Electronic Supporting Information

Production of oxymethylene ethers (OME) as sustainable diesel fuel substitutes: continuous synthesis from dimethyl ether and trioxane and evaluation of catalyst stability Marius Drexler, Victor Zaghini Francesconi, Ulrich Arnold,* Thomas A. Zevaco and Jörg Sauer

Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research and Technology (IKFT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany. E-mail: ulrich.arnold@kit.edu

Content

Α.	Detailed description of analytical procedures	2
В.	TGA curves	4
	Figure B.1: TGA analysis of the calcined KIT-Z80PU and KIT-Z80AE catalyst	4
	Figure B.2: TGA analysis of the used KIT-Z80PU and KIT-Z80AE catalyst samples of all four runs	4
C.	Tables	5
	Table C.1: Composition of feed used in the experiments, mass of catalyst employed.	5
	Table C.2: Conversion of reactants as well as selectivity to product species in continuous experiment with Feed C1 and KIT-Z80PU catalyst	5
	Table C.3: Conversion of reactants as well as selectivity to product species in continuous experiment with Feed C1 and KIT-Z80PU catalyst (continued).	5
	Table C.4: Conversion of reactants as well as selectivity to product species in continuous experiment with Feed C1 and KIT-Z80AE catalyst	6
	Table C.5: Conversion of reactants as well as selectivity to product species in continuous experiment with Feed C1 and KIT-Z80AE catalyst (continued).	6
	Table C.6: Conversion of reactants as well as selectivity to product species in continuous experiment with Feed C2 and KIT-Z80PU catalyst	7
	Table C.7: Conversion of reactants as well as selectivity to product species in continuous experiment with Feed C2 and KIT-Z80PU catalyst (continued).	7
	Table C.8: Conversion of reactants as well as selectivity to product species in continuous experiment with Feed C2 and KIT-Z80AE catalyst	8
	Table C.9: Conversion of reactants as well as selectivity to product species in continuous experiment with Feed C2 and KIT-Z80AE catalyst (continued).	8
	Table C.10: Conversion of TRI as well as selectivity to product species in batch experiment with Feed B1	9
	Table C.11: Conversion of TRI as well as selectivity to product species in batch experiment with Feed B1 (continued).	9

A. Detailed description of analytical procedures

Product analysis via gas chromatography

For online analysis samples of the product stream were drawn and analyzed employing an Agilent 8860 GC equipped with a liquid sampling valve system and flame ionization detector (FID). An Agilent DB-5 MS+DG column with 30 m length, 0.25 mm diameter and 0.25 μ m film thickness was used for compound separation and helium was employed as carrier gas. A Polyarc system (Activated Research Company) was installed in between column and detector to improve the FIDs sensitivity for highly oxygenated compounds such as TRI or MeFo. A sample of 0.5 μ l was injected into the inlet and a split ratio of 100:1 was used. The temperature program of the GC oven was as follows: 30 °C hold for 4 min, 30 °C/min to 300 °C, hold for 2 min.

Analysis of the batch experiment product mixture was performed offline using a Hewlett Packard 6890 series GC equipped with FID. As with the online GC, an Agilent DB-5 MS+DG column with 30 m length, 0.25 mm diameter and 0.25 μ m film thickness was used for compound separation and helium was employed as carrier gas. The injection was 1 μ l and the split ratio 100:1. The oven temperature program was similar to the program used for online GC: 30 °C hold for 4 min, 30 °C/min to 300 °C, hold for 8 min.

Within this study, TRI, OME_{1-10} , MeFo, MeOH and dodecane were quantified in the product mixtures. Response factors of TRI, OME_1 , OME_2 , OME_3 , OME_4 , OME_5 , MeFo, MeOH and dodecane have been determined by calibration with well-defined mixtures. Calibration mixtures have been produced from pure compounds using a precision balance (Precisa BJ 2200C) to determine the exact composition. The compositions of those mixtures were chosen similar to reactant and product mixtures, to avoid matrix effects. The accuracy of the measurements was estimated to be within the repeatability of the calibration measurements (ca. <5% for the offline GC and <3% for the online GC). Response factors of higher OME were correlated based on the values of OME_{1-5} as they were not available in pure form. For all experiments, no signal for MeOH could be detected in the product mixture.

NMR measurement parameters

¹³C MAS NMR spectra were recorded at a resonance frequency of 100.11 MHz with a sample spinning frequency of 15 kHz using the standard pulse sequence single_pulse_dec_solid.jxp from the Jeol library. The recording parameters were accordingly optimized: 8192 scans were accumulated upon $\pi/2$ single pulse excitation of 2.2 µs pulse width and 5 s recycle delay (offset 100 ppm, spectral width = 40 kHz / 400 ppm; acquisition time = 40.63232 ms; decoupling mode TPPM).

The standard proton.jxp pulse sequence was used for the ¹H spectra: Dim_size 16K, 512 scans were accumulated with an excitation pulse of $3.34 \,\mu\text{s}$ (45° pulse), relaxation time of 5 s between scans, spectral width of 14 ppm (offset 5 ppm). The chemical shifts were calibrated with the remaining ¹H signal of the solvent (DMSO 99.8%). The standard carbon.jxp pulse sequence was used for the ¹³C spectra: Dim_size 32K, 20480 scans were accumulated by an excitation pulse of $3.06 \,\mu\text{s}$ (90° pulse @ 9.18 $\,\mu\text{s}$), relaxation delay of 2 s between scans, spectral width of 250 ppm (offset 100 ppm). The chemical shifts were calibrated with the characteristic deuterium-coupled ¹³C signal of the solvent (52 ppm; CD2Cl2 99.8%).

The adiabatic version of the HSQC experiment was chosen for the 2D C,H-measurement: ghsqcad.jxp. The use of so-called adiabatic pulses in a C-H correlated experiment often leads to better data sets, as the scattering of the J(C,H)-coupling values encountered in complex mixtures can be somewhat alleviated with this specific method. The experiment was performed using the following parameters:

1024 X_points; 256 Y_points; 64 scans per experiments – with a total scan number of 16384; 90° pulse: 6.71 μ s; relaxation delay of 1.3 s, ¹H spectral width of 12 ppm (offset 5 ppm), ¹³C spectral width of 180 ppm (offset 85 ppm), measuring time ca. 14 hours.

B. TGA curves



Figure B.1: TGA analysis of the calcined KIT-Z80PU and KIT-Z80AE catalyst.



Figure B.2: TGA analysis of the used KIT-Z80PU and KIT-Z80AE catalyst samples of all four runs.

C. Tables

Feed	Run	Catalyst	m _{Catalyst}	DME	TRI	Dodecane
			[g]	[wt%]	[wt%]	[wt%]
C1	1	KIT-Z80PU	26.5	30.01	15.03	54.96
C1	1	KIT-Z80AE	25.3	30.01	15.00	54.99
C2	1	KIT-Z80PU	26.5	42.06	32.96	24.98
	2			42.01	33.00	24.99
C2	1	KIT-Z80AE	25.3	42.03	32.98	24.99
	2			42.02	32.99	24.99
B1	1	Fresh (KIT-Z80PU)	0.52	33.22	16.62	50.16
	2		0.52	33.26	16.55	50.19
B1	1	Used (KIT-Z80PU)	0.52	33.47	16.73	49.80
	2		0.52	33.36	16.78	49.86
B1	1	R1 (KIT-Z80PU)	0.52	33.51	16.48	50.01
	2		0.52	33.08	16.59	50.34
B1	1	R2 (KIT-Z80PU)	0.52	33.26	16.65	50.09
	2		0.52	33.02	16.51	50.47
B1	1	R3 (KIT-Z80PU)	0.52	32.98	16.56	50.46
	2		0.52	33.28	16.62	50.10

Table C.1: Composition of feed used in the experiments, mass of catalyst employed.

Table C.2: Conversion of reactants as well as selectivity to product species in continuous experiment with Feed C1 and KIT-Z80PU catalyst.

Time on stream	m _{Feed,total}	T _{Reactor}	X _{TRI}	X _{DME}	S _{OME1}	S _{OME2}	S _{OME3}	S _{OME4}
[h]	[g]	[°C]	[%]	[%]	[%]	[%]	[%]	[%]
0.5	500	102.7	95.52	22.26	21.08	14.22	14.13	11.40
1.0	1000	102.6	84.42	18.87	19.95	14.38	13.94	13.14
1.5	1500	102.7	76.79	16.49	19.03	14.33	14.80	10.81
2.0	2000	102.6	72.70	14.66	16.81	14.68	14.91	11.76
2.5	2500	102.6	68.14	13.03	15.37	14.17	14.76	12.30
3.0	2990	102.4	66.46	11.88	14.22	13.90	14.46	12.63
3.5	3500	102.4	62.96	10.47	12.92	13.70	14.49	11.99
4.0	4000	102.4	61.05	9.65	12.15	13.30	13.78	12.95
4.5	4520	102.3	57.83	8.57	11.17	12.57	13.29	12.99
5.1	5100	102.3	55.30	7.61	10.25	12.24	12.97	13.13

Table C.3: Conversion of reactants as well as selectivity to product species in continuous experiment with Feed C1 and KIT-Z80PU catalyst (continued).

Time on stream	S _{OME5}	S _{OME6}	S _{OME7}	S _{OME8}	S _{OME9}	S _{OME10}	S _{MeFo}	ACL
[h]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[mol _{FA} /mol _{OME}]
0.5	4.55	2.70	1.09	0.51	0.00	0.00	30.31	1.87
1.0	6.07	3.79	1.78	0.85	0.00	0.00	26.10	1.98
1.5	7.55	4.97	2.83	1.24	0.28	0.00	24.15	2.06
2.0	8.48	5.98	3.67	1.80	0.46	0.00	21.45	2.21
2.5	9.28	6.85	4.33	2.13	0.67	0.00	20.13	2.32
3.0	9.71	7.46	4.95	2.44	0.89	0.00	19.34	2.41
3.5	10.23	8.07	5.67	3.09	1.18	0.00	18.65	2.52
4.0	10.19	8.29	5.96	3.25	1.24	0.00	18.88	2.58
4.5	10.72	8.84	6.28	3.55	1.35	0.23	19.01	2.68
5.1	10.81	9.18	6.86	3.87	1.48	0.50	18.72	2.77

Time on stream	m _{Feed,total}	T _{Reactor}	X _{TRI}	X _{DME}	S _{OME1}	S _{OME2}	S _{OME3}	S _{OME4}
[h]	[g]	[°C]	[%]	[%]	[%]	[%]	[%]	[%]
0.5	500	102.2	88.47	21.97	22.16	15.15	15.64	9.48
1.0	1000	102	78.78	18.70	20.22	16.10	15.46	11.44
1.5	1500	102.1	74.45	16.43	18.12	15.24	15.80	12.36
2.0	2000	102	70.16	14.50	16.20	15.02	15.60	13.01
2.5	2500	102.1	66.70	12.65	14.70	14.63	15.46	13.15
3.0	3000	102	63.92	11.03	12.96	13.97	15.13	13.91
3.5	3500	101.7	59.98	9.56	11.62	13.38	14.64	13.99
4.0	4005	101.8	60.59	8.34	10.50	12.70	13.93	14.21
4.5	4500	101.9	58.09	7.53	9.80	12.68	13.62	14.22
5.1	5100	101.8	55.79	6.64	8.97	11.93	13.07	14.28

Table C.4: Conversion of reactants as well as selectivity to product species in continuous experiment with Feed C1 and KIT-Z80AE catalyst.

Table C.5: Conversion of reactants as well as selectivity to product species in continuous experiment with Feed C1 and KIT-Z80AE catalyst (continued).

Time on stream	S _{OME5}	S _{OME6}	S _{OME7}	S _{OME8}	S _{OME9}	S _{OME10}	S _{MeFo}	ACL
[h]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[mol _{FA} /mol _{OME}]
0.5	5.46	3.41	1.70	0.65	0.00	0.00	26.34	1.87
1.0	7.65	5.02	2.90	1.29	0.26	0.00	19.66	2.05
1.5	8.94	6.34	3.89	1.99	0.58	0.00	16.75	2.20
2.0	9.80	7.39	4.87	2.49	0.79	0.00	14.84	2.34
2.5	10.60	8.23	5.60	3.12	1.06	0.00	13.43	2.45
3.0	11.08	9.01	6.31	3.61	1.35	0.00	12.67	2.59
3.5	11.54	9.61	7.01	4.22	1.50	0.44	12.06	2.72
4.0	11.87	10.14	7.72	4.65	1.89	0.48	11.90	2.84
4.5	12.04	10.60	8.19	4.82	2.07	0.79	11.19	2.91
5.1	12.09	10.75	8.37	5.25	2.25	0.86	12.17	3.00

Time on stream	m _{Feed,total}	T _{Reactor}	X _{TRI}	X _{DME}	S _{OME1}	S _{OME2}	S _{OME3}	S _{OME4}
լոյ	เยา	[L]	[%]	[%]	[%]	[%]	[%]	[%]
1.1	1090	103.1	68.50	24.05	14.01	13.98	17.17	12.31
1.6	1640	102.9	63.25	20.94	11.83	13.57	16.94	13.17
2.2	2165	103.0	61.52	19.53	11.02	13.36	16.10	13.03
2.7	2680	103.0	57.73	17.32	10.00	12.22	16.23	13.26
3.2	3200	102.6	55.79	15.91	9.26	12.19	15.61	13.01
3.7	3730	102.6	52.51	14.15	8.57	11.10	15.40	13.04
4.3	4250	102.5	49.95	12.73	7.87	10.77	15.03	12.97
4.8	4790	102.8	47.91	11.70	7.50	10.64	14.74	12.74
5.3	5320	102.5	46.12	10.78	7.16	10.50	14.25	12.51
6.4	6394	102.2	27.66	3.13	6.16	6.58	13.35	13.03
7.4	7364	102.2	27.43	3.56	5.34	5.70	18.27	12.27
7.8	7844	102.2	25.88	2.82	4.40	5.93	12.07	12.69
8.9	8864	123.4	56.78	11.97	8.56	8.81	11.09	8.97
9.4	9364	123.4	53.48	9.84	7.21	7.34	10.52	8.89
9.9	9864	108.8	29.78	2.13	2.65	3.26	7.83	9.48
10.9	10864	102.0	23.57	1.14	2.68	2.79	6.94	8.47
2.2 2.7 3.2 3.7 4.3 4.8 5.3 6.4 7.4 7.8 8.9 9.4 9.9 10.9	2165 2680 3200 3730 4250 4790 5320 6394 7364 7844 8864 9364 9864 10864	103.0 102.6 102.6 102.5 102.8 102.5 102.2 102.2 102.2 102.2 102.2 123.4 123.4 108.8 102.0	61.52 57.73 55.79 52.51 49.95 47.91 46.12 27.66 27.43 25.88 56.78 53.48 29.78 23.57	19.53 17.32 15.91 14.15 12.73 11.70 10.78 3.13 3.56 2.82 11.97 9.84 2.13 1.14	11.02 10.00 9.26 8.57 7.87 7.50 7.16 6.16 5.34 4.40 8.56 7.21 2.65 2.68	13.36 12.22 12.19 11.10 10.77 10.64 10.50 6.58 5.70 5.93 8.81 7.34 3.26 2.79	16.10 16.23 15.61 15.40 15.03 14.74 14.25 13.35 18.27 12.07 11.09 10.52 7.83 6.94	13.03 13.26 13.01 13.04 12.97 12.74 12.51 13.03 12.27 12.69 8.97 8.89 9.48 8.47

Table C.6: Conversion of reactants as well as selectivity to product species in continuous experiment with Feed C2 and KIT-Z80PU catalyst.

Table C.7: Conversion of reactants as well as selectivity to product species in continuous experiment with Feed C2 and KIT-Z80PU catalyst (continued).

Time on stream	S _{OME5}	S _{OME6}	S _{OME7}	S _{OME8}	S _{OME9}	S _{OME10}	S _{MeFo}	ACL
[h]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[mol _{FA} /mol _{OME}]
1.1	9.66	6.92	4.22	2.25	0.59	0.00	18.90	2.40
1.6	10.95	8.54	5.33	2.86	0.65	0.11	16.07	2.59
2.2	11.46	9.24	6.09	3.17	0.74	0.17	15.63	2.68
2.7	12.00	10.02	6.90	3.44	0.86	0.25	14.81	2.80
3.2	12.13	10.49	7.54	3.53	1.05	0.27	14.93	2.87
3.7	12.59	11.12	8.11	3.63	1.21	0.29	14.95	2.97
4.3	12.90	11.63	8.65	3.71	1.31	0.39	14.78	3.05
4.8	12.97	11.88	9.05	3.66	1.41	0.42	15.00	3.10
5.3	13.01	12.14	9.12	3.63	1.58	0.45	15.65	3.14
6.4	11.93	11.44	8.77	4.10	0.52	0.00	24.13	3.26
7.4	11.66	10.76	8.49	4.10	0.98	0.00	22.42	3.33
7.8	13.18	11.83	9.14	4.82	2.02	0.29	23.63	3.58
8.9	8.13	6.30	4.25	2.00	0.44	0.15	41.30	2.61
9.4	8.18	6.56	4.81	2.38	0.81	0.25	43.04	2.79
9.9	9.79	10.19	8.39	4.83	2.46	0.83	40.28	3.96
10.9	9.44	9.82	8.09	5.69	5.27	3.21	37.60	4.21

Time on stream	m _{Feed,total}	T _{Reactor}	X _{TRI}	X _{DME}	S _{OME1}	S _{OME2}	S _{OME3}	S _{OME4}
[h]	[g]	[°C]	[%]	[%]	[%]	[%]	[%]	[%]
0.5	510	102.6	74.29	26.44	15.86	13.33	15.92	11.76
1.0	1000	102.4	67.44	23.24	13.97	13.44	16.43	12.69
1.5	1500	102.5	66.17	21.98	13.22	12.63	16.29	13.16
2.0	2000	102.3	61.20	19.66	11.71	11.69	16.97	13.17
2.5	2500	102.3	58.16	17.73	10.83	10.98	16.51	13.21
3.0	2950	102.4	54.50	15.56	9.55	9.96	16.24	13.32
4.3	4290	102.2	48.57	11.72	7.69	8.03	14.26	12.56
5.4	5400	102.1	48.67	10.15	5.72	6.51	11.94	11.05
6.4	6400	101.6	20.42	1.04	5.95	5.12	11.30	7.26
6.9	6900	101.4	17.63	0.78	4.78	5.33	8.90	7.77
7.4	7410	101.5	17.33	0.93	5.16	5.38	9.43	9.44
7.9	7900	101.5	17.51	1.13	4.98	6.04	7.70	9.11
8.4	8400	101.5	17.20	1.17	5.58	4.80	8.73	9.54
8.9	8890	122.6	51.30	11.02	6.67	9.94	11.84	11.10
9.4	9390	122.4	47.57	8.39	5.48	6.07	10.60	10.67
9.9	9900	122.4	43.93	6.63	4.55	5.19	9.58	10.04
11.4	11400	101.4	19.98	0.93	2.05	1.47	2.29	3.75

Table C.8: Conversion of reactants as well as selectivity to product species in continuous experiment with Feed C2 and KIT-Z80AE catalyst.

Table C.9: Conversion of reactants as well as selectivity to product species in continuous experiment with Feed C2 and KIT-Z80AE catalyst (continued).

Time on stream	S _{OME5}	S _{OME6}	S _{OME7}	S _{OME8}	S _{OME9}	S _{OME10}	S _{MeFo}	ACL
[h]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[mol _{FA} /mol _{OME}]
0.5	9.23	6.43	3.88	1.69	0.34	0.00	21.56	2.27
1.0	10.88	7.86	5.02	2.34	0.58	0.06	16.73	2.46
1.5	11.40	8.65	5.96	2.90	0.86	0.12	14.81	2.56
2.0	12.15	9.65	6.80	3.41	1.14	0.27	13.05	2.71
2.5	12.55	10.27	7.57	3.87	1.46	0.37	12.38	2.82
3.0	13.11	11.28	8.58	4.43	1.74	0.48	11.29	2.98
4.3	13.63	12.61	10.19	6.18	2.72	1.14	10.99	3.29
5.4	12.92	12.99	11.40	8.87	5.69	3.39	9.53	3.74
6.4	11.53	11.20	9.06	13.49	6.01	0.00	19.08	3.69
6.9	16.46	16.06	12.13	9.02	3.44	0.00	16.12	3.89
7.4	16.36	16.07	11.69	6.97	3.04	1.03	15.43	3.80
7.9	14.84	14.67	11.93	8.95	5.80	3.36	12.60	3.96
8.4	13.70	15.01	11.59	9.49	4.03	2.45	15.07	3.85
8.9	11.50	10.66	8.73	6.54	2.72	0.67	19.63	3.23
9.4	11.39	11.85	9.41	7.83	4.09	1.31	21.30	3.60
9.9	11.19	12.12	9.81	8.43	4.54	1.66	22.88	3.81
11.4	7.94	11.01	11.34	15.23	22.15	14.99	7.78	5.99

Catalyst	Run	T _{Reactor} [°C]	X _{tri} [%]	S _{ome1} [%]	S _{OME2} [%]	S _{OME3} [%]	S _{OME4} [%]
Fresh (KIT-Z80PU)	1	98	42.07	17.36	19.42	16.86	12.76
	2	100	45.74	20.07	20.27	16.43	11.85
Used (KIT-Z80PU)	1	97	1.43	15.47	17.62	14.96	12.08
	2	100	1.73	14.81	16.39	13.66	10.93
R1 (KIT-Z80PU)	1	98	1.43	16.34	18.25	15.60	12.64
	2	100	1.48	17.27	18.67	15.65	12.18
R2 (KIT-Z80PU)	1	98	31.10	17.41	21.25	17.86	12.95
	2	98	28.10	18.70	21.17	17.15	12.26
R3 (KIT-Z80PU)	1	98	32.62	15.20	18.15	16.97	13.65
	2	100	35.78	15.73	18.57	17.11	13.50

Table C.10: Conversion of TRI as well as selectivity to product species in batch experiment with Feed B1.

Table C.11: Conversion of TRI as well as selectivity to product species in batch experiment with Feed B1 (continued).

Catalyst	Run	S _{omes} [%]	S _{OME6} [%]	S _{ome7} [%]	S _{ome8} [%]	S _{OME9} [%]	S _{MeFo} [%]
Fresh (KIT-Z80PU)	1	9.33	6.57	4.43	2.74	1.30	9.23
	2	8.33	5.69	3.66	2.14	0.93	10.63
Used (KIT-Z80PU)	1	9.77	8.08	0.00	0.00	0.00	22.01
	2	9.03	7.51	6.16	0.00	0.00	21.51
R1 (KIT-Z80PU)	1	10.36	0.00	0.00	0.00	0.00	26.82
	2	9.80	0.00	0.00	0.00	0.00	26.43
R2 (KIT-Z80PU)	1	9.05	6.05	3.89	2.43	1.36	7.77
	2	8.61	5.85	3.81	2.40	1.33	8.71
R3 (KIT-Z80PU)	1	10.34	7.34	5.03	3.19	1.58	8.57
	2	10.06	7.02	4.78	3.09	1.77	8.36