Alkali Earth Metal Molybdates as Catalysts for the Selective Oxidation of Methanol to Formaldehyde — Selectivity, Activity, and Stability

Thrane, Joachim; Lundegaard, Lars Fahl; Beato, Pablo; Mentzel, Uffe Vie; Thorhauge, Max; Jensen, Anker Degn; Høj, Martin

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**Supplementary Material for:**

*Alkali Earth Metal Molybdates as Catalysts for the Selective Oxidation of Methanol to Formaldehyde - Selectivity, Activity and Stability*

Joachim Thrane\(^1\)*, Lars Fahl Lundegaard\(^2\), Pablo Beato\(^2\), Uffe Vie Mentzel\(^2\), Max Thorhauge\(^2\), Anker Degrn Jensen\(^1\), Martin Høj*\(^1\)

\(^1\) Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs. Lyngby, Denmark.

\(^2\) Haldor Topsøe A/S, Kgs. Lyngby, Denmark.

*mh@kt.dtu.dk

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1 **Motivation for choice of catalyst synthesis methods**

It was planned to synthesize all the alkali earth metal molybdates by the sol-gel method. However, as discussed below, the syntheses of SrMoO\(_4\) and BaMoO\(_4\) by this method resulted in low phase purity according to XRD. Hence, the co-precipitation method was used, which in contrast to the sol-gel method gave good phase purity for SrMoO\(_4\) and BaMoO\(_4\) by XRD, but the exact Mo:M ratios were difficult to control. For SrMoO\(_4\) and BaMoO\(_4\) slightly over stoichiometric
Mo:M ratios were achieved, but for CaMoO$_4$ the co-precipitation method gave under stoichiometric Mo:Ca ratio with poor selectivity for formaldehyde in the catalytic activity and selectivity test. MgMoO$_4$ was not possible to precipitate under the employed conditions.

The full XRD and BET characterizations and activity measurements on both the phase pure and the non-phase pure catalysts are disclosed in this supplementary material.

## 2 Characterization by XRD

In the following, XRD results for all the prepared catalysts as function of preparation method, Mo:M ratio and calcination temperature are given. As can be seen from Table S1 and Figure S1, MgMoO$_4$ was formed by calcination already at 400°C. Increasing the temperature sintered the material somewhat.

**Table S1. Relative amounts of phases in wt.% and the crystallite size in Å found by XRD for the fresh MgMoO$_4$ samples prepared by sol-gel synthesis after calcination at 400°C and 500°C.**

| Mo:Mg   | 1.1     | 1.0     |
|---------|---------|---------|
| T$_{calc}$ | 400°C | 500°C | 400°C | 500°C |
| MoO$_3$  | [wt%]  |   -   | 2.4   |   -   |   -   |
|         | [Å]    |   -   | 300   |   -   |   -   |
| Mo$_3$O$_9$·H$_2$O | [wt%] | 2.3   | 2.0   |   -   |   -   |
|         | [Å]    | 50    | 50    |   -   |   -   |
| MgMoO$_4$ | [wt%] | 97.7  | 95.5  | 100   | 100   |
|         | [Å]    | 133   | 100   | 105   | 211   |
Figure S1. XRD of the fresh MgMoO₄ samples prepared by sol-gel synthesis after calcination at 400°C and 500°C.

CaMoO₄ was, as for the MgMoO₄, formed after calcination at 400°C (Table S2, Figure S2). The co-precipitated CaMoO₄ sample was found by ICP to have a substoichiometric ratio of Mo:Ca = 0.90, however no Ca phases, e.g. CaO, Ca(OH)₂, CaCO₃, were found by XRD.

Table S2. Relative amounts of phases in wt.% and the crystallite size in Å found by XRD for the fresh CaMoO₄ samples prepared by sol-gel synthesis and co-precipitation after calcination at 400°C and 500°C.

| Mo:Ca | 1.1 | 1.0 | 0.9* |
|-------|-----|-----|------|
|       | 400°C | 500°C | 400°C | 500°C | 400°C | 500°C |
| MoO₃  | [wt%] |       | [Å]  |       | [Å]  |       |
|       | 3.5   | 5.1   | 682  | 747   | -    | -    |
| CaMoO₄| [wt%] | 96.4  | 94.9 | 547   | 977  | 260  |
|       | [Å]   | 100   | 100  | 415   | 173  | 335  |

* found by ICP-OES.
Figure S2. XRD of the fresh CaMoO₄ samples prepared by sol-gel synthesis and co-precipitation after calcination at 400°C and 500°C.
SrMoO$_4$ was difficult to form, as calcination temperatures of 600°C was needed to get only SrMoO$_4$ and MoO$_3$ by XRD for the samples prepared by the sol-gel method (Table S3 and Figure S3), possibly arising from an inhomogeneous solid formed by sol-gel. In contrast, SrMoO$_4$ was readily formed after calcination at 400°C from the co-precipitated sample.

**Table S3. Relative amounts of phases in wt.% and the crystallite size in Å found by XRD for the fresh SrMoO$_4$ samples prepared by sol-gel synthesis and co-precipitation after calcination at 400°C, 500°C and 600°C.**

| Mo:Sr   | T$_{calc}$ | 400°C | 500°C | 600°C | 400°C | 500°C | 600°C | 400°C | 500°C |
|---------|------------|-------|-------|-------|-------|-------|-------|-------|-------|
| MoO$_3$ (orthorhombic) | [wt%]       | 18.7  | -     | 0.7   | 16.4  | -     | -     | -     | -     |
|         | [Å]        | 394   | -     | 2892  | 565   | -     | -     | -     | -     |
| MoO$_3$ (monoclinic) | [wt%]       | 16.1  | 7.1   | 4.9   | 18.7  | 3.3   | -     | -     | 2.5   |
|         | [Å]        | 579   | 680   | 1161  | 660   | 810   | -     | -     | 518   |
| SrCO$_3$ | [wt%]       | -     | 6.7   | -     | -     | 4.4   | -     | -     | -     |
|         | [Å]        | -     | 475   | -     | -     | 418   | -     | -     | -     |
| Sr(NO$_3$)$_2$ | [wt%]       | 46.4  | 1.8   | -     | 45.4  | -     | -     | -     | -     |
|         | [Å]        | 2202  | 1633  | -     | 2396  | -     | -     | -     | -     |
| Sr$_{11}$Mo$_4$O$_{23}$ | [wt%]       | -     | 3     | -     | -     | 1.8   | -     | -     | -     |
|         | [Å]        | -     | 599   | -     | -     | 533   | -     | -     | -     |
| SrMoO$_3$ | [wt%]       | -     | 0.3   | -     | -     | -     | -     | -     | -     |
|         | [Å]        | -     | 1093  | -     | -     | -     | -     | -     | -     |
| SrMoO$_4$ | [wt%]       | 18.7  | 81.1  | 94.4  | 19.4  | 90.5  | 100   | 100   | 97.5  |
|         | [Å]        | 389   | 1106  | 2091  | 421   | 1197  | 2601  | 618   | 1777  |

* found by ICP-OES.
Figure S3. XRD of the fresh SrMoO$_4$ samples prepared by sol-gel synthesis and co-precipitation after calcination at 400°C, 500°C and 600°C.
For the BaMoO₄ samples, the pure phases were difficult to obtain by sol-gel synthesis (Table S4, Figure S4). Many phases were observed (including non-decomposed precursor material), uncertain phases and non-identified phases. BaMoO₄ was, as for SrMoO₄, readily formed by the co-precipitation route.

Table S4. Relative amounts of phases in wt.% and the crystallite size in Å found by XRD for the fresh BaMoO₄ samples prepared by sol-gel synthesis and co-precipitation after calcination at 400°C, 500°C and 600°C. The quantification of phases is in general uncertain due to the presence of non-identified phases.

| Mo:Ba | 1.1 | 1.0 | 1.12* |
|-------|-----|-----|-------|
|       | 400°C | 500°C | 600°C | 400°C | 500°C | 600°C | 400°C | 500°C |
| MoO₃ (ortho) | [wt%] | 55.6 | - | - | 18.7 | / | - | - | - |
|         | [Å] | 375 | - | - | 660 | 516 | - | - | - |
| MoO₃ (mono) | [wt%] | - | - | - | - | / | 0.9 | - | - |
|         | [Å] | - | - | - | - | / | 1442 | - | - |
| BaCO₃ | [wt%] | 0.7 | 3.7 | 2.5 | 0.5 | - | - | - | - |
|         | [Å] | 445 | 515 | 631 | 459 | - | 1.9 | - | - |
| Ba(NO₃)₂ | [wt%] | 25.6 | 1.2 | - | 25.2 | - | 550 | - | - |
|         | [Å] | 2385 | 1201 | - | 2359 | - | - | - | - |
| BaMo₃O₁₀ | [wt%] | - | 16.6 | 5.5 | - | / | - | - | 4.7 |
|         | [Å] | - | 500 | 1733 | - | / | - | - | 400 |
| BaO₂ | [wt%] | - | - | - | 7.5 | - | - | - | - |
|         | [Å] | - | 257 | - | - | - | - | - | - |
| BaO | [wt%] | 0.9 | 0.3 | 0.6 | - | / | 0 | - | - |
|         | [Å] | 1093 | 610 | - | 599 | 417 | - | - | - |
| BaMoO₃ | [wt%] | - | - | 1.1 | - | / | 0.6 | - | - |
|         | [Å] | - | 873 | - | / | 279 | - | - | - |
| BaMoO₄ | [wt%] | 17.2 | 78.5 | 90.3 | 11.5 | / | 96.6 | 100 | 95.3 |
|         | [Å] | 759 | 1171 | 1632 | 1148 | 508 | 1716 | 873 | 2054 |

* found by ICP-OES. / quantification was not possible
Figure S4. XRD of the fresh BaMoO$_4$ samples prepared by sol-gel synthesis and co-precipitation after calcination at 400°C, 500°C and 600°C.
3 Characterization by BET

Increasing calcination temperature was found to decrease the surface area (Table S5).

Table S5. Overview of BET surface areas measured on the alkali earth metal molybdate catalysts prepared dependent on calcination temperature.

| M      | Method | Mo:M | SSA [m²/g] |
|--------|--------|------|------------|
|        |        |      | 400°C  | 500°C  | 600°C |
| Mg     | Sol-Gel| 1.1  | 66.1    | 33.0    | -     |
| Mg     | Sol-Gel| 1.0  | 71.8    | 45.3    | -     |
| Ca     | Sol-Gel| 1.1  | 24.0    | 13.1    | -     |
| Ca     | Sol-Gel| 1.0  | 39.6    | 34.4    | -     |
| Ca     | Co-prec| 0.90*| 30.2    | 11.3    | -     |
| Sr     | Sol-Gel| 1.1  | 5.3     | 3.7     | 1.2   |
| Sr     | Sol-Gel| 1.0  | 5.7     | 6.0     | 2.1   |
| Sr     | Co-prec| 1.20*| 9.7     | 3.1     | -     |
| Ba     | Sol-Gel| 1.1  | -       | -       | 0.9   |
| Ba     | Sol-Gel| 1.0  | -       | -       | 0.8   |
| Ba     | Co-prec| 1.12*| 3.9     | 1.2     | -     |

* found by ICP-OES.

4 Activity Tests

All activity and selectivity data for the catalysts calcined at 400 and 500°C are given in Table S6 to Table S9 and Figure S5 to Figure S6. The trends of selectivity and activity as function of temperature were very similar irrespective of calcination at 400°C or 500°C. The main difference was the conversion due to the difference in surface area. The samples calcined at 500°C were used for the further investigation (up to 100 h on stream) to decrease the effect of sintering during the long measurements. The Arrhenius plots all gave good correlations with R² >0.99.
Table S6. Conversions and selectivities of the “phase pure” catalyst samples calcined at 500°C at 250°C, 300°C, 350°C and 400°C with a flow of 150 NmL/min with MeOH/O₂/N₂ = 5/10/85 molar ratio over a bed of 25 mg catalyst (150-250 μm) diluted in 150 mg SiC.

| Mo:M | Tsp [°C] | k [L/(m²s)] | X [%] | Xcor [%] | Scor [%] | Si [%] | CH₃O | DME | DMM | MF | CO | CO₂ |
|------|----------|-------------|-------|----------|---------|-------|-------|-----|-----|----|----|----|-----|
| MgMoO₄ | 1.0 | 250 | 2.14×10⁻³ | 0.6 | 0.6 | 96.6 | 96.6 | 0.0 | 0.0 | 2.3 | 0.0 | 1.1 |
| | 300 | 1.08×10⁻³ | 2.6 | 2.3 | 97.6 | 87.5 | 5.0 | 5.3 | 1.7 | 0.0 | 0.5 |
| | 350 | 4.24×10⁻⁴ | 9.1 | 8.0 | 95.9 | 84.5 | 6.8 | 4.9 | 2.6 | 0.6 | 0.5 |
| | 400 | 1.61×10⁻³ | 28.6 | 26.7 | 94.3 | 87.2 | 3.9 | 3.5 | 0.9 | 3.3 | 1.1 |
| | 1.1 | 250 | 1.43×10⁻³ | 2.7 | 1.9 | 99.0 | 61.2 | 7.1 | 31.0 | 0.0 | 0.0 | 0.7 |
| | 300 | 9.51×10⁻⁴ | 15.2 | 11.6 | 99.3 | 67.3 | 6.0 | 26.1 | 0.4 | 0.0 | 0.1 |
| | 350 | 4.07×10⁻⁴ | 48.0 | 40.1 | 99.1 | 76.5 | 3.6 | 19.1 | 0.3 | 0.4 | 0.1 |
| | 400 | 1.04×10⁻² | 78.7 | 75.0 | 97.6 | 91.5 | 1.6 | 4.7 | 0.1 | 2.1 | 0.1 |
| CaMoO₄ | 1.0 | 250 | 2.34×10⁻³ | 0.5 | 0.4 | 90.5 | 53.5 | 0.0 | 39.5 | 0.0 | 0.0 | 7.0 |
| | 300 | 9.23×10⁻³ | 1.7 | 1.3 | 83.5 | 56.7 | 5.4 | 25.1 | 8.3 | 0.0 | 4.5 |
| | 350 | 4.28×10⁻⁴ | 7.2 | 5.6 | 87.5 | 62.8 | 2.6 | 24.4 | 6.2 | 1.0 | 2.9 |
| | 400 | 1.94×10⁻³ | 27.0 | 22.5 | 83.5 | 63.0 | 1.8 | 21.2 | 1.6 | 7.5 | 4.7 |
| | 1.1 | 250 | 1.66×10⁻⁴ | 1.3 | 0.9 | 98.8 | 54.4 | 18.7 | 26.2 | 0.0 | 0.0 | 0.8 |
| | 300 | 9.02×10⁻⁴ | 6.5 | 4.8 | 99.7 | 69.5 | 15.9 | 14.4 | 0.0 | 0.0 | 0.2 |
| | 350 | 4.12×10⁻⁴ | 24.6 | 20.8 | 99.2 | 81.1 | 8.5 | 9.8 | 0.4 | 0.2 | 0.1 |
| | 400 | 1.41×10⁻⁴ | 59.5 | 55.3 | 98.5 | 90.1 | 3.6 | 4.9 | 0.3 | 1.0 | 0.1 |
| | 0.9* | 250 | 8.39×10⁻³ | 0.6 | 0.4 | 86.4 | 55.5 | 0.0 | 34.0 | 4.0 | 0.0 | 6.5 |
| | 300 | 2.38×10⁻⁴ | 1.5 | 0.9 | 87.2 | 45.7 | 2.2 | 43.2 | 2.8 | 0.0 | 6.1 |
| | 350 | 5.85×10⁻⁴ | 3.4 | 44.2 | 2.3 | 45.1 | 2.4 | 41.4 | 2.9 | 1.1 | 7 |
| | 400 | 1.53×10⁻³ | 8.1 | 81.6 | 46.8 | 1.5 | 36.2 | 1.5 | 2.2 | 10 |
| SrMoO₄ | 1.20* | 250 | 1.40×10⁻⁴ | 0.2 | 0.2 | 100.0 | 56.5 | 17.7 | 25.8 | 0.0 | 0.0 | 0.0 |
| | 300 | 8.05×10⁻⁵ | 1.3 | 1.1 | 96.3 | 73.6 | 8.2 | 15.2 | 1.3 | 0.9 | 0.9 |
| | 350 | 2.96×10⁻⁵ | 4.4 | 3.7 | 98.7 | 80.0 | 6.3 | 12.5 | 0.5 | 0.3 | 0.4 |
| | 400 | 8.23×10⁻⁵ | 10.9 | 9.8 | 98.2 | 84.9 | 1.8 | 11.6 | 1.1 | 0.3 | 0.3 |
| BaMoO₄ | 1.12* | 250 | 1.03×10⁻⁴ | 0.1 | 0.1 | 81.5 | 81.5 | 0.0 | 0.0 | 0.0 | 0.0 | 18.5 |
| | 300 | 6.20×10⁻⁵ | 0.4 | 0.4 | 91.4 | 85.0 | 7.0 | 0.0 | 4.8 | 0.0 | 3.3 |
| | 350 | 4.57×10⁻⁵ | 2.7 | 2.5 | 98.3 | 88.8 | 2.4 | 7.3 | 0.4 | 0.5 | 0.7 |
| | 400 | 1.35×10⁻² | 7.3 | 7.0 | 99.3 | 92.3 | 1.3 | 5.8 | 0.0 | 0.2 | 0.4 |

* found by ICP-OES.
Figure S5. Arrhenius plot for “phase pure” samples calcined at 500°C.

Table S7. Activation energies and pre-exponential factors calculated from the Arrhenius equation for “phase pure” samples calcined at 500°C.

|          | \( E_a \) [kJ/mol] | \( k_0 \) [L/(m^2s)] |
|----------|-------------------|----------------------|
| Mo:Mg = 1.0 | 83.8              | 4.85 \times 10^3     |
| Mo:Mg = 1.1 | 84.4              | 4.23 \times 10^4     |
| Mo:Ca = 1.0 | 86.1              | 7.90 \times 10^3     |
| Mo:Ca = 1.1 | 87.0              | 7.96 \times 10^4     |
| Mo:Ca = 0.9 | 56.1              | 3.22 \times 10^4     |
| Mo:Sr = 1.20 | 79.6              | 1.32 \times 10^4     |
| Mo:Ba = 1.12 | 97.6              | 5.60 \times 10^5     |
Table S8. Conversions and selectivities of the “phase pure” catalyst samples calcined at 400°C at 250°C, 300°C, 350°C and 400°C with a flow of 150 NmL/min with MeOH/O₂/N₂ = 5/10/85 molar ratio over a bed of 25 mg catalyst (150-250 µm) diluted in 150 mg SiC.

| Mo:M | Tsp [°C] | k [L/(m²s)] | X [%] | Xcor [%] | Scor [%] | Si [%] | CH₂O | DME | DMM | MF | CO | CO₂ |
|------|---------|-------------|-------|----------|----------|--------|-------|-----|-----|----|----|----|
| 1.0  | 250     | 1.06·10⁻²  | 0.8   | 0.6      | 95.7     | 67.4   | 7.4   | 21.8| 0.0 | 0.0 | 3.4 |
|      | 300     | 6.58·10⁻³  | 4.9   | 4.2      | 95.3     | 77.5   | 3.9   | 14.5| 2.0 | 0.1 | 1.9 |
|      | 350     | 2.85·10⁻³  | 22.1  | 20.2     | 96.0     | 86.5   | 3.5   | 6.3 | 1.4 | 1.0 | 1.3 |
|      | 400     | 9.08·10⁻⁴  | 58.4  | 56.2     | 93.8     | 89.7   | 2.1   | 2.2 | 0.2 | 4.7 | 1.1 |
| 1.1  | 250     | 1.86·10⁻³  | 4.0   | 3.3      | 99.7     | 74.9   | 7.4   | 17.4| 0.0 | 0.0 | 0.2 |
|      | 300     | 1.29·10⁻³  | 20.9  | 19.3     | 98.8     | 90.4   | 4.9   | 3.6 | 0.6 | 0.4 | 0.1 |
|      | 350     | 6.86·10⁻⁴  | 61.0  | 58.4     | 98.2     | 93.7   | 3.0   | 1.6 | 0.3 | 1.4 | 0.0 |
|      | 400     | 2.58·10⁻⁴  | 93.9  | 92.4     | 95.7     | 94.3   | 1.4   | 0.2 | 0.1 | 4.0 | 0.1 |
| 1.0  | 250     | 1.30·10⁻⁴  | 0.3   | 0.3      | 70.3     | 66.5   | 5.4   | 0.0 | 16.6| 0.0 | 11.5|
|      | 300     | 1.12·10⁻⁴  | 2.5   | 2.1      | 87.9     | 73.7   | 4.6   | 11.0| 7.2 | 0.4 | 3.1 |
|      | 350     | 6.23·10⁻⁴  | 12.4  | 10.9     | 88.6     | 77.5   | 3.8   | 8.4 | 5.5 | 1.8 | 3.0 |
|      | 400     | 2.99·10⁻⁴  | 44.5  | 42.0     | 82.6     | 76.7   | 2.0   | 4.7 | 0.8 | 10.7| 5.0 |
| 1.1  | 250     | 2.19·10⁻⁴  | 3.3   | 1.8      | 98.3     | 41.9   | 19.1  | 38.0| 0.0 | 0.0 | 0.9 |
|      | 300     | 1.30·10⁻⁴  | 16.7  | 11.5     | 99.2     | 59.9   | 13.9  | 25.6| 0.3 | 0.0 | 0.2 |
|      | 350     | 5.81·10⁻⁴  | 53.0  | 43.7     | 99.1     | 77.0   | 7.5   | 14.7| 0.3 | 0.3 | 0.1 |
|      | 400     | 1.81·10⁻⁴  | 88.7  | 85.5     | 97.4     | 93.5   | 2.7   | 1.3 | 0.1 | 2.2 | 0.1 |
| 0.9* | 250     | 2.81·10⁻⁵  | 0.5   | 0.3      | 80.0     | 45.1   | 1.4   | 39  | 4.3 | 0.0 | 10.3|
|      | 300     | 7.88·10⁻⁵  | 1.3   | 0.9      | 78.3     | 47.1   | 3.2   | 33.5| 6.4 | 2.3 | 7.5 |
|      | 350     | 2.22·10⁻⁴  | 3.2   | 2.5      | 82.5     | 54.6   | 2.5   | 29.2| 1.7 | 3.5 | 8.4 |
|      | 400     | 5.37·10⁻⁴  | 7.1   | 5.5      | 72.3     | 46.7   | 2.8   | 28.9| 1.5 | 7.9 | 12.1|
| 1.20*| 250     | 1.80·10⁻⁴  | 1.0   | 0.7      | 98.4     | 64.8   | 11.1  | 22.9| 0.0 | 0.0 | 1.2 |
|      | 300     | 8.36·10⁻⁴  | 4.1   | 3.2      | 99.1     | 70.3   | 11.2  | 17.7| 0.4 | 0.0 | 0.3 |
|      | 350     | 4.50·10⁻⁴  | 18.8  | 15.9     | 99.4     | 79.6   | 5.9   | 14.0| 0.3 | 0.1 | 0.1 |
|      | 400     | 2.02·10⁻²  | 58.1  | 52.9     | 99.2     | 87.4   | 2.7   | 9.2 | 0.2 | 0.5 | 0.0 |
| 1.12*| 250     | 1.99·10⁻⁴  | 0.5   | 0.3      | 94.4     | 51.6   | 0.0   | 44.4| 0.0 | 0.0 | 4.0 |
|      | 300     | 7.84·10⁻⁴  | 1.7   | 1.2      | 98.0     | 54.4   | 3.4   | 40.9| 0.0 | 0.0 | 1.4 |
|      | 350     | 3.10·10⁻⁴  | 6.0   | 4.4      | 98.8     | 60.6   | 1.1   | 37.3| 0.3 | 0.0 | 0.6 |
|      | 400     | 1.05·10⁻²  | 17.8  | 13.1     | 98.9     | 60.7   | 0.6   | 37.8| 0.3 | 0.2 | 0.4 |

* found by ICP-OES.
Figure S6. Arrhenius plot for “phase pure” samples calcined at 400°C.

Table S9. Activation energies and pre-exponential factors calculated from the Arrhenius equation for “phase pure” samples calcined at 400°C.

|               | $E_a$ [kJ/mol] | $k_0$ [L/(m$^2$s)] |
|---------------|----------------|---------------------|
| Mo:Mg = 1.0   | 87.1           | 5.42·10$^4$         |
| Mo:Mg = 1.1   | 96.6           | 8.31·10$^4$         |
| Mo:Ca = 1.0   | 105.7          | 4.70·10$^5$         |
| Mo:Ca = 1.1   | 86.6           | 9.94·10$^4$         |
| Mo:Ca = 0.9   | 57.8           | 1.57·10$^4$         |
| Mo:Sr = 1.20  | 92.4           | 2.67·10$^3$         |
| Mo:Ba = 1.12  | 77.5           | 1.02·10$^4$         |
Table S10. Conversions and selectivities of the SrMoO$_4$ catalyst samples prepared by sol-gel synthesis at 250°C, 300°C, 350°C and 400°C with a flow of 150 NmL/min with MeOH/O$_2$/N$_2$ = 5/10/85 molar ratio over a bed of 25 mg catalyst (150-250 µm) diluted in 150 mg SiC.

| Type, Mo:M | T$_{calc}$ | T$_{sp}$ | k | X | X$_{cor}$ | S$_{cor}$ | Si [%] |
|------------|------------|----------|---|---|-----------|----------|--------|
|            | [°C]       | [°C]     | [L/(m$^2$)] | [%] | [%]       |           |        |
|            |            |          |               |     |           | CH$_2$O | DME | DMM | MF | CO | CO$_2$ |
| SrMoO$_4$, 1.0 | 400        | 250      | 2.17·10$^{-4}$ | 0.6 | 0.4       | 97.6     | 56.2  | 11.2 | 31  | 0.0 | 0.0 | 1.6 |
|            |            | 300      | 1.52·10$^{-3}$ | 4.1 | 2.7       | 91.4     | 51.2  | 8.8  | 34.1 | 5.7 | 0.0 | 0.2 |
|            |            | 350      | 5.45·10$^{-3}$ | 13  | 9.5       | 99.2     | 63.4  | 8.1  | 27.9 | 0.5 | 0.0 | 0.1 |
|            |            | 400      | 1.95·10$^{-2}$ | 37.3| 29.7      | 99.3     | 70.9  | 3.5  | 25   | 0.3 | 0.2 | 0.1 |
|            | 500        | 250      | 1.30·10$^{-4}$ | 0.4 | 0.3       | 95.4     | 86.1  | 9.7  | 0.0  | 0.0 | 0.0 | 4.2 |
|            |            | 300      | 1.10·10$^{-3}$ | 2.8 | 1.7       | 98.6     | 45.2  | 9.1  | 44.8 | 0.0 | 0.0 | 0.9 |
|            |            | 350      | 4.48·10$^{-3}$ | 10.2| 6.3       | 99.3     | 46.7  | 7.0  | 45.9 | 0.2 | 0.0 | 0.2 |
|            |            | 400      | 1.69·10$^{-2}$ | 31.4| 22.2      | 98.9     | 57.0  | 2.8  | 39.4 | 0.5 | 0.1 | 0.2 |
|            | 600        | 250      | 2.05·10$^{-4}$ | 0.2 | 0.16      | 83.1     | 38.3  | 0.0  | 50.4 | 2.5 | 0.0 | 8.8 |
|            |            | 300      | 5.62·10$^{-4}$ | 0.6 | 0.38      | 90.4     | 38.3  | 2.5  | 53.2 | 1.0 | 1.6 | 3.4 |
|            |            | 350      | 1.69·10$^{-3}$ | 1.7 | 1.04      | 94.8     | 41.5  | 3.6  | 51.6 | 1.5 | 0.3 | 1.5 |
|            |            | 400      | 5.74·10$^{-3}$ | 5.2 | 3.23      | 96.3     | 42.0  | 2.4  | 53.3 | 1.0 | 0.3 | 1.0 |
| SrMoO$_4$, 1.1 | 400        | 250      | 1.72·10$^{-4}$ | 0.5 | 0.3       | 96.4     | 50.8  | 11.9 | 34.9 | 0.0 | 0.0 | 2.3 |
|            |            | 300      | 1.26·10$^{-3}$ | 3.4 | 2.2       | 99.2     | 54.4  | 9.4  | 35.7 | 0.0 | 0.0 | 0.6 |
|            |            | 350      | 5.34·10$^{-3}$ | 12.5| 9.3       | 99.0     | 63.8  | 6.2  | 29.3 | 0.3 | 0.2 | 0.2 |
|            |            | 400      | 1.72·10$^{-2}$ | 33.7| 28.2      | 98.5     | 75.9  | 2.6  | 20.2 | 0.6 | 0.5 | 0.1 |
|            | 500        | 250      | 1.58·10$^{-4}$ | 0.3 | 0.2       | 93.7     | 49.4  | 4.2  | 42.1 | 0.0 | 0.0 | 4.2 |
|            |            | 300      | 7.55·10$^{-4}$ | 1.3 | 1.0       | 95.3     | 59.9  | 8.2  | 28.5 | 0.8 | 0.9 | 1.8 |
|            |            | 350      | 2.76·10$^{-3}$ | 4.4 | 3.3       | 98.8     | 66.1  | 5.0  | 28   | 0.0 | 0.3 | 0.6 |
|            |            | 400      | 8.40·10$^{-3}$ | 11.9| 9.3       | 98.2     | 66.8  | 2.8  | 28.9 | 0.3 | 0.5 | 0.6 |
|            | 600        | 250      | 4.31·10$^{-4}$ | 0.2 | 0.1       | 80.8     | 33.0  | 0.0  | 54.8 | 2.4 | 0.0 | 9.7 |
|            |            | 300      | 1.46·10$^{-3}$ | 0.6 | 0.4       | 94.2     | 40.4  | 0.0  | 55.9 | 0.5 | 0.0 | 3.1 |
|            |            | 350      | 3.66·10$^{-3}$ | 1.6 | 1.0       | 96.6     | 43.8  | 3.8  | 50.3 | 0.6 | 0.0 | 1.5 |
|            |            | 400      | 1.01·10$^{-2}$ | 5.2 | 3.2       | 96.8     | 42.2  | 2.6  | 53.2 | 0.9 | 0.0 | 1.0 |
Figure S7. Arrhenius plot for SrMoO₄ catalyst samples prepared by sol-gel synthesis calcined at 400°C, 500°C and 600°C.

Table S11. Activation energies and pre-exponential factors calculated from the Arrhenius equation for SrMoO₄ catalyst samples prepared by sol-gel synthesis calcined at 400°C, 500°C and 600°C.

| Mo:Sr | Tcalc [°C] | Eₐ [kJ/mol] | k₀[L/(m²s)] |
|-------|-----------|-------------|-------------|
| 1.0   | 400       | 86.8        | 1.08⋅10⁵    |
|       | 500       | 94.1        | 3.57⋅10⁵    |
|       | 600       | 64.5        | 4.95⋅10²    |
| 1.1   | 400       | 89.8        | 1.72⋅10⁵    |
|       | 500       | 77.5        | 8.69⋅10³    |
|       | 600       | 60.7        | 4.94⋅10²    |
Table S12. Conversions and selectivities of the BaMoO$_4$ catalyst samples prepared by sol-gel synthesis at 250°C, 300°C, 350°C and 400°C with a flow of 150 NmL/min with MeOH/O$_2$/N$_2$ = 5/10/85 molar ratio over a bed of 25 mg catalyst (150-250 µm) diluted in 150 mg SiC.

| Type, Mo:M | $T_{\text{calc}}$ [°C] | $T_{\text{sp}}$ [°C] | $k$ [L/(m$^2$s)] | $X$ [%] | $X_{\text{cor}}$ [%] | $S_{\text{cor}}$ [%] | CH$_2$O | DME | DMM | MF | CO | CO$_2$ |
|------------|----------------|----------------|----------------|--------|----------------|----------------|-------|-----|-----|----|----|------|
| BaMoO$_4$, 1.0 | 600 | 250 | 3.17$\times$10$^{-5}$ | 0.0 | 33.8 | 33.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 66.2 |
| | | 300 | 2.40$\times$10$^{-4}$ | 0.1 | 71.5 | 71.5 | 0.0 | 0.0 | 0.0 | 0.0 | 13.7 | 14.8 |
| | | 350 | 7.72$\times$10$^{-4}$ | 0.3 | 85.1 | 85.1 | 0.0 | 0.0 | 0.0 | 0.0 | 4.5 | 10.4 |
| | | 400 | 2.42$\times$10$^{-3}$ | 0.9 | 91.1 | 91.1 | 0.0 | 0.0 | 0.0 | 0.0 | 1.8 | 7.1 |
| BaMoO$_4$, 1.1 | 600 | 250 | 4.97$\times$10$^{-4}$ | 0.2 | 69.5 | 30.0 | 0.0 | 49.5 | 0.0 | 8.4 | 12.1 |
| | | 300 | 1.01$\times$10$^{-3}$ | 0.5 | 82.0 | 31.5 | 5.2 | 52.6 | 0.0 | 2.5 | 8.3 |
| | | 350 | 3.64$\times$10$^{-3}$ | 1.5 | 83.7 | 44.5 | 3.9 | 40.3 | 1.6 | 1.3 | 8.3 |
| | | 400 | 8.51$\times$10$^{-3}$ | 3.2 | 88.0 | 49.2 | 3.2 | 39.1 | 1.0 | 0.6 | 6.8 |

Figure S8. Arrhenius plot for BaMoO$_4$ catalyst samples prepared by sol-gel synthesis calcined at 600°C.
Table S13. Activation energies and pre-exponential factors calculated from the Arrhenius equation for BaMoO$_4$ catalyst samples prepared by sol-gel synthesis calcined at 600°C.

|          | $E_a$ [kJ/mol] | $k_0$ [L/(m$^2$s)] |
|----------|---------------|---------------------|
| Mo:Ba = 1.0 | 83.5          | 7.90·10$^3$        |
| Mo:Ba = 1.1 | 57.0          | 2.09·10$^2$        |

5 CO$_2$-TPD

5.1 Procedure:
The CO$_2$-TPD procedure was performed in the setup used for the activity tests. A Pfeiffer Vacuum OMNIStar™ MS, measuring N$_2$ (m/z=28), O$_2$ (m/z=32), H$_2$O (m/z=18) on the faraday detector and CO$_2$ on the SEM detector, was connected to the effluent line in front of the GC. For the analysis 200 mg of sample (150-250 µm) was mounted between two quarts wool plugs in the 4 mm quartz U-reactor. The samples were heated to 450°C at 10°C/min in a 150 NmL/min flow of 10% O$_2$ in N$_2$ and stayed for 2 h. The reactor was cooled to 80°C. The reactor was bypassed and a calibration curve for the MS was made by running a 5:145, 10:140, and 15:135 mol:mol ratio of CO$_2$ and N$_2$ in a 150 NmL/min flow (7 min each). CO$_2$ was adsorbed for 9 min from a 5 NmL/min CO$_2$ in 145 NmL/min N$_2$ flow. Non adsorbed CO$_2$ was flushed for 300 min with 150 NmL/min N$_2$. The temperature was decreased to 70°C to get a better baseline. The desorption was performed with a ramp of 10°C/min until 600°C in 150 NmL/min of N$_2$. The baseline subtraction, peak fitting and integration was done in the Fityk software (Wojdyr, M. (2010). J. Appl. Cryst. 43, 1126-1128.) using the VoigtA peaks.

5.2 Results
The samples calcined at 500°C were investigated by CO$_2$-TPD (See Figure S1). The Temperature ramp was conducted until 600°C, but only results until 450°C (the drying temperature)
was used as it could be seen from the other tracked species (particularly water) that the large peaks there stemmed from decomposition.

Figure S9. CO₂-TPD curves, peaks fitted and sum of fitted peaks for samples calcined at 500°C (a) Mo:Ca = 1.0, (b) Mo:Sr = 1.20, (c) Mo:Mg = 1.0, (d) Mo:Ba = 1.12, (e) Mo:Ca = 1.1, (f) Mo:Mg = 1.1. Flow: 150 NmL/min N₂. Ramp: 10°C/min.

The total surface basicity of the samples calculated from the peak fits is shown in Table S14.
Table S14: Overview of total mass based and surface areas based basicity calculated from fits of CO$_2$-TPD curves.

| Sample       | Total Basicity  | Total Basicity  |
|--------------|-----------------|-----------------|
|              | [µmol CO$_2$/g] | [µmol CO$_2$/m$^2$] |
| Mo:Mg = 1.0  | 7.4·10^-2       | 1.6·10^-3       |
| Mo:Mg = 1.1  | 4.3·10^-2       | 1.3·10^-3       |
| Mo:Ca = 1.0  | 2.7·10^-1       | 7.8·10^-3       |
| Mo:Ca = 1.1  | 1.5·10^-2       | 1.1·10^-3       |
| Mo:Sr = 1.20 | 2.9·10^-2       | 9.4·10^-3       |
| Mo:Ba = 1.12 | -               | -               |

Figure S9 and Table S14 show that the sample with Mo:Ca = 1.0 had the highest mass based basicity of 0.27 µmol CO$_2$/g, while the other samples had much lower (3.5-9 times) values. This sample also showed significantly lower formaldehyde selectivity (Figure 4 and 7) and was the only one with desorption of CO$_2$ at low temperature, with major peaks at 100 and 150°C. On surface area basis, see Table S14 column 2, the Mo:Ca = 1.0 sample still had the second highest value, only surpassed by the Mo:Sr = 1.20 sample which had a low surface area of 3.1 m$^2$/g and a noisy desorption signal, due to the low total amount of adsorbed CO$_2$ being close to the detection limit for the samples with low surface basicity on mass basis. No fit was made for Mo:Ba = 1.12 in Figure S9(d) as the apparent peak was believed to be a measurement artefact.
6 Sample preparation

There were used two different preparation methods in this article: A Sol-gel synthesis and a co-precipitation method. The exact amounts of chemicals used are shown in Table S15 and Table S16.

**Table S15. Overview of amounts of chemicals used for the sol-gel synthesis of alkali earth metal molybdates.**

| Mo:M | Mg(NO$_3$)$_2$·6H$_2$O [g] | Ca(NO$_3$)$_2$·4H$_2$O [g] | Sr(NO$_3$)$_2$ [g] | Ba(NO$_3$)$_2$ [g] | (NH$_4$)$_6$MO$_7$O$_{24}$·4H$_2$O [g] | C$_6$H$_8$O$_7$·H$_2$O [g] |
|------|--------------------------|--------------------------|-----------------|-----------------|---------------------------------|--------------------------|
| 1.1$^a$ | 5.1655                  | -                        | -               | -               | 3.9155                          | 4.2459                  |
| 1.0$^a$ | 5.5695                  | -                        | -               | -               | 3.8320                          | 4.5746                  |
| 1.1$^b$ | -                       | 8.8290                   | -               | -               | 7.2490                          | 7.8485                  |
| 1.0$^b$ | -                       | 9.4537                   | -               | -               | 7.0623                          | 8.4020                  |
| 1.1$^a$ | -                       | -                        | 4.0418          | -               | 3.7092                          | 4.8136                  |
| 1.0$^a$ | -                       | -                        | 6.2734          | -               | 3.5770                          | 5.1315                  |
| 1.1$^a$ | -                       | -                        | -               | 4.1929          | 3.1258                          | 4.1457                  |
| 1.0$^a$ | -                       | -                        | -               | 4.4048          | 2.9795                          | 4.2806                  |

$^a$ 4 g of sample.
$^b$ 8 g of sample.

**Table S16: Overview of amounts of chemicals used for the co-precipitation synthesis of 5 g samples of alkali earth metal molybdates.**

| Mg(NO$_3$)$_2$·6H$_2$O [g] | Ca(NO$_3$)$_2$·4H$_2$O [g] | Sr(NO$_3$)$_2$ [g] | Ba(NO$_3$)$_2$ [g] | (NH$_4$)$_6$MO$_7$O$_{24}$·4H$_2$O [g] | C$_6$H$_8$O$_7$·H$_2$O [g] |
|--------------------------|--------------------------|-----------------|-----------------|---------------------------------|--------------------------|
| 6.9545                  | -                        | -               | -               | 47.9296                          | 5.7036                  |
| -                       | 5.9060                   | -               | -               | 44.1327                          | 5.2594                  |
| -                       | -                        | 4.2718          | -               | 35.6513                          | 4.2461                  |
| -                       | -                        | -               | 4.4056          | 29.8031                          | 3.5319                  |

For the BaMoO$_4$ samples prepared by sol-gel method, it was difficult to keep the sample from premature precipitation during the evaporation of the water.

Before deciding on precipitation at pH = 7, it was tried to co-precipitate SrMoO$_4$ without addition of 25 wt.% NH$_3$, but this gave extreme excess of MoO$_3$ as identified by XRD after
calcination. Precipitation with stoichiometric and 10 % excess of Mo compared to Sr had also previously been tried at pH = 10.4, but only yielded SrCO$_3$.

MgMoO$_4$ was tried co-precipitated by the route described in the article, but no precipitation took place due to too high solubility of MgMoO$_4$. Addition of 100 mL of ethanol gave a precipitate but with extreme excess of Mo. No further efforts was made to precipitate MgMoO$_4$.

7 Corrected selectivity and activity

The selectivity and conversion were corrected for reversible byproducts (DME, DMM and MF), as these will mostly be converted under industrial operation. DME was treated as two MeOH, DMM as two MeOH and one CH$_2$O, and MF as one MeOH and one CO, as they would be converted back to these species at high MeOH conversion. The reversible byproducts corrected selectivity and conversion made the comparison of the catalysts clearer. This is illustrated in Figure S10 for the industrial reference (MoO$_3$/Fe$_2$(MoO$_4$)$_3$), where the reversible byproducts corrected selectivity remains constant even though the specific selectivities undergo large changes as function of increasing temperature and conversion. Particularly the DMM selectivity, but also the DME selectivity, decreased when the conversion increased.
Figure S10. Conversion and selectivity vs. temperature for the industrial reference catalyst, MoO$_3$/Fe$_2$(MoO$_4$)$_3$. 25 mg 150-250 µm sample diluted in 150 µm SiC. Flow of 150 NmL/min, 5% MeOH, 10% O$_2$ in N$_2$. 