

## Supplementary Information

Carbonylation of dimethoxymethane: A study on reactivity of different solid acid catalysts

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### GC Method:

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Agilent 8890

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#### **GC**

GC Summary

|               |         |
|---------------|---------|
| Run Time      | 7.6 min |
| Post Run Time | 0 min   |

#### **Oven**

|                    |           |
|--------------------|-----------|
| Equilibration Time | 0 min     |
| Max Temperature    | 240 °C    |
| (Initial)          | 40 °C     |
| Hold Time          | 2 min     |
| Post Run           | 110 °C    |
| #1 Rate            | 25 °C/min |
| #1 Value           | 180 °C    |
| #1 Hold Time       | 0 min     |

#### **ALS**

Front Injector

|                            |       |
|----------------------------|-------|
| Syringe Size               | 10 µL |
| Injection Volume           | 1 µL  |
| Solvent A Washes (PreInj)  | 5     |
| Solvent A Washes (PostInj) | 5     |
| Solvent A Volume           | 8 µL  |
| Sample Washes              | 1     |
| Sample Wash Volume         | 8 µL  |

|                             |             |
|-----------------------------|-------------|
| Sample Pumps                | 3           |
| Solvent Wash Draw Speed     | 150 µL/min  |
| Solvent Wash Dispense Speed | 6000 µL/min |
| Sample Wash Draw Speed      | 150 µL/min  |
| Sample Wash Dispense Speed  | 6000 µL/min |
| Injection Dispense Speed    | 6000 µL/min |
| Viscosity Delay             | 0 sec       |
| L1 Airgap                   | 0.2 µL      |

### Front SS Inlet He

|                   |   |
|-------------------|---|
| Mode              | Split   |
| Heater            | On 180 °C   |
| Pressure          | On 0  |
| Total Flow        | On 133.4 mL/min   |
| Septum Purge Flow | On 3 mL/min   |
| Pre-Run Flow Test | Off   |
| Gas Saver         | On 20 After 2 min mL/min  |
| Split Ratio       | 50 :1   |
| Split Flow        | 127.84 mL/min   |
| Liner             | Agilent 5190-3165: 870 µL (Split, taper, wool, low pressure drop) |

### PolyArc

|             |        |
|-------------|--------|
| Temperature |        |
| Setpoint    | On     |
| (Initial)   | 450 °C |

### Column #1

|                    |                                   |
|--------------------|-----------------------------------|
| Column Information | Agilent 123-7033UI DB-WAX Ultra I |
| Temperature Range  | 20 °C—240 °C (240 °C)             |
| Dimensions         | 30 m x 320 µm x 0.5 µm            |

|                  |                   |
|------------------|-------------------|
| In               | Front SS Inlet He |
| Out              | Aux EPC 1         |
| (Initial)        | 40 °C             |
| Pressure         | 0                 |
| Flow             | 2.5568 mL/min     |
| Average Velocity | 33.826 cm/sec     |
| Holdup Time      | 1.4781 min        |
| Control Mode     | Constant Flow     |
| (Initial)        | 2.5568 mL/min     |
| Post Run         | 1 mL/min          |

#### **Column #2**

|                    |                        |
|--------------------|------------------------|
| Column Information | Agilent FS, Deactivate |
| Temperature Range  | 20 °C—240 °C (240 °C)  |
| Dimensions         | 2.5 m x 250 µm x 0 µm  |
| Out                | Front Detector FID     |
| (Initial)          | 40 °C                  |
| Pressure           | 0                      |
| Flow               | 4 mL/min               |
| Average Velocity   | 122.56 cm/sec          |
| Holdup Time        | 0.033996 min           |
| Control Mode       | Constant Flow          |
| Setpoint           | On                     |
| (Initial)          | 4 mL/min               |
| Post Run           | 9.5407 mL/min          |

#### **Front Detector FID**

|          |               |
|----------|---------------|
| Makeup   | He            |
| Heater   | On 250 °C     |
| H2 Flow  | On 1.5 mL/min |
| Air Flow | On 350 mL/min |

|                             |                                    |
|-----------------------------|------------------------------------|
| Makeup Flow                 | On 25 mL/min                       |
| Carrier Gas Flow Correction | Constant Makeup and Fuel FlowFlame |
| Initial Baseline Minimum    | 2 pA                               |
| Initial Baseline Maximum    | 20 pA                              |
| Initial Baseline Noise      | 0.3 pA                             |
| Final Baseline Minimum      | 2 pA                               |
| Final Baseline Maximum      | 40 pA                              |
| Final Baseline Noise        | 0.6 pA                             |
| Total Peak Area             | 100 pA*sec                         |
| Maximum Peak Height         | 3 pA                               |
| Time Window Start           | 0 min                              |
| Time Window End             | 0.5333333333 min                   |

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 Column(s)  
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Column Description : DB-WAX Ultra I

Inventory# : autoID-2  
 Model# : 123-7033UI  
 Manufacturer : Agilent  
 Diameter : 320.0 µm  
 Length : 30.0 m  
 Film thickness : 0.50 µm  
 Void time : 1.478 min  
 Maximum Temperature: 240.0 °C  
 Comment :

Column Description: FS, Deactivate

Inventory# : autoID-3  
 Model# :

Manufacturer : Agilent  
Diameter : 250.0  $\mu\text{m}$   
Length : 2.5 m  
Film thickness : 0.00  $\mu\text{m}$   
Void time : 0.034 min  
Maximum Temperature: 240.0  $^{\circ}\text{C}$

**GC-MS:**

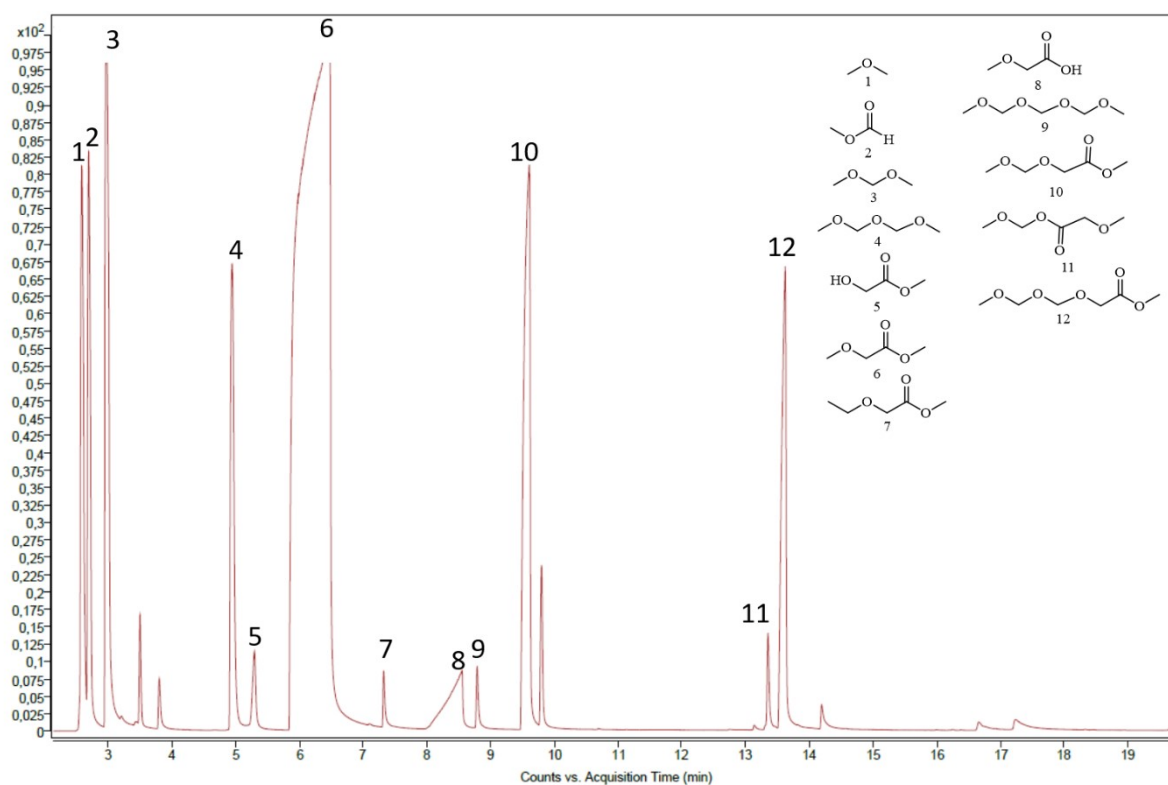
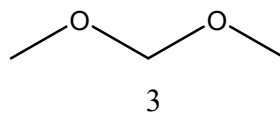
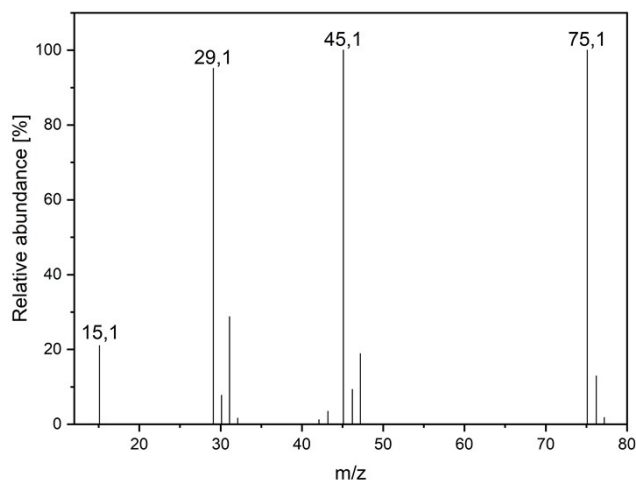
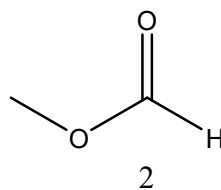
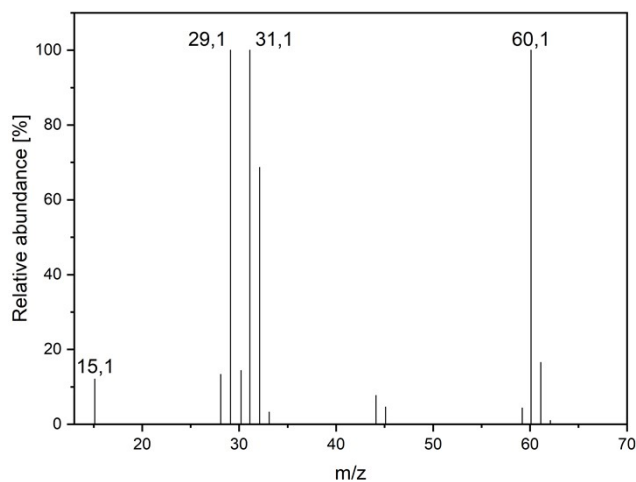
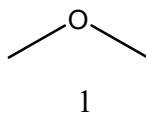
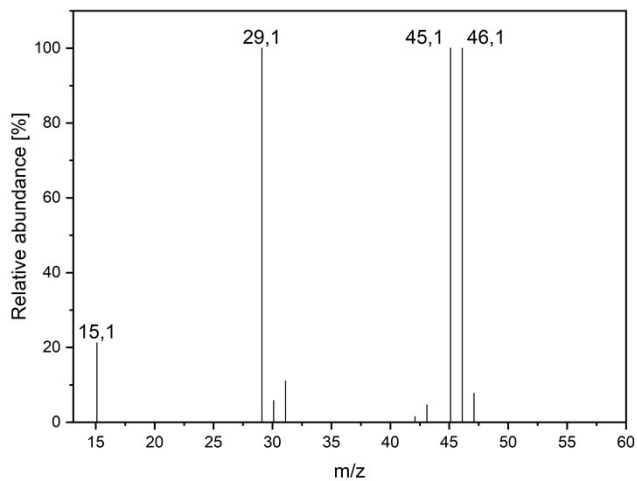
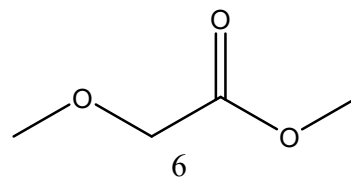
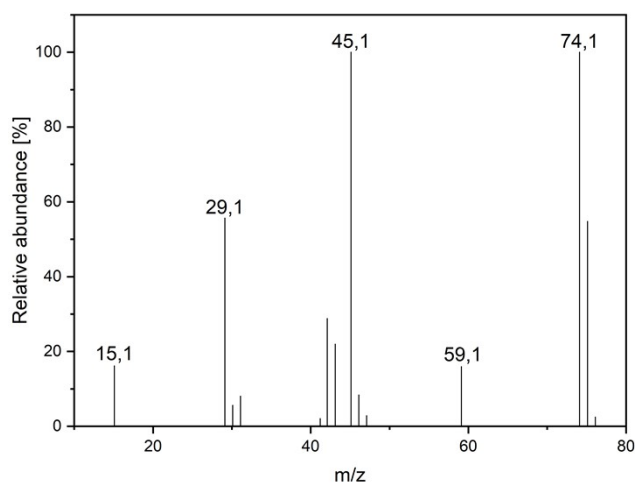
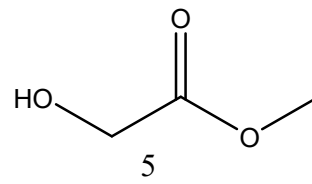
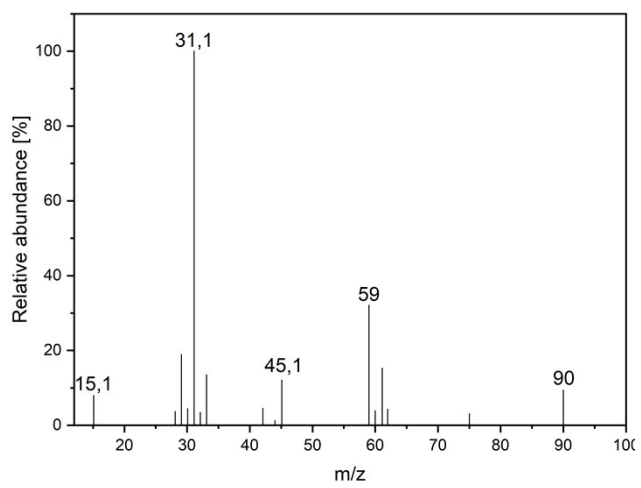
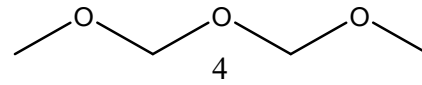
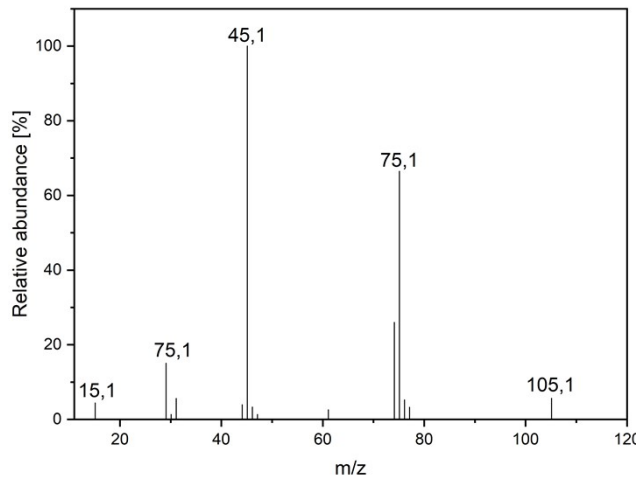
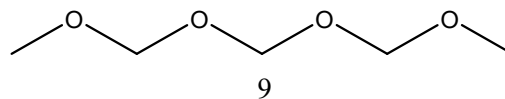
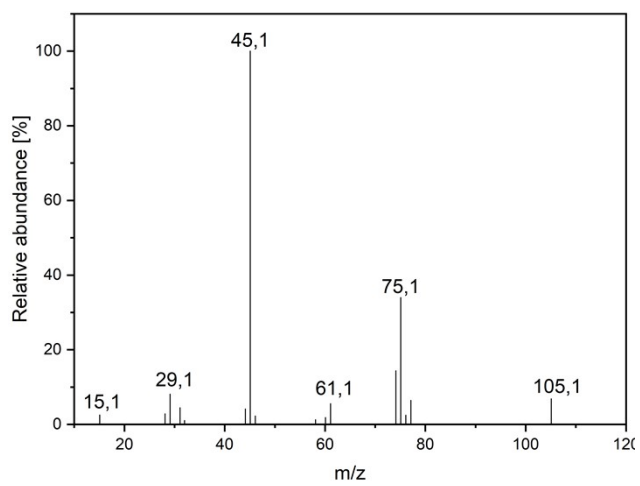
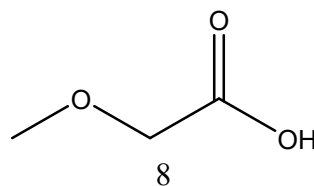
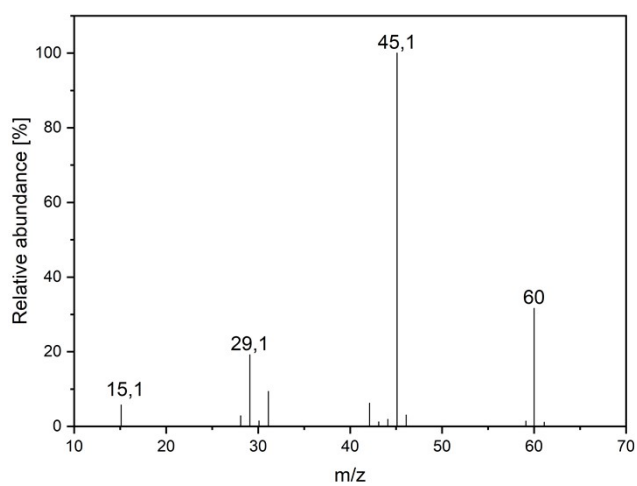
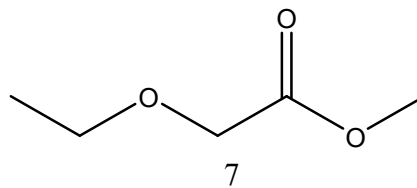
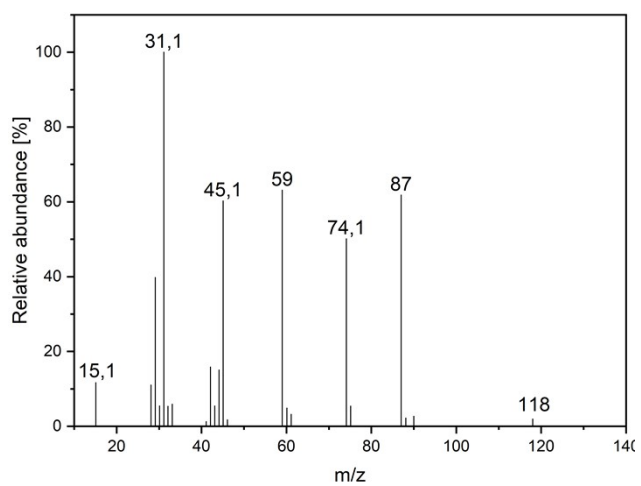


Figure S1: GC-MS Measurements of the liquid phase after the DMM Carbonylation reaction. 1 g of A36, 60 bar of CO, 110  $^{\circ}\text{C}$  and 43.0293 g of DMM.

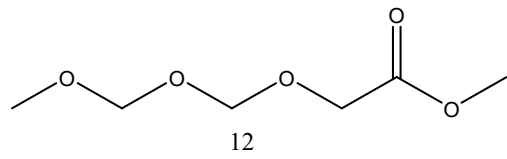
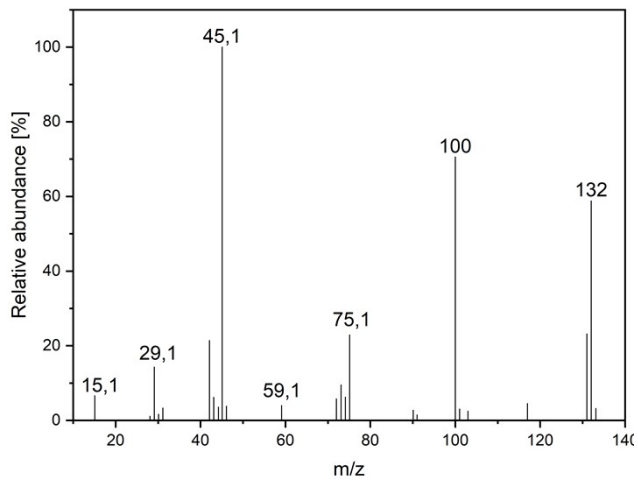
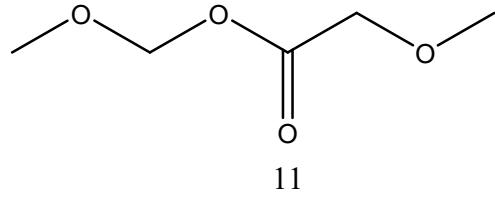
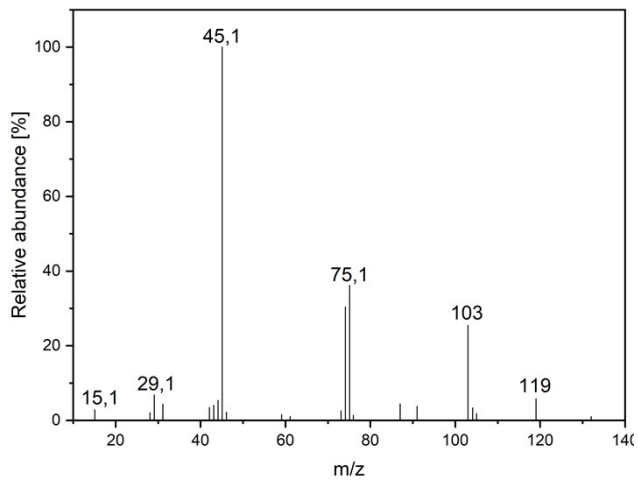
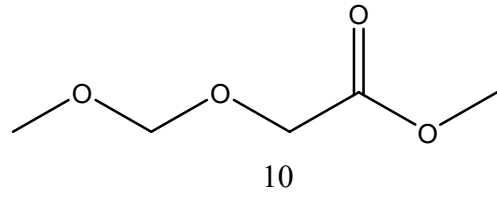
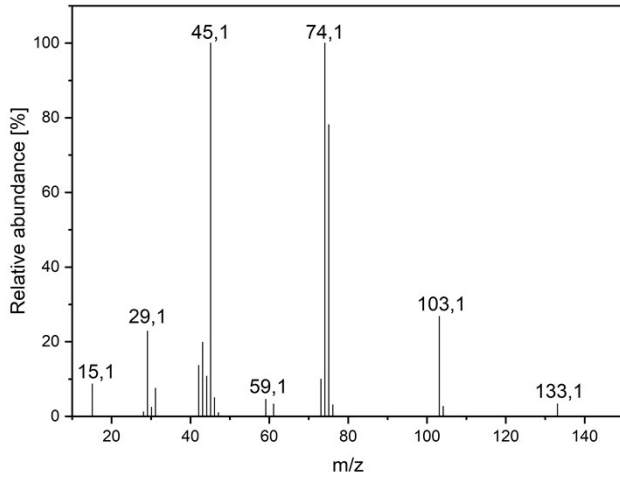
Figure S2: Fragmentation pattern for all considered compounds (1-12) measured by GC-MS. Since compounds 1, 3, 4, 9 are all acetals with the same oxymethylene repetition unit  $-CH_2O-$ , their fragmentation pattern is quite similar and often the ion peak is not detected due to fragmentation of long-chained compounds (e.g. 9). For each new oligomer with a higher chain length, there is typically a new peak with an increase of 30 g/mol due to the oxymethylene repetition unit.











### Catalytic results for catalyst screening

Table S1: Table of catalytic results for figures 4 and 6 in the main text (catalyst screening); performed at 90 °C, with 10 g of DMM, 0.5 g of catalyst powder, 55 bar of CO and 6 h of runtime.

| Catalyst | c(FA)<br>[mol·l <sup>-1</sup> ·<br>g <sub>cat</sub> <sup>-1</sup> ] | c(MeFo)<br>[mol·l <sup>-1</sup> ·<br>g <sub>cat</sub> <sup>-1</sup> ] | c(MMA)<br>[mol·l <sup>-1</sup> ·<br>g <sub>cat</sub> <sup>-1</sup> ] | c(OME-2)<br>[mol·l <sup>-1</sup> ·<br>g <sub>cat</sub> <sup>-1</sup> ] | c(OME-3)<br>[mol·l <sup>-1</sup> ·<br>g <sub>cat</sub> <sup>-1</sup> ] |
|----------|---|---|--|--|--|
| B-25     | 306.87  | 508.57  | 229.57   | 13.47  | 6.00   |
| H-Y-30   | 206.22  | 352.76  | 98.86  | 27.47  | 0.23   |
| F-20     | 248.98  | 327.22  | 84.59  | 441.51   | 9.82   |
| M-20     | 260.38  | 402.46  | 190.24   | 82.71  | 0.26   |
| Z-30     | 611.88  | 756.32  | 845.52   | 160.27   | 1.29   |
| Z-80     | 2264.59   | 446.11  | 217.86   | 52.74  | 0.12   |
| Z-280    | 443.56  | 218.47  | 215.87   | 75.46  | 0.25   |
| DX2      | 295.04  | 574.76  | 15965.40   | 198.05   | 2.27   |
| DX4      | 524.09  | 627.79  | 22791.37   | 191.51   | 3.54   |
| DX8      | 410.40  | 797.39  | 27408.61   | 224.87   | 6.28   |
| A15      | 534.83  | 600.32  | 24651.50   | 209.95   | 6.00   |
| A16      | 354.91  | 558.82  | 21326.16   | 212.17   | 5.71   |
| A36      | 534.90  | 880.82  | 40012.18   | 193.23   | 14.46  |
| A46      | 238.54  | 216.34  | 706.05   | 191.40   | 1.49   |

| Catalyst | S(FA)<br>[%] | S(MeFo)<br>[%] | S(MMA)<br>[%] | S(OME-2)<br>[%] | S(OME-3)<br>[%] | X(DMM)<br>[%] | X(CO)<br>[%] |
|----------|--------------|----------------|---------------|-----------------|-----------------|---------------|--------------|
| B-25     | 28.83        | 47.78          | 21.57         | 1.27            | 0.56            | 4.44          | 0.91         |
| H-Y-30   | 30.08        | 51.46          | 14.42         | 4.01            | 0.03            | 1.22          | 0.52         |
| F-20     | 22.39        | 29.42          | 7.61          | 39.70           | 0.88            | 4.48          | 6.54         |
| M-20     | 27.82        | 43.00          | 20.32         | 8.84            | 0.03            | 4.85          | 0.39         |
| Z-30     | 25.76        | 31.84          | 35.60         | 6.75            | 0.05            | 12.97         | 10.14        |
| Z-80     | 75.96        | 14.96          | 7.31          | 1.77            | 0.00            | 8.61          | 27.89        |
| Z-280    | 46.51        | 22.91          | 22.64         | 7.91            | 0.03            | 4.40          | 31.69        |
| DX2      | 1.73         | 3.37           | 93.72         | 1.16            | 0.01            | 25.38         | 9.45         |
| DX4      | 2.17         | 2.60           | 94.42         | 0.79            | 0.01            | 34.26         | 16.21        |
| DX8      | 1.42         | 2.76           | 95.01         | 0.78            | 0.02            | 39.06         | 21.58        |
| A15      | 2.06         | 2.31           | 94.80         | 0.81            | 0.02            | 27.43         | 16.34        |
| A16      | 1.58         | 2.49           | 94.96         | 0.94            | 0.03            | 23.36         | 14.32        |
| A36      | 1.28         | 2.12           | 96.10         | 0.46            | 0.03            | 54.84         | 26.61        |
| A46      | 17.62        | 15.98          | 52.15         | 14.14           | 0.11            | 5.95          | 2.00         |

### Effect of catalyst amount

Table S2: Table of catalytic results for figures 7 and 8 in the main text (variation of catalyst amount); performed at 110 °C, with 43 g of DMM, 60 bar of CO and 6 h of runtime for 0.5 g A36.

| Time<br>[h] | c(FA)<br>[mol·l <sup>-1</sup> ·<br>g <sub>cat</sub> <sup>-1</sup> ] | c(MeFo)<br>[mol·l <sup>-1</sup> ·<br>g <sub>cat</sub> <sup>-1</sup> ] | c(MMA)<br>[mol·l <sup>-1</sup> ·<br>g <sub>cat</sub> <sup>-1</sup> ] | c(OME-2)<br>[mol·l <sup>-1</sup> ·<br>g <sub>cat</sub> <sup>-1</sup> ] | c(OME-3)<br>[mol·l <sup>-1</sup> ·<br>g <sub>cat</sub> <sup>-1</sup> ] |
|-------------|---|---|--|--|--|
| 1           | 281.22  | 337.55  | 2756.55  | 45.15  | 0.14   |

|   |        |         |          |        |      |
|---|--------|---------|----------|--------|------|
| 2 | 222.90 | 681.68  | 10370.82 | 125.03 | 0.68 |
| 3 | 286.93 | 892.54  | 15749.45 | 187.70 | 2.08 |
| 4 | 279.78 | 975.15  | 20343.01 | 230.38 | 5.39 |
| 6 | 322.00 | 1165.35 | 27505.04 | 264.48 | 3.18 |

| Time [h] | S(FA) [%] | S(MeFo) [%] | S(MMA) [%] | S(OME-2) [%] | S(OME-3) [%] | X(DMM) [%] | X(CO) [%] |
|----------|-----------|-------------|------------|--------------|--------------|------------|-----------|
| 1        | 8.22      | 9.87        | 80.59      | 1.32         | 0.00         | 6.71       | 13.84     |
| 2        | 1.96      | 5.98        | 90.96      | 1.10         | 0.01         | 18.71      | 27.33     |
| 3        | 1.68      | 5.21        | 92.00      | 1.10         | 0.01         | 27.98      | 32.13     |
| 4        | 1.28      | 4.47        | 93.17      | 1.06         | 0.02         | 37.74      | 32.13     |
| 6        | 1.10      | 3.98        | 94.00      | 0.90         | 0.01         | 55.66      | 38.59     |

Table S3: Table of catalytic results for figures 7 and 8 in the main text (variation of catalyst amount); performed at 110 °C, with 43 g of DMM, 60 bar of CO and 6 h of runtime for 1.0 g A36.

| Time [h] | c(FA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MeFo) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MMA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-2) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-3) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] |
|----------|--|--|---|---|---|
| 1        | 81.09  | 276.99   | 2922.99   | 51.67   | 0.42  |
| 2        | 182.63   | 459.39   | 8457.78   | 114.75  | 2.05  |
| 3        | 155.50   | 510.24   | 11849.68  | 137.38  | 4.39  |
| 4        | 181.51   | 481.62   | 16043.93  | 150.16  | 6.91  |
| 6        | 167.59   | 609.88   | 19420.01  | 105.61  | 7.62  |

| Time [h] | S(FA) [%] | S(MeFo) [%] | S(MMA) [%] | S(OME-2) [%] | S(OME-3) [%] | X(DMM) [%] | X(CO) [%] |
|----------|-----------|-------------|------------|--------------|--------------|------------|-----------|
| 1        | 2.43      | 8.31        | 87.69      | 1.55         | 0.01         | 12.80      | 18.13     |
| 2        | 1.98      | 4.98        | 91.77      | 1.24         | 0.02         | 31.94      | 34.21     |
| 3        | 1.23      | 4.03        | 93.62      | 1.09         | 0.03         | 43.11      | 39.83     |
| 4        | 1.08      | 2.86        | 95.14      | 0.89         | 0.04         | 60.26      | 39.83     |
| 6        | 0.83      | 3.00        | 95.61      | 0.52         | 0.04         | 75.97      | 47.39     |

Table S4: Table of catalytic results for figures 7 and 8 in the main text (variation of catalyst amount); performed at 110 °C, with 43 g of DMM, 60 bar of CO and 6 h of runtime for 1.5 g A36.

| Time [h] | c(FA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MeFo) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MMA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-2) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-3) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] |
|----------|--|--|---|---|---|
| 1        | 72.91  | 167.37   | 1951.48   | 35.47   | 0.61  |
| 2        | 118.21   | 316.20   | 6739.98   | 90.61   | 2.10  |
| 3        | 141.25   | 365.57   | 9828.64   | 98.81   | 4.75  |
| 4        | 116.14   | 361.30   | 12186.25  | 88.50   | 5.69  |
| 6        | 104.50   | 345.26   | 12183.45  | 28.66   | 2.91  |

| Time | S(FA) | S(MeFo) | S(MMA) | S(OME-2) | S(OME-3) | X(DMM) | X(CO) |
|------|-------|---------|--------|----------|----------|--------|-------|
|------|-------|---------|--------|----------|----------|--------|-------|

| [h] | [%]  | [%]  | [%]   | [%]  | [%]  | [%]   | [%]   |
|-----|------|------|-------|------|------|-------|-------|
| 1   | 3.27 | 7.51 | 87.60 | 1.59 | 0.03 | 12.19 | 16.95 |
| 2   | 1.63 | 4.35 | 92.75 | 1.25 | 0.03 | 37.45 | 33.47 |
| 3   | 1.35 | 3.50 | 94.15 | 0.95 | 0.05 | 54.47 | 39.57 |
| 4   | 0.91 | 2.83 | 95.52 | 0.69 | 0.04 | 69.97 | 39.57 |
| 6   | 0.83 | 2.73 | 96.20 | 0.23 | 0.02 | 91.72 | 46.89 |

### Effect of temperature

Table S5: Table of catalytic results for figure 9 in the main text (temperature variation); performed with 43 g of DMM, 60 bar of CO and 3 h of runtime.

| Temperature [°C] | c(FA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MeFo) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MMA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-2) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-3) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] |
|------------------|--|--|---|---|---|
| 40               | 113.79   | 0.00   | 255.69  | 30.74   | 0.08  |
| 50               | 88.43  | 66.04  | 685.05  | 29.37   | 0.08  |
| 60               | 131.59   | 67.78  | 2231.17   | 23.89   | 0.16  |
| 110              | 165.90   | 599.20   | 16005.82  | 159.74  | 7.31  |
| 120              | 218.74   | 650.22   | 18467.46  | 115.57  | 8.29  |
| 130              | 155.68   | 794.09   | 19186.47  | 61.80   | 12.62   |
| 140              | 126.04   | 778.54   | 15735.91  | 34.71   | 1.71  |

| T [°C] | S(FA) [%] | S(MeFo) [%] | S(MMA) [%] | S(OME-2) [%] | S(OME-3) [%] | X(DMM) [%] | X(CO) [%] |
|--------|-----------|-------------|------------|--------------|--------------|------------|-----------|
| 40     | 28.43     | 0.00        | 63.87      | 7.68         | 0.02         | 1.85       | 5.01      |
| 50     | 10.18     | 7.60        | 78.83      | 3.38         | 0.01         | 7.61       | 5.24      |
| 60     | 5.36      | 2.76        | 90.90      | 0.97         | 0.01         | 7.50       | 11.62     |
| 110    | 0.98      | 3.54        | 94.50      | 0.94         | 0.04         | 51.62      | 36.68     |
| 120    | 1.12      | 3.34        | 94.90      | 0.59         | 0.04         | 79.95      | 37.94     |
| 130    | 0.77      | 3.93        | 94.93      | 0.31         | 0.06         | 89.86      | 36.37     |
| 140    | 0.76      | 4.67        | 94.36      | 0.21         | 0.01         | 93.43      | 29.49     |

Table S6: Table of catalytic results for figure 9 in the main text (temperature variation); performed with 43 g of DMM, 60 bar of CO and 6 h of runtime.

| Temperature [°C] | c(FA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MeFo) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MMA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-2) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-3) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] |
|------------------|--|--|---|---|---|
| 110              | 43.63  | 677.39   | 21165.78  | 61.82   | 2.26  |
| 120              | 55.97  | 639.20   | 21896.49  | 32.38   | 5.15  |
| 130              | 76.89  | 745.58   | 20214.32  | 9.99  | 3.00  |
| 140              | 30.85  | 906.54   | 18470.50  | 3.97  | 3.03  |

| T [°C] | S(FA) [%] | S(MeFo) [%] | S(MMA) [%] | S(OME-2) [%] | S(OME-3) [%] | X(DMM) [%] | X(CO) [%] |
|--------|-----------|-------------|------------|--------------|--------------|------------|-----------|
| 110    | 0.20      | 3.09        | 96.42      | 0.28         | 0.01         | 84.28      | 47.47     |

|     |      |      |       |      |      |       |       |
|-----|------|------|-------|------|------|-------|-------|
| 120 | 0.25 | 2.82 | 96.76 | 0.14 | 0.02 | 94.25 | 48.56 |
| 130 | 0.37 | 3.54 | 96.03 | 0.05 | 0.01 | 94.66 | 42.19 |
| 140 | 0.16 | 4.67 | 95.14 | 0.02 | 0.02 | 97.50 | 33.04 |

Table S7: Table of catalytic results for figure 9 in the main text (temperature variation); performed with 43 g of DMM, 60 bar of CO and 24 h of runtime.

| Temperature [°C] | c(FA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MeFo) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MMA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-2) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-3) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] |
|------------------|--|--|---|---|---|
| 40               | 173.62   | 46.81  | 1520.79   | 29.95   | 0.17  |
| 50               | 165.77   | 86.96  | 3789.92   | 32.99   | 0.25  |
| 60               | 280.88   | 104.48   | 9039.88   | 59.86   | 1.07  |

| T [°C] | S(FA) [%] | S(MeFo) [%] | S(MMA) [%] | S(OME-2) [%] | S(OME-3) [%] | X(DMM) [%] | X(CO) [%] |
|--------|-----------|-------------|------------|--------------|--------------|------------|-----------|
| 40     | 9.80      | 2.64        | 85.86      | 1.69         | 0.01         | 4.22       | 23.90     |
| 50     | 4.07      | 2.13        | 92.98      | 0.81         | 0.01         | 11.89      | 29.94     |
| 60     | 2.96      | 1.10        | 95.30      | 0.63         | 0.01         | 19.82      | 39.09     |

### Effect of pressure

Table S8: Table of catalytic results for figures 10 and 11 in the main text (pressure variation); performed at CO pressure of 20 bar, 110 °C, with 43 g of DMM, 1.0 g of A36 and 6 h of runtime.

| Time [h] | c(FA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MeFo) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MMA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-2) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-3) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] |
|----------|--|--|---|---|---|
| 1        | 102.47   | 171.14   | 524.09  | 27.08   | 0.41  |
| 2        | 76.55  | 452.29   | 2173.42   | 81.35   | 0.49  |
| 3        | 156.70   | 628.14   | 3451.51   | 138.85  | 1.33  |
| 4        | 142.96   | 769.23   | 4618.84   | 190.54  | 4.11  |
| 6        | 56.91  | 825.93   | 5998.88   | 225.88  | 9.34  |

| Time [h] | S(FA) [%] | S(MeFo) [%] | S(MMA) [%] | S(OME-2) [%] | S(OME-3) [%] | X(DMM) [%] | X(CO) [%] |
|----------|-----------|-------------|------------|--------------|--------------|------------|-----------|
| 1        | 12.42     | 20.74       | 63.51      | 3.28         | 0.05         | 2.72       | 16.88     |
| 2        | 2.75      | 16.25       | 78.07      | 2.92         | 0.02         | 16.86      | 29.80     |
| 3        | 3.58      | 14.35       | 78.86      | 3.17         | 0.03         | 21.25      | 38.75     |
| 4        | 2.50      | 13.43       | 80.67      | 3.33         | 0.07         | 27.34      | 45.31     |
| 6        | 0.80      | 11.61       | 84.29      | 3.17         | 0.13         | 49.44      | 53.63     |

Table S9: Table of catalytic results for figures 10 and 11 in the main text (pressure variation); performed at CO pressure of 40 bar, 110 °C, with 43 g of DMM, 1.0 g of A36 and 6 h of runtime.

| Time [h] | c(FA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MeFo) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MMA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-2) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-3) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] |
|----------|--|--|---|---|---|
|----------|--|--|---|---|---|

|   |        |        |          |        |      |
|---|--------|--------|----------|--------|------|
| 1 | 95.02  | 186.09 | 1309.11  | 40.16  | 0.25 |
| 2 | 131.68 | 388.77 | 4361.35  | 82.47  | 0.97 |
| 3 | 135.73 | 465.54 | 7426.11  | 131.75 | 2.68 |
| 4 | 109.87 | 512.09 | 9810.08  | 147.22 | 4.97 |
| 6 | 44.67  | 513.91 | 10099.69 | 130.01 | 2.77 |

| Time [h] | S(FA) [%] | S(MeFo) [%] | S(MMA) [%] | S(OME-2) [%] | S(OME-3) [%] | X(DMM) [%] | X(CO) [%] |
|----------|-----------|-------------|------------|--------------|--------------|------------|-----------|
| 1        | 5.83      | 11.41       | 80.28      | 2.46         | 0.02         | 4.00       | 17.85     |
| 2        | 2.65      | 7.83        | 87.84      | 1.66         | 0.02         | 22.73      | 30.52     |
| 3        | 1.66      | 5.70        | 90.99      | 1.61         | 0.03         | 32.39      | 38.49     |
| 4        | 1.04      | 4.84        | 92.69      | 1.39         | 0.05         | 46.27      | 45.02     |
| 6        | 0.41      | 4.76        | 93.59      | 1.20         | 0.03         | 69.43      | 52.83     |

Table S10: Table of catalytic results for figures 10 and 11 in the main text (pressure variation); performed at CO pressure of 60 bar, 110 °C, with 43 g of DMM, 1.0 g of A36 and 6 h of runtime.

| Time [h] | c(FA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MeFo) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MMA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-2) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-3) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] |
|----------|--|--|---|---|---|
| 1        | 81.09  | 276.99   | 2922.99   | 51.67   | 0.42  |
| 2        | 182.63   | 459.39   | 8457.78   | 114.75  | 2.05  |
| 3        | 155.50   | 510.24   | 11849.68  | 137.38  | 4.39  |
| 4        | 181.51   | 481.62   | 16043.93  | 150.16  | 6.91  |
| 6        | 167.59   | 609.88   | 19420.01  | 105.61  | 7.62  |

| Time [h] | S(FA) [%] | S(MeFo) [%] | S(MMA) [%] | S(OME-2) [%] | S(OME-3) [%] | X(DMM) [%] | X(CO) [%] |
|----------|-----------|-------------|------------|--------------|--------------|------------|-----------|
| 1        | 2.43      | 8.31        | 87.69      | 1.55         | 0.01         | 12.80      | 11.87     |
| 2        | 1.98      | 4.98        | 91.77      | 1.24         | 0.02         | 31.94      | 24.29     |
| 3        | 1.23      | 4.03        | 93.62      | 1.09         | 0.03         | 43.11      | 32.78     |
| 4        | 1.08      | 2.86        | 95.14      | 0.89         | 0.04         | 60.26      | 38.99     |
| 6        | 0.83      | 3.00        | 95.61      | 0.52         | 0.04         | 75.97      | 46.27     |

Table S11: Table of catalytic results for figures 10 and 11 in the main text (pressure variation); performed at CO pressure of 80 bar, 110 °C, with 43 g of DMM, 1.0 g of A36 and 6 h of runtime.

| Time [h] | c(FA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MeFo) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(MMA) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-2) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] | c(OME-3) [mol·l <sup>-1</sup> ·g <sub>cat</sub> <sup>-1</sup> ] |
|----------|--|--|---|---|---|
| 1        | 121.81   | 192.67   | 2542.05   | 43.22   | 0.23  |
| 2        | 94.83  | 322.36   | 8455.59   | 88.67   | 1.35  |
| 3        | 123.22   | 325.81   | 14411.98  | 117.87  | 4.61  |
| 4        | 148.85   | 337.86   | 18061.72  | 113.45  | 6.59  |
| 6        | 39.45  | 497.81   | 21612.66  | 55.92   | 6.31  |

| Time [h] | S(FA) [%] | S(MeFo) [%] | S(MMA) [%] | S(OME-2) [%] | S(OME-3) [%] | X(DMM) [%] | X(CO) [%] |
|----------|-----------|-------------|------------|--------------|--------------|------------|-----------|
| 1        | 4.20      | 6.64        | 87.66      | 1.49         | 0.01         | 5.59       | 8.08      |
| 2        | 1.06      | 3.60        | 94.34      | 0.99         | 0.02         | 29.97      | 18.63     |
| 3        | 0.82      | 2.17        | 96.19      | 0.79         | 0.03         | 56.75      | 25.45     |
| 4        | 0.80      | 1.81        | 96.75      | 0.61         | 0.04         | 69.47      | 30.57     |
| 6        | 0.18      | 2.24        | 97.30      | 0.25         | 0.03         | 84.91      | 36.27     |

#### **Pictures of the catalysts used in this study**



Figure S3: Picture of the zeolite catalysts used in this study. From left to right: H-Y-30, H-BEA-25, H-FER-20, H-MOR-20, H-ZSM-5-30, H-ZSM-5-80 and H-ZSM-5-280.

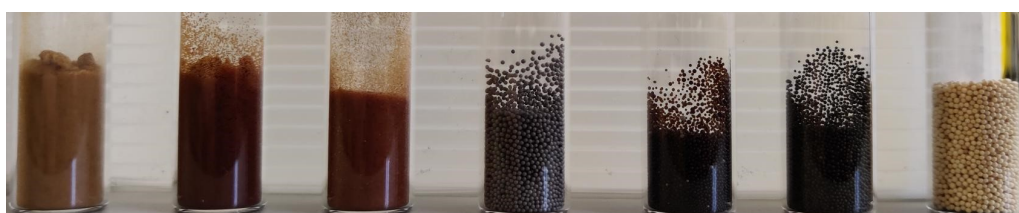


Figure S4: Picture of the ion exchange resins used in this study. From left to right: Dowex50WX2, Dowex50WX4, Dowex50WX8, Amberlyst15, Amberlyst16, Amberlyst36, Amberlyst46.

#### **Calculation of the CO-Conversion**

Because of the high pressures used in this study all calculations were done using the Van-der-Waals equation to calculate molar amounts of CO. For this the volumes of the reactors with and without the dosing line were determined.

Volumes Reactors with dosing line:

Reactor 1: 132.27 ml

Reactor 2: 132.51 ml

Reactor 3: 130.51 ml

Volume dosing line:

Reactor 1 dosing line: 15.04 ml

Reactor 2 dosing line: 16.10 ml

Reactor 3 dosing line: 15.05 ml

From integrating the flow over time diagram of the MFCs the total amount of dosed CO could be calculated. To get the total amount of CO which is able to react inside the reactor the total amount of dosed CO was subtracted from the total amount of CO in the dosing line. Dividing the total amount of CO able to react from the used CO, which was calculated by the pressure drop in the reactor the CO-Conversion was calculated.

#### **Calculation of the percentage contribution of the desorption peaks to the total NH<sub>3</sub> uptake:**

For the evaluation of the percentage contribution of the desorption peaks to the total  $\text{NH}_3$  uptake the baseline was subtracted using OriginPro. Further normalisation of the thermograms lead to the normed and baseline corrected thermograms shown in the main manuscript. The desorption peaks were deconvoluted and the area% of each peak was calculated (see Figure S5).

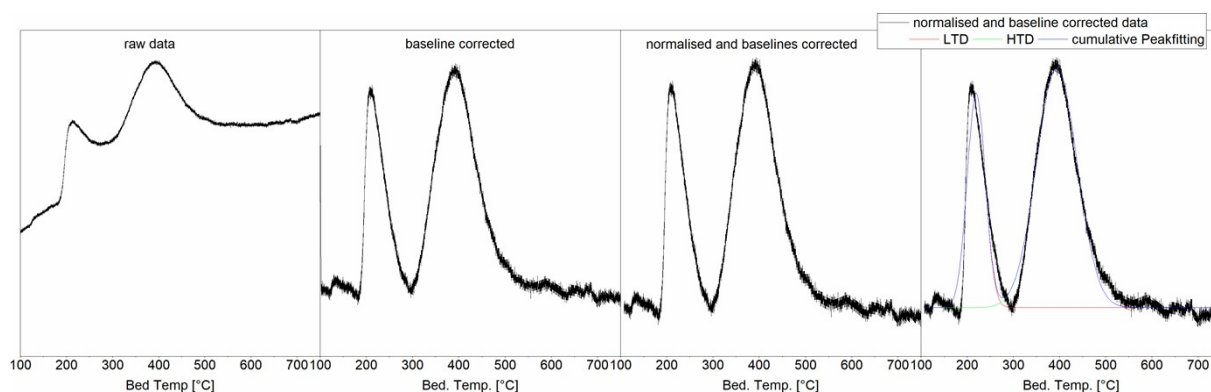


Figure S5: Exemplary evaluation step for the deconvolution of the two desorption peaks for the H-ZSM-5-80 catalyst.

### Pressure curves of the screening runs:

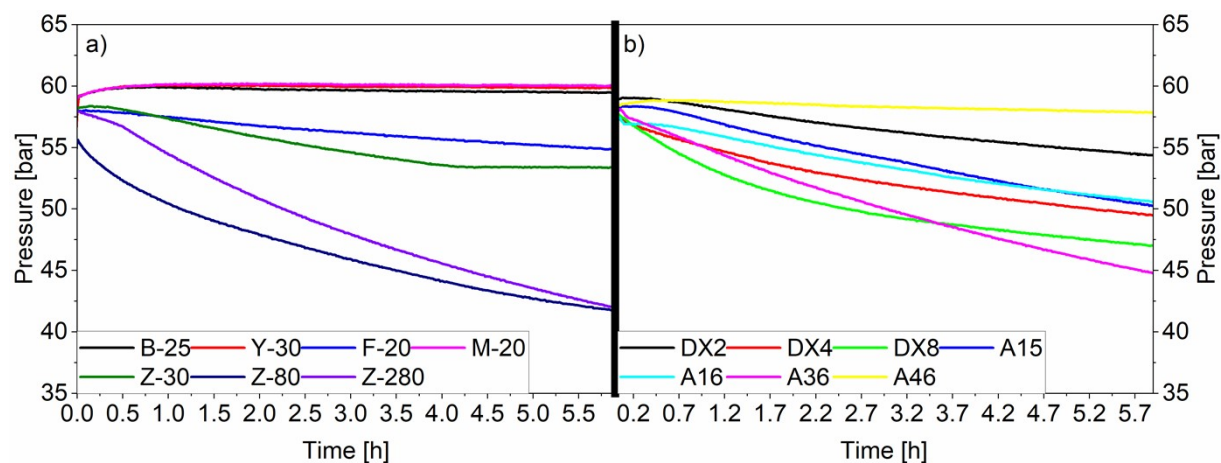


Figure S6: The pressure over time diagram for all screening runs done with all SAC. a) shows the pressure curves of the screening runs with the zeolites and b) shows the pressure curves of the screening runs with ion exchange resins.