52.2	29.8	18	31.9	107
									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} yield	C_5-C_{11}					ref
						CH_4	C_5-C_{11}		lin paraffins	iso-paraffins	olefins	aromatics	octane number	
		°C	bar(g)	%	$\%_C$	$\%_C$	$\%_C$	$\%_C$	$\%_C$	$\%_C$	$\%_C$	$\%_C$		
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	
									21.0	39.4	4.5	35.0	86.9	88
									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	
									13.4	48.9	18	19.6	83.4	111
									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	
									15.8	39.5	18	26.7	86.4	111
									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	
									16.9	30.8	18	34.3	90.7	111
									16.9	0	48.8	34.3	98.3	
Fe-Z-30-5	H-ZSM-5	300	20.0	25.6	*45*	27.3	12.9	1.8	3.3	26.3	3.3	67	96.4	
					estimation				6.6	51.9	6.5	35	67.9	112
									10.1	79.8	10.1	0	36.7	
Fe-Z-50-5	H-ZSM-5	300	20.0	30.9	*45*	28	10.2	1.7	2.9	22.8	3.5	70.8	99.1	
					estimation				6.4	50.8	7.8	35	66.6	112
									9.9	78.2	11.9	0	34.9	
Fe-Z-80-5	H-ZSM-5	300	20.0	69.4	*45*	23.8	32.0	12.2	4.1	30.3	7.8	57.9	90.5	
					estimation				6.3	46.7	12	35	72.0	112
									9.6	71.9	18.5	0	43.9	
Fe-Z-80-10	H-ZSM-5	300	20.0	35	*45*	21.3	36.2	7.0	3.4	26.1	13.4	57	90.7	
					estimation				5.1	39.5	20.3	35	73.1	112
									7.9	60.8	31.3	0	45.0	
Fe-Z-80-15	H-ZSM-5	300	20.0	56.3	*45*	18.7	43.1	13.3	3	23.7	19.6	53.7	89.8	
					estimation				4.3	33.2	27.5	35	75.3	112
									6.6	51.1	42.3	0	48.3	
Fe-Z-100-5	H-ZSM-5	300	20.0	65.3	*45*	25	24.9	8.9	4.5	33.2	18.9	43.4	82.5	
					estimation				5.2	38.1	21.7	35	76.2	112
									7.9	58.6	33.4	0	50.4	
Fe-Z-300-5	H-ZSM-5	300	20.0	73.3	*45*	27.7	15.6	6.3	3.7	27.8	34.5	34	79.2	
					estimation				3.7	44.3	18	34	74.5	112
									3.7	62.3	0	34	69.4	
Fe/SiO2-M	H-ZSM-5	280	10	60	29.9	7	49.3	20.7	14.5	26.2	59.3	0	88.3	
									29.1	52.9	18	0	64.5	113
									35.5	64.5	0	0	54.2	
Fe/SiO2-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	
									25.2	56.8	18	0	68.4	113
									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	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	bar(g)	%	$\%_C$	$\%_C$	$\%_C$	$\%_C$	$\%_C$	$\%_C$	$\%_C$	$\%_C$		
Zn2Mn1Ox/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
ZnAl2O4/SAPO-11	SAPO-11	350	30	36	44	2.4	70.0	14.1	5.5	77.2	17.3	0	73.1	43
ZnAl2O4/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_5-C_{11}	C_5-C_{11} yield	lin paraffins	iso-paraffins	olefins	aromatics	octane number	
		°C	bar(g)	%	$\%_C$	$\%_C$	$\%_C$	$\%_C$	$\%_C$	$\%_C$	$\%_C$	$\%_C$		
CZA + Al2O3[1] nano-H-ZSM-5[2]	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/Al2O3	8.6	0	97.7			8.4	30
2Cu_MCF 10.7	10.7	0	97			10.4	31
Cu/ZnO/Al2O3	29.9	0	99.6			29.8	30
Cu/ZnO/Al2O3	34.4	0	99.8			34.3	30
Cu/ZnO/Al2O3	40.3	0	98.7			39.8	30
Cu/ZnO/Al2O3	47	0	98.9			46.5	30
MTG							
CUO/NH4-ZSM-5(%3)	99.6	0		100		99.6	117
CUO/NH4-ZSM-5(%5)	99.7	0		100		99.7	117
CUO/NH4-ZSM-5(%7)	99.9	0		100		99.9	117
CUO/NH4-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/Al2O3	8.6	0			97	8.4	30,117
2Cu_MCF 10.7	10.7	0			96	10.3	31,117
Cu/ZnO/Al2O3	29.9	0			99	29.6	30,117
Cu/ZnO/Al2O3	34.4	0			99	34.1	30,117
Cu/ZnO/Al2O3	40.3	0			98	39.6	30,117
Cu/ZnO/Al2O3	47	0			98	46.2	30,117

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