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

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Abstract: Alkali earth metal molybdates (MMOx, M = Mg, Ca, Sr, and Ba) were investigated as catalysts for the selective oxidation of methanol to formaldehyde in the search for more stable alternatives to the current industrial iron molybdate catalyst. The catalysts were prepared by either sol-gel synthesis or co-precipitation with both stoichiometric ratio (Mo:M = 1.0) and 10 mol% to 20 mol% excess Mo (Mo:M = 1.1 to 1.2). The catalysts were characterized by X-ray diffraction (XRD), nitrogen physisorption, Raman spectroscopy, temperature programmed desorption of CO2 (CO2-TPD), and inductively coupled plasma (ICP). The catalytic performance of the catalysts was measured in a lab-scale, packed bed reactor setup by continuous operation for up to 100 h on stream at 400 °C. Initial selectivities towards formaldehyde of above 97% were achieved for all samples with excess molybdenum oxide at MeOH conversions between 5% and 75%. Dimethyl ether (DME) and dimethoxyxymethane (DMM) were the main byproducts, but CO (0.1%–2.1%) and CO2 (0.1%–0.4%) were also detected. It was found that excess molybdenum oxide evaporated from all the catalysts under operating conditions within 10 to 100 h on stream. No molybdenum evaporation past the point of stoichiometry was detected.

Keywords: formox process; selective oxidation; formaldehyde; molybdate; methanol; heterogeneous catalysis

1. Introduction

Formaldehyde is a major industrial chemical used in the production of urea-, phenol-, melamine, and polyacetal resins, accounting for 70% of the consumption, but with other important products as well [1]. Formaldehyde is commercially available as formalin, which is an aqueous solution of formaldehyde (typically 37 wt.%), as formaldehyde is very reactive and, in pure form, polymerizes to the solid paraformaldehyde. In 2017, the annual production was 50 million metric tons of formalin [2] and it is expected to grow to 60 million tons per year in the late 2020s [3], with a growth rate of 5.76% per year of the market value from 2018 to 2022 [4].

The synthesis of formaldehyde was first reported by Butlerov in 1859, and industrial production started in Germany in 1889. There are two processes applied industrially today—the silver process, which was patented in 1910, and the Formox process using a metal oxide catalyst, which was first patented in 1921 [5]. Today, around two-thirds of the global capacity is based on the Formox technology [6].
In the Formox process, an iron molybdate catalyst with excess molybdenum oxide (MoO$_3$/Fe$_2$(MoO$_4$)$_3$) has been used since 1952 [7], giving overall plant yields of 90%–95% depending, among other things, on the degree of catalyst deactivation [3]. The main cause of deactivation for the industrial catalyst is the volatilization of molybdenum species [8–10], which leads to a catalyst lifetime of only 12–18 months [7]. The active phase has been shown to be a thin amorphous surface layer of MoO$_3$ [11–16], where the role of the crystalline MoO$_3$ is only to replenish the MoO$_3$ surface upon evaporation [11]. Thus, it is of major interest to either increase the stability of the iron molybdate or find alternative catalysts with similar activity and selectivity, but better stability and less volatile components. In the literature, much investigation has gone into various vanadium-based systems such as vanadium phosphates (90%–96% selectivity) [17,18], iron vanadates (90% selectivity) [3,19–26], supported V$_2$O$_5$ [27–32], and other vanadium-based catalysts [33,34]. The vanadium-based catalysts mostly show good activity, lower selectivity than iron molybdate, and the vanadium is also subject to volatilization [22,35]. On the other hand only few publications looking into alternative molybdate catalysts are found in the literature [3,36–38], and have mostly been done by Popov et al. [36–38] during the 1970s and 1980s and, more recently, by the Andersson group at Lund University (Sweden) [3,20]. Unfortunately, details on the stability of the systems are often not provided, even though this is the main motivation for finding an alternative catalyst system for the industry. The iron molybdate catalysts are deliberately sintered during the synthesis to decrease the activity of the catalyst for better temperature control; hence the activity is not an issue for the industry, though this is often the focus in the scientific literature. The CaMoO$_4$ system was tested by Popov et al. [38] for methanol oxidation, achieving 96% selectivity to formaldehyde, and by Said and Goda [39] for the anaerobic dehydrogenation to anhydrous formaldehyde, where a yield of 98% was reported. Also, SrMoO$_4$ and BaMoO$_4$ have been tested by Popov et al. [36], but the selectivities to CH$_2$O, CO, and CO$_2$ were not clearly presented.

In this study, an investigation of alkali earth metal molybdates as catalysts for the selective oxidation of methanol to formaldehyde was conducted with respect to selectivity; activity; and, importantly, stability for a period of up to 100 h under conditions of accelerated deactivation at 400 °C. This is correlated to the catalyst composition and structure determined by nitrogen physisorption using BET theory, X-ray diffraction (XRD), Raman spectroscopy, inductively coupled plasma (ICP), and surface basicity by temperature programmed desorption of CO$_2$ (CO$_2$-TPD). The potential of using the alkali earth metal molybdates for industrial production of formaldehyde is discussed.

2. Results

2.1. Characterization

2.1.1. XRD, BET, and ICP

All the catalyst samples were characterized by X-ray powder diffraction both as fresh and spent samples, see Figure 1.
Figure 1. Normalized X-ray powder diffractograms for all catalyst samples. Symbols mark the peaks for the different phases. x = MMoO₄ (M = Ca, Sr, Ba) with a scheelite-CaWO₄ tetragonal structure, + = MgMoO₄ with a CoMoO₄ monoclinic structure, o = MoO₃ with orthorhombic structure, * = Mo₃O₉·H₂O from the ICSD database [40] (collection codes: 20418, 194078, 239418, 193795, 35076, 420492). Arrows: reflections unaccounted for.

The diffractograms of CaMoO₄, SrMoO₄, and BaMoO₄ were very similar as they all had the scheelite-CaWO₄ structure. The peaks shifted towards lower diffraction angles owing to the increasing size of the tetragonal unit cell when going down the alkali earth group. MgMoO₄ displayed several peaks in comparison, because the unit cell of MgMoO₄ is monoclinic. The phase compositions from Rietveld analysis as well as the crystallite sizes for the fresh catalysts are shown in Table 1.

Table 1. Overview of the stoichiometric ratios between molybdenum and the alkali earth metal (M = Mg, Ca, Sr, or Ba), the specific surface area (SSA) measured by BET, and the phase composition and crystallite size of the stoichiometric molybdate determined by XRD on fresh samples.

<table>
<thead>
<tr>
<th>Mo:M</th>
<th>SSA [m²/g]</th>
<th>MMoO₄ [wt.%]</th>
<th>Mo₃O₉ [Å]</th>
<th>Mo₃O₉·H₂O [wt.%]</th>
<th>Mo₃O₉ (Ortho) [wt.%]</th>
<th>MMoO₄ [wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgMoO₄</td>
<td>1.0</td>
<td>45.3</td>
<td>100</td>
<td>211</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgMoO₄</td>
<td>1.1</td>
<td>33.0</td>
<td>95.5</td>
<td>378</td>
<td>2.0</td>
<td>2.4</td>
</tr>
<tr>
<td>CaMoO₄</td>
<td>1.0</td>
<td>34.4</td>
<td>100</td>
<td>415</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrMoO₄</td>
<td>1.20*</td>
<td>3.1</td>
<td>97.5</td>
<td>1777</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>BaMoO₄</td>
<td>1.12*</td>
<td>1.2</td>
<td>95.3</td>
<td>2054</td>
<td>2.5</td>
<td>4.7</td>
</tr>
</tbody>
</table>

* Measured by inductively coupled plasma optical emission spectrometry (ICP-OES).
All the fresh samples consisted of a stoichiometric alkali earth molybdate phase and, for the cases where Mo was in excess, one additional molybdenum oxide phase (see Table 1). The MoO$_3$-H$_2$O phase was believed to come from solvation of MoO$_3$ by water in the air and is expected to dehydrate under operating conditions. It should be noted that all the molybdenum phases have Mo in the +6 oxidation state. The crystallite size increased down through the group and, in addition, samples with excess Mo had larger crystal sizes compared with the stoichiometric samples (see Table 1), indicating that molybdenum promotes sintering. These observations from XRD were in agreement with the trends for the specific surface area determined by BET, as the specific surface area decreased down through the group, and the samples with excess Mo had lower specific surface areas (see Table 1). For information on the effect of calcination temperature, see Tables S1 to S5 and Figures S1 to S4 in the Supplementary Material (SM). For the spent Mo:Ba = 1.12, Mo:Sr = 1.20, and Mo:Ca = 1.1 samples, it was observed that the peaks from excess Mo (MoO$_3$ and BaMoO$_4$) had disappeared after the activity tests and no new peaks appeared (Figure 1). Thus, the catalysts were phase pure molybdates after the reaction. There were no differences between the spent Mo:Ca = 1.1 and spent Mo:Ca = 1.0 samples. The Mo:Mg = 1.0 and Mo:Mg = 1.1 samples showed the formation of new peaks after the reaction, but also the disappearance of the excess MoO$_3$. The new peaks were mostly visible for the Mo:Mg = 1.1 catalyst. The new peaks were likely a partially reduced Mo phase, as it was most visible in the Mo:Mg = 1.1 catalyst. The HighScore+ and software in combination with the ICDD PDF-4+ database and the Topas 4 software were used in an attempt to index the additional peaks, however, no reasonable match could be identified.

2.1.2. Raman Spectroscopy

All samples were investigated with Raman spectroscopy both as fresh samples and after the catalytic tests.

The spectrum for the fresh Mo:Mg = 1.1 (Figure 2a) showed clear bands from crystalline MoO$_3$ as peaks at 994, 818, and 666 cm$^{-1}$, but the double peak at 282 and 290 cm$^{-1}$ were also visible, which corresponds to the peaks described for MoO$_3$ by various authors [41-43] (ID: R100217). A very small peak has also been reported for MoO$_3$ at 471 cm$^{-1}$ [42], which was also seen for the fresh Mo:Mg = 1.1. The peak at 740 cm$^{-1}$ could indicate the presence of MoO$_2$ [44,45], which was not seen by XRD. If comparing the spectra to the literature on MgMoO$_4$, the general shape of the Mo:Mg = 1.1 spent and Mo:Mg = 1.0 spent samples were in good agreement with these spectra [41,42]. The peaks were reported at 116, 153, 178, 204, 277, 335, 349, 371, 384, 856, 910, 958, and 970 cm$^{-1}$, with small “shoulders” at 302, 425, and 876 cm$^{-1}$ [41,42]. This leaves one clear, non-explained peak at 551 cm$^{-1}$, which was especially well defined for the spent Mo:Mg = 1.1 sample. This may be the same non-identified phase observed with XRD. From the spectra, it was observed that the free MoO$_3$ in the Mo:Mg = 1.1 catalyst evaporated during the 100 h on stream, leaving only the MgMoO$_4$ phase. The spectrum for Mo:Mg = 1.0 fresh was not obtainable because of fluorescence.

Also, the Mo:Ca = 1.1 sample was synthesized to have 10 mol% excess of Mo, which, from the XRD, was found as crystalline MoO$_3$. For the fresh catalyst, a MoO$_3$ phase was also found by Raman spectroscopy (Figure 2b), as there were distinguished peaks at 994, 818, and 666 cm$^{-1}$, and the double peak at 291 and 283 cm$^{-1}$ [41–43] (ID: R100217). However, the spent Mo:Ca = 1.1 catalyst no longer displayed the peaks attributed to MoO$_3$. The spent Mo:Ca = 1.1 catalyst exhibited the same peaks as the Mo:Ca = 1.0 catalyst did (both fresh and spent), showing that all excess MoO$_3$ evaporated from the Mo:Ca = 1.1 sample, and that no free MoO$_3$ was present in the Mo:Ca = 1.0 sample (neither fresh or spent). Furthermore, the Mo:Ca = 1.0 catalyst did not show any change in the peaks after the reaction, only smaller variations in the relative magnitude of the peaks. The peaks could be assigned to the CaMoO$_3$ phase, which has all of the peaks at 877, 845, 792, 388, 322 [43] (ID: R100180, R050355) [46,47], 188 cm$^{-1}$ [47] (192 cm$^{-1}$ [46]), and 111 cm$^{-1}$ [43] (ID: R050355) [46,47]. However, the position of the last peak at 135 cm$^{-1}$ differed from the value of 145 cm$^{-1}$ reported in the literature [43] (ID: R100180, R050355) [46,47]. There was no evidence of the molybdenum evaporating from the CaMoO$_3$ phase under reaction conditions by Raman, as there were no signs of CaO, Ca(OH)$_2$, or CaCO$_3$ in the spectra (peaks at 155, 282, 680, 713, and 1080 cm$^{-1}$) [48].
For the Mo:Ca = 1.2 sample (Figure 3a), the excess of Mo was again found as MoO₆ from the peaks at 994, 818, 666, and 290 cm⁻¹ [41–43] (ID: R100217), in agreement with the XRD results for the fresh catalyst. After 8 h on stream, the sample no longer exhibited the peaks at 994, 818, 666, 290, 240, 154, and 127 cm⁻¹. Thus, the MoO₆ had evaporated already after 8 h on stream, which was also observed for an iron molybdate catalyst [49]. The peaks at 885, 842, 793, 380, 366, 326, 231, and 181 cm⁻¹ were attributed to the vibrational modes of the MoO₆²⁻ in SrMoO₄ [46,47]. Additionally, SrMoO₄ was reported to have external optical modes at 111, 137, and 157 cm⁻¹ [46,47], thus accounting for all the observed bands in the Raman spectrum. Comparing the spectrum of the spent strontium molybdate catalyst with the spectrum of the CaMoO₄ (Mo:Ca = 1.0) catalyst, the similarity was striking. The same applies for comparing with the spent barium molybdate catalyst (Figure 3b). This is also in agreement with peaks for BaMoO₄ in the literature at 891, 838, 792, 360, 346, 325, 189, 143, 136, and 107 cm⁻¹. This shows that in all three cases, the spent samples consisted of the stoichiometric molybdates, as these all have a scheelite structure and exhibit bands from the same symmetry operations. For the fresh barium molybdate catalyst, it was found that it did not contain the excess Mo in the form of MoO₆, in agreement with XRD; however, it did show extra bands compared with the spent catalyst. The spent catalyst only showed the BaMoO₄ bands [46,50] (890, 837, 790, 359, 346, 324, 185, 132, and 107 cm⁻¹, all reported with small variations) after only 8 h on stream. The additional peaks in the fresh barium molybdate catalyst were likely attributed to the BaMoO₄⁰ phase found by XRD, however, a reference Raman spectrum was not found.

Figure 2. Raman spectra measured for (a) magnesium molybdate and (b) calcium molybdate catalysts before and after 100 h on stream at 400 °C.
2.2. Catalytic Activity

The activity and selectivity of the catalysts were evaluated at 250 °C, 300 °C, 350 °C, and 400 °C in a lab-scale, packed bed reactor. The results are shown as the corrected selectivity versus the corrected conversion in Figure 4. Furthermore, the samples were compared to a molybdenum trioxide/iron molybdate industrial reference catalyst.

Figure 3. Raman spectra measured for (a) strontium molybdate and (b) barium molybdate catalysts before and after 8 h on stream at 400 °C.

Figure 4. Reversible byproducts corrected selectivity towards formaldehyde vs. the corrected conversion obtained by measurements at 250 °C, 300 °C, 350 °C, and 400 °C, in a flow of 150 NmL/min.
with MeOH/O₂/N₂ = 5/10/85 molar ratio with 25 mg of 150–250 μm catalyst diluted in 150 mg SiC. (a) catalysts with low maximum conversion; (b) catalysts with high maximum conversion.

The mass based activity decreased down the group (i.e., with increasing molar mass) for the samples with excess Mo, which was in correspondence with the tendency of the specific surface areas shown in Table 1. It should be noted that the MgMoO₄ and CaMoO₄ samples with Mo:M = 1.1 behaved almost identically. Both the selectivity and activity of the stoichiometric samples were significantly lower, even though the surface areas were significantly higher. Thus, the corrected selectivity, for all catalysts with an excess molybdenum oxide phase detected by XRD, was above 97%. However, they do not have quite as high selectivity as the industrial reference for which the selectivity was above 99.3%. The individual selectivities and activity are visualized Figures 5 and 6, and full details are shown in Tables S6 and S7 and Figure S5 in the SM. See also Tables S8 and S13 and Figures S6 and S8 for information on the calcination temperature and preparation method.

![Figure 5](image_url)

Figure 5. Selectivities and conversions for the alkali earth metal molybdates at 250 °C, 300 °C, 350 °C, and 400 °C in a flow of 150 NmL/min with MeOH/O₂/N₂ = 5/10/85 molar ratio with 25 mg of 150–250 μm catalyst diluted in 150 mg SiC.
The selectivity towards DMM was significant for most samples, except for the BaMoO₄ catalyst and the MgMoO₄ catalyst with Mo:Mg = 1.0. The presence of the over-oxidation products (CO and CO₂) indicates the presence of sites with stronger basic character [51]. All the samples also formed some DME, which was generally recognized to stem from strong acidic sites [51]. All the samples with excess Mo had a surface area normalized, non-corrected activity on the order of 1×10⁻² L/(m²·s) at 400 °C, which indicates that the excess Mo was important for the activity for all the samples. This may be explained by the excess MoO₃ being needed to form a surface monolayer acting as the most active phase in the catalysts, in agreement with previous studies [11–16].

The stability of the samples was investigated with time on stream for up to 100 h at 400 °C, see Figure 7, which may be considered as the maximum temperature in the hot spot region in industrial reactors under normal operation. This was done in order to investigate accelerated deactivation corresponding to a longer time on stream at a lower temperature in the industrial reactor.
The selectivity and activity of all the samples (including the industrial reference) decreased with time on stream, but the industrial reference reactivated after about 20 h on stream. The reactivation was observed previously by Raun et al. [49], who found that the reactivation started when the excess crystalline MoO₃ had evaporated from the catalyst. For the stoichiometric Ca- and MgMoO₄, an initial increase in the selectivity was also observed within the first 10 h (Figure 7a), which was believed to stem from a restructuring of the Mo on the surface, as the surface of mixed metal oxide catalysts was reported to consist of only a single metal oxide under reaction conditions [52].

The stability of the catalysts with Mo in excess decreased down through the group, so the BaMoO₄ lost 80% of the activity within 8 h, whereas it took 37 h and 55 h for the CaMoO₄ and MgMoO₄, respectively, to lose 80% activity. After 100 h on stream, the activity of the catalysts with excess Mo came close to the activity of the stoichiometric molybdates and, in the case of MgMoO₄, the selectivities of the two samples were also identical after 100 h. This indicates that the catalysts became very similar once the excess molybdenum evaporated. CaMoO₄ with excess MoO₃ even became less active than the stoichiometric sample, though the selectivity did not fall to the same level. Comparing the surface area based activity of the samples after 100 h (with an assumption of no change in surface area to be able to make the comparison, as the sample size was too small to measure the change in surface area by BET), the rate constants became very close, being 1.1×10⁻³ L/(m²-s) and 1.3×10⁻³ L/(m²-s) for the Mo:Ca = 1.0 and 1.1, respectively. For MgMoO₄, the same comparison showed 2.6×10⁻⁴ L/(m²-s) and 8.3×10⁻⁴ L/(m²-s) for the Mo:Mg = 1.0 and 1.1 samples, respectively, which is not as close as for the CaMoO₄ samples. The reason for this difference is perhaps the assumption of no change in the surface area, and it is likely that the two samples approach each other with further time on stream.

3. Discussion

The Raman spectra showed that excess molybdenum oxide evaporated from all samples under reaction conditions of 400 °C, 150 NmL/min of 5% MeOH, 10% O₂ and 85% N₂, and 25 mg catalyst, yielding only the stoichiometric alkali earth metal molybdates. This was shown to happen within 8 h for the strontium and barium molybdates. The stoichiometric molybdates, however, did not undergo significant structural or chemical changes during the time on stream, as the Raman spectra before and after reaction were essentially identical. This is different from the industrial MoO₃/Fe₂(MoO₄)₃ catalysts, where the Mo has been shown by Raun et al. [49] to evaporate from the ferric molybdate phase, first forming ferrous molybdate and then iron oxide: Fe₄(MoO₄) → Fe₃MoO₄ → Fe₂O₃.

The corrected formaldehyde selectively measured initially was on a similar level, between 94% and 99% for all samples, when the conversion was large enough to measure selectivity accurately (Figure 4, when above 2% conversion approximately), except for the stoichiometric CaMoO₄ sample. Also, with time on stream, the selectivity of this sample was significantly lower than the selectivities of the other samples. The low selectivity of the stoichiometric CaMoO₄ could stem from small variations in the surface Mo distribution leading to Mo deficient zones, which is detrimental to the formaldehyde selectivity, as shown by Popov et al. [38]. Increased selectivity towards over-oxidation products (MF, CO, and CO₂) owing to increased basicity/nucleophilicity has also been reported after the addition of K₂O to a V₂O₅/Al₂O₃ catalyst by Wachs et al. [29], from the difference in adsorption products of methanol on SiO₂, Al₂O₃, F/Al₂O₃, MgO, TiO₂, ZrO₂, ThO₂, and Fe₂O₃ by Busca et al. [53], and proposed as a way of probing a catalyst surface by Tatibouet [51]. This was supported by the 3.5–9 times higher surface basicity (μmol CO₂/g) for this sample as measured by CO₂-TPD (see Figure S9 and Table S14 in the SM for more details). The SrMoO₄ and BaMoO₄ samples lost their selectivity at the same rate as the Mo:Ca = 1.1 sample, for the first 8 h on stream. This may point towards the MoO₃ evaporation happening at the same rate, and thus the excess MoO₃ in the calcium sample may mostly be gone after 8 h on stream, as seen with Raman spectroscopy for the strontium and barium samples.
The activity measurements showed that the activity and selectivity of the samples with and without initial excess of molybdenum became almost equal after 100 h on stream. Combined with the Raman and XRD measurements, this points towards having essentially the same catalyst in the reactor after operation independent of the initial Mo:M ratio.

From the literature [49,54], it seemed the MoO$_3$ evaporation from the industrial catalyst pellets (ring shaped cylinders with outer diameter = 4.55 mm, hole diameter = 1.70 mm, and length = 4.00 mm) was a diffusion limited process, as it took much longer time for the excess MoO$_3$ to disappear from pellets than the sieve fraction used here (150–250 μm), under similar conditions. Additionally, a reactor model indicated that reducing MoO$_3$ evaporation only for the catalyst layer near the inlet might to a large extent solve the problem of increasing pressure drop [55]. In this study, the CaMoO$_4$, MgMoO$_4$, and Mo:Mg = 1.1 samples initially showed a smaller relative decrease of the activity than the industrial reference (Figure 7), and much less MoO$_3$ per catalyst mass evaporated from them according to Raman spectroscopy. The selectivity of the CaMoO$_4$ sample was probably too low to be used industrially. However, the MgMoO$_4$ samples had high enough selectivity to be of interest as inlet layer catalyst, in front of the regular industrial catalyst, to partly convert the feed. In this way, the methanol concentration would be decreased and the problem of MoO$_3$ evaporation from the iron molybdate catalyst would be less severe, as it would not experience as high methanol concentrations as normal. This could increase the longevity of the industrial type catalyst, but further studies are needed to confirm this.

4. Materials and Methods

4.1. Catalyst Synthesis

Two different methods, sol-gel and co-precipitation, were used to synthesize the catalysts in order to achieve sufficiently high purity, surface area, and catalytic activity of all the alkali earth metal molybdates. For the synthesis, Mg(NO$_3$)$_2$·6H$_2$O (Alfa Aesar, 98%), Ca(NO$_3$)$_2$·4H$_2$O (Sigma-Aldrich, puriss. P.a., ACS reagent, 99%–103%), citric acid C$_3$H$_6$O$_7$·H$_2$O (Sigma-Aldrich, ≥99.0%), (NH$_4$)$_6$Mo$_7$O$_24$·4H$_2$O (Sigma-Aldrich, puriss. p.a., ACS reagent, ≥99.0% (T)), Sr(NO$_3$)$_2$ (Fluka, puriss. P.a. ACS; ≥99.0% (KT)), Ba(NO$_3$)$_2$ (Alfa Aesar, ACS, 99+%), and 25 wt.% aqueous NH$_3$ (VWR AnalaR NORMAPUR) were used. Water was demineralized in all cases.

4.1.1. Sol-Gel

Samples with stoichiometric and 10 mol% excess of Mo were prepared for MgMoO$_4$ and CaMoO$_4$ using a citric acid sol-gel method. Mg(NO$_3$)$_2$·6H$_2$O (5.16 g or 5.56 g) or Ca(NO$_3$)$_2$·4H$_2$O (8.82 g or 9.45 g) was dissolved in 100 mL of H$_2$O together with a 1/1 molar amount of C$_3$H$_6$O$_7$·H$_2$O and a 1/0.143 or 1/0.157 molar amount of (NH$_4$)$_6$Mo$_7$O$_24$·4H$_2$O (giving Mo:M ratios of 1.0 and 1.1) (see Table S15 in the SM for full details). The water was evaporated in a rotary evaporator until the liquid became highly viscous and greenish. The samples were then slowly dried in an oven at 80 °C, where they swelled to multiple times the original liquid volume. The samples were calcined in static air in a muffle furnace at 500 °C for 4 h with a heating rate of 5 °C/min.

4.1.2. Co-Precipitation

For SrMoO$_4$ and BaMoO$_4$, a co-precipitation procedure was used to synthesize phase pure materials. Sr(NO$_3$)$_2$ (4.27 g) or Ba(NO$_3$)$_2$ (4.41 g) was dissolved in 100 mL of H$_2$O together with a 1/1 molar amount of C$_3$H$_6$O$_7$·H$_2$O. Then, 10/7 molar amounts of (NH$_4$)$_6$Mo$_7$O$_24$·4H$_2$O (giving Mo:M = 10 in the solution, see Table S16 in the SM for more details) were dissolved separately in 130 mL of H$_2$O. The nitrate/citric acid solution was heated to 45 °C on a magnetic stirrer. The molybdate solution was added slowly under stirring and, finally, the pH was adjusted to 7.0 with 25 wt.% aqueous NH$_3$. The solution was aged for 10 min at 45 °C under stirring, filtered hot, and washed with 600 mL of H$_2$O. The samples were dried at 110 °C and subsequently calcined at 500 °C for 4 h with a heating rate of 5 °C/min.
4.2. Catalytic Activity and Selectivity

The samples were tested in a lab-scale, packed bed reactor setup described in detail elsewhere [49,56,57]. For the tests, 25 mg of sample in a 150–250 μm sieve fraction was diluted with 150 mg of SiC (150–355 μm sieve fraction). The bed was held in place by two quartz wool plugs. The flow rate was 150 NmL/min with 5 vol.% MeOH and 10 vol.% O2 in N2. The MeOH was fed by bubbling the gas mixture through liquid methanol kept at 5 °C. The temperature of the catalyst bed was controlled by a Siemens PLC running a PID loop with a LabVIEW application as the interface. A thermocouple touching the top of the catalyst bed was used to control the temperature. The effluent was analyzed by a ThermoFisher Trace Ultra GC equipped with both TCD and FID, quantifying MeOH, DME, DMM, MF, CO, and CO2. The catalyst temperature was ramped stepwise with activity measurements performed at 250 °C, 300 °C, 350 °C, and 400 °C (one GC analysis at each temperature, after 15 min of stabilization with 40 min in total at each temperature), after which the conditions were kept steady for up to 100 h (SrMoO4 and BaMoO4 were only kept for 8 h).

The selectivities and conversion were calculated based on the GC measurements on the effluent according to Equations (1)–(4).

\[ S_i = \frac{v_i \chi_i}{\sum v_i \chi_i} \]  
\[ X = \frac{\sum v_i \chi_i}{v_{\text{CH}_2\text{OH}} + \sum v_i \chi_i} \]  
\[ S_{\text{cor}} = \frac{s_{\text{CH}_2\text{O}} + \frac{3}{2}s_{\text{DMM}}}{s_{\text{CH}_2\text{O}} + \frac{3}{2}s_{\text{DMM}} + \frac{1}{2}s_{\text{MF}} + \frac{1}{2}s_{\text{CO}} + s_{\text{CO}_2}} \]  
\[ X_{\text{cor}} = \left(1 - \frac{3}{2}s_{\text{DMM}} - \frac{1}{2}s_{\text{MF}} - s_{\text{DME}}\right)X \]  

where \( v_i \) is the gas mole fraction of the ith product, and \( v_i \) is the number of carbons in the ith product. \( X_{\text{cor}} \) and \( S_{\text{cor}} \) are the reversible byproduct corrected conversion and selectivity towards formaldehyde. Here, DME was treated like two MeOH, DMM like two MeOH and one CH3O, and MF as one MeOH and one CO, as they would be converted back to these species at high MeOH conversion. This made the comparison between catalysts easier as the reversible byproduct corrected selectivity was mostly independent of temperature and conversion. This is further illustrated in Figure S10 in the SM. The reaction rate was assumed to follow (pseudo-)first order kinetics, as reported in the literature [58–62], and the rate constant was calculated from the design equation for a PFR reactor as in Equation (5) [63].

\[ k = -\frac{V_0}{w} \ln(1 - X) \]  

where \( V_0 \) is the volumetric feed flow at reaction conditions, \( w \) is the catalyst mass, and \( X \) is the conversion. For the calculation of \( k_{\text{cor}} \) (corrected rate constant), \( X_{\text{cor}} \) was used instead.

4.3. Characterization

4.3.1. X-Ray Powder Diffraction

The fresh samples were investigated with a PanAlytical X’Pert Pro instrument in Bragg-Brentano Geometry in reflectance mode using a Cu Kα radiation source (\( \lambda = 1.541 \text{ Å} \)) at ambient conditions. The scan range was 5–70° with a step size of 0.017°. The Rietveld analysis was performed using the Topas Software. Spent samples were investigated using a PanAlytical Empyrean instrument using a Cu Kα radiation source (\( \lambda = 1.541 \text{ Å} \)) mounted with a Ni beta filter, a pair of 0.04 radian soller slits, a beam stop, and a capillary spinner. The scan range was 5–75° with a step size of 0.14°. The samples were measured in open capillaries at ambient conditions. Relevant fresh samples were measured for comparison.
4.3.2. Surface Area Measurement

The surface areas of the samples were measured using a Quantachrome NOVATouch instrument and analyzed using the BET method. The samples were degassed at 350 °C for 4 h under vacuum before the nitrogen physisorption at 77 K with up to six points in the p/p0 range of 0.05–0.3, depending on the R²-value of the linear regression.

4.3.3. Elemental Analysis

The samples prepared by precipitation were subjected to inductively coupled plasma optical emission spectrometry (ICP-OES), to determine the Mo to alkali earth metal ratio. The samples were melted with K₂S₂O₇ and dissolved with HCl. Calibration curves including a blank were made before measurement. The apparatus was a Perkin Elmer model Optima 3000, Agilent 720 ICP, or a similar instrument. Samples prepared by the sol-gel method were assumed to have the nominal composition.

4.3.4. Raman Spectroscopy

Raman spectroscopy was performed on all the samples as prepared (fresh) and after the performance tests (spent). The Raman spectra were recorded with a Horiba LabRam microscope at ambient conditions. For the measurement, a HeNe laser (red, λ = 633 nm) was used as a monochromatic light source, however, owing to large fluorescence, the Mo:Ca = 1.0 samples (both fresh and spent) were measured with an argon laser (blue, λ = 488 nm). The Mo:Mg = 1.0 fresh fluoresced so much that a Raman spectrum was not obtainable, neither by changing excitation wavelength or by initial dehydration. The raw data were baseline subtracted in OriginPro software using the Peak Analyzer. The spectra were normalized with respect to peak height before plotting.

4.3.5. CO₂-TPD

Temperature programmed desorption of CO₂ (CO₂-TPD) was performed in the setup used for the activity test by a modification connecting a Pfeiffer Vacuum OMNISTar™ MS before the GC. For the measurements, 200 mg of sample was used, which was mounted between two quartz wool plugs. The samples were dried in a mixture of 10% O₂ and 90% N₂ to ensure no change in the surface. Full details on the procedure are given in the SM.

5. Conclusions

Alkali earth metal molybdates have successfully been synthesized by sol-gel synthesis and co-precipitation, as confirmed by XRD and Raman spectroscopy. The specific surface areas of the stoichiometric molybdates were higher than for the respective molybdates with excess MoO₃, indicating that molybdenum promotes sintering. It was further observed that the surface area decreased down through group 2 (Mg > Ca > Sr > Ba). The most active catalyst (on mass basis) was the MgMoO₄ catalyst with 10 mol% Mo in excess, which achieved over 75% conversion at 400 °C and more than 97% reversible byproduct corrected selectivity towards formaldehyde. All the catalysts with excess MoO₃ had similar surface area based activity at 400 °C on the order of 1·10⁻² L/(m²·s). Among the samples with excess MoO₃, the MgMoO₄ showed the highest stability through 100 h on stream, while the most stable catalyst tested was the stoichiometric CaMoO₄ catalyst. However, this catalyst only had a corrected selectivity towards formaldehyde of 85%. The surface area based activity of the CaMoO₄ catalysts with Mo:Ca = 1.0 and 1.1 catalysts was very similar after 100 h on stream, indicating that the catalyst with initial excess of Mo approached the stoichiometric samples, as excess Mo was lost by volatilization. This was substantiated by Raman measurements on fresh and spent samples. As the selectivity of the industrial reference was significantly better than even the Mo:Mg = 1.1 sample, and also with time on stream, the industrial applicability of these catalysts seemed limited. The Mo:Mg = 1.1 may be applicable as the inlet layer catalyst to increase the longevity of the current industrial catalyst, but further studies would be needed to confirm this.
Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1: Motivation for choice of different synthesis methods for the different alkali earth metal molybdates, XRD and BET analysis of additional samples by variation in calcination temperature and non-phase pure samples not reported in the main manuscript, full results of activity and selectivity measurements, and full details of sample preparation.


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