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Highly Stable Apatite Supported Molybdenum Oxide Catalysts for Selective Oxidation of Methanol to Formaldehyde: Structure, Activity and Stability

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Molybdenum oxide (5 to 20 wt.%) supported on calcium or strontium hydroxyapatite were investigated as catalysts for selective oxidation of methanol to formaldehyde. These catalysts were both active and selective, with a maximum yield achieved at 95% conversion and 96% selectivity. The main byproducts were CO (3.2%) and dimethyl ether (DME, 0.7%). The catalytic performance of the catalysts was measured for up to 600 h at 350 °C. Compared to an industrial iron molybdate catalyst, the hydroxyapatite based catalysts deactivated slower.

1. Introduction

Formaldehyde (CH₂O) is an important bulk chemical, as it is the smallest aldehyde and an important C₁-building block used for a variety of different products and processes.[1] The global production of formaldehyde is about 50 million metric tons of formalin, an aqueous solution of 37–57 wt% formaldehyde, per year. The market is expected to grow to 60 million tons per year in the late 2020s, with a growth rate in the total market value of 5.76% per year from 2018–2022.[2] The industrial production of formaldehyde mainly takes place by two processes, the silver catalyst process running with excess methanol at 600–720 °C (86.5-92% yield),[3–6] and the Formox process, using a metal oxide catalyst, running at 250–400 °C with excess oxygen[7,4] (overall plant yield of 90–95%)[8]. Today the Formox process is responsible for two thirds of the annual global formaldehyde production.[9] The preferred catalyst for the Formox process is an iron molybdate catalyst with excess molybdenum oxide (MoO₃/Fe₂(MoO₄)₃), referred to as FeMo in this paper.[5] Excess MoO₃, giving Mo/Fe ratios of 2–3 in typical industrial catalysts, is added to increase the stability of the catalyst.[7–10] This is needed as the lifetime of the FeMo catalyst is only 6–18 months.[9] The active component in the catalyst is the molybdenum oxide, and more specifically it has been found that the active component is a thin layer of amorphous MoO₃ on the surface of the catalyst.[11–18] This MoO₃ and excess crystalline MoO₃ form volatile species with methanol leading to a loss of Mo from the catalyst over time.[9,19,20] The methanol inlet concentration has increased significantly over the years (from 6.5% to 11% MeOH) to increase productivity,[7,12] which is one reason for the short catalyst lifetime. The volatile Mo species evaporate and flow with the gas down the reactor, where they decompose and deposit as needle like MoO₃ crystals, when the temperature and methanol concentration decreases.[9,21] This leads to increasing pressure drop[22] and decreasing selectivity over time. The stabilizing effect of the excess MoO₃ is partly to replenish the surface layer of MoO₃, as it evaporates.[9,11] For many processes it is advantageous to have a very active catalyst and catalytic activity is typically the focus in the academic literature. However, FeMo catalysts for producing formaldehyde are calcined at high temperature to decrease the surface area and thereby moderate the activity of the catalyst to have better temperature control in the reactor. The main motivation for the industry is thus not to find a more active catalyst, but a more stable catalyst to decrease the
frequent and expensive shutdowns and catalyst replacements, without compromising the selectivity and activity. For methanol selective oxidation catalysts it has been shown that acidic and basic surfaces are responsible for formation of by-products such as DME and CO, respectively, while redox sites are responsible for formation of formaldehyde. Thus a prospective catalyst should have a low surface acidity and basicity to decrease by-product formation and significant redox activity for both reduction and re-oxidation of the active sites, as the selective oxidation of methanol follows the Mars-van Krevelen mechanism.

Our group has recently conducted an in-depth characterization of the deactivation phenomena of the FeMo catalyst as powder over 600 h. The results showed increased rate of volatilization when the MeOH concentration increases, O₂ concentration decreases and temperature increases.

In the search for alternative catalysts we recently published an investigation of alkali earth metal molybdates (MgMoO₄, CaMoO₄, SrMoO₄ and BaMoO₄). Though higher stability was found for stoichiometric molybdates, an excess of MoO₃ was needed to obtain selectivity and activity similar to what was reported by the Popov group. However, these catalysts deactivated quickly due to evaporation of the excess MoO₃.

A variety of alternative catalytic systems for this reaction has been reported in the academic literature, mostly focusing on vanadium containing systems including various vanadates (e.g. Fe(VO₄)₂ with selectivity >90%), vanadium phosphates and vanadium oxides. Also molybdenum oxide and other metal oxide catalysts have been reported.

A screening study in our group evaluating numerous of the promising alternatives to the FeMo catalyst reported in the literature, found that MoO₃/hydroxyapatite was a very promising candidate as it showed activity and selectivity close to the FeMo catalyst and, importantly, superior stability.

Thus, in this paper we report that molybdenum oxide supported on hydroxyapatite (Ca₅(PO₄)₃OH) and the Sr analogue (written as CaHAP and SrHAP) are highly stable catalysts for the selective oxidation of methanol to formaldehyde. To understand the structure-activity-stability relationship various characterization techniques were applied, including nitrogen physisorption, TEM, SEM, XRD, XAS, total X-ray scattering with PDF analysis, ICP, CO₂-TPD, NH₃-TPD and H₂-TPR on the fresh catalyst samples and XRD, XAS and STEM on powder samples used on stream for up to 600 h at 350 °C in a lab scale fixed bed reactor.

Under anaerobic conditions a 5 wt% MoO₃/CaHAP catalyst has previously been reported to have high selectivity and stability for the dehydrogenation of methanol to formaldehyde, although at very low activity, but to the best of our knowledge we report the first investigation with oxygen in the feed, making the catalysts relevant for industrial application in the Formox process. This paper reports part one of the investigation, part two was performed on industrial sized catalyst pellets, investigating the influence of pellet density.

### Experimental

#### Catalyst Synthesis

The synthesis of the catalysts was performed in two steps: Initial co-precipitation of the apatite supports followed by impregnation with ammonium heptamolybdate. For the synthesis the following chemicals were used. Ca(NO₃)₂·4H₂O (Sigma-Aldrich, puriss. P.a., ACS reagent, 99–103 %), Sr(NO₃)₂ (Fluka, puriss. P.a. ACS ≥99.0 % (KT)), 25 wt% aqueous NH₃ (VWR AnalaR NORMAPUR), citric acid C₆H₈O₇·H₂O (Sigma-Aldrich), ACS Reagent ≥99.0 %, (NH₄)₂MoO₄·4H₂O (Sigma-Aldrich, puriss. p.a., ACS reagent, ≥99.0 % (T)), (NH₄)₂HPO₄ (Sigma-Aldrich, BioUltra, ≥99.0 % (T)).

#### Precipitation of Apatite Support

The apatite supports were prepared by a co-precipitation procedure inspired by. It was aimed to prepare 0.029 mol of apatite from each precipitation. 0.149 mol of the respective metal nitrate and a stoichiometric amount of citric acid was dissolved in 350 mL of demineralized water. 0.130 mol of (NH₄)₂HPO₄ was dissolved in 250 mL of demineralized water to have a final M/P ratio of 1.15. The metal nitrate/citric acid solution was heated to 75 °C on a hot plate magnetic stirrer, after which the (NH₄)₂HPO₄ solution was added dropwise (no visible change). Monitoring of pH by a Methrom 744 pH-meter (calibrated at pH = 7.00 and pH = 4.00) showed an increase of pH from 1.05 to 2.85 during the addition of the phosphate solution. The solution was made basic by dropwise addition of 25 wt% aqueous NH₃ until pH = 9.3, still at 75 °C, during which visible white powder precipitated. The mixture was aged for 20 min under stirring with unrestricted pH. The precipitate was filtered hot and washed with 500 mL of demineralized water. The filter cake was dried at 110 °C over night and calcined at 600 °C for 4 hours with a ramping rate of 5 °C/min in static air in a muffle furnace. After calcination, the solid apatite filter cake was crushed and sieved to 150–250 μm.

#### Impregnation

The support materials were impregnated using the incipient wetness method. Corresponding amounts of AHM to the aimed nominal MoO₃ loadings were dissolved in demineralized water corresponding to the pore volume, determined by incipient wetness with water (CaHAP: 52.6 m²/g and water pore volume of 1.13 g H₂O/g CaHAP, SrHAP: 32.7 m²/g and water pore volume of 0.96 g H₂O/g SrHAP). The impregnation solution and powder were mixed thoroughly by stirring with a glass spatula for 5 min before drying over night at 50 °C. The impregnated samples were calcined at 500 °C for 4 hours with a ramping rate of 5 °C/min in static air in a muffle furnace. The samples were impregnated with Mo loadings past an expected monolayer (~4.5 Mo atoms per nm²), to track structure, activity, and stability, as improvements were observed beyond monolayer loading.

#### Catalytic Activity and Selectivity

Catalytic activity, selectivity and stability were measured using a lab scale, fixed bed reactor setup described in detail elsewhere. The measurements were carried out using 25 mg of catalyst in a 150–250 μm sieve fraction diluted with 150 mg of SiC (150–355 μm) in a feed of 150 NmL/min, 5 vol.% MeOH, 10 vol.% O₂ in N₂. The activity tests, data acquisition and data treatment were conducted as described previously. Formaldehyde oxidation tests over the apatite supports were done by a dual bed system as shown in
Figure S1 with a FeMo catalyst bed, followed by a quartz wool plug and then a pure support bed.

The selectivity was calculated according to Equation (1) and conversion according to Equation (2).

\[ S_i = \frac{\nu_i y_i}{\sum \nu_i y_i} \]  \hspace{1cm} (1)

\[ X = \frac{\nu_i y_i}{y_{CH,O} + \sum y_i} \]  \hspace{1cm} (2)

Where \( \nu_i \) was the number of carbon atoms in the \( i \)th product and \( y_i \) its mol fraction. In this paper the reversible by-product corrected selectivity and conversion will mostly be used, as it takes into account that DME, DMM and MF are reversible products and will form 2 MeOH, 2 MeOH and 1 formaldehyde, and 1 MeOH and 1 CO molecule, respectively, at high conversion. They were calculated according to Equations (3) and (4).

\[ S_{\text{raw}} = \frac{S_{\text{CH,O}} + \frac{1}{2} S_{\text{DMM}}}{S_{\text{CH,O}} + S_{\text{DMM}} + S_{\text{CO}} + S_{\text{CO,2}}} \]  \hspace{1cm} (3)

\[ X_{\text{raw}} = \left( 1 - \frac{2}{3} S_{\text{DMM}} - \frac{1}{2} S_{\text{MF}} - S_{\text{DME}} \right) X \]  \hspace{1cm} (4)

(Pseudo-1\textsuperscript{st} order kinetics have been reported in the literature\cite{59-63} for the selective oxidation of methanol to formaldehyde, thus the mass based reaction rate constant was calculated according to the design equation for 1\textsuperscript{st} order reaction in a plug flow reactor \cite{Eq. (5)},\cite{64}

\[ k = -\frac{V_s}{W} \ln(1 - X) \]  \hspace{1cm} (5)

For calculation of \( K_{\text{raw}} \), \( X_{\text{raw}} \) was used instead of \( X \). \( W \) is the weight of sample loaded and \( V_s \) the volumetric flow rate at reaction conditions.

Characterization

X-ray Powder Diffraction, ICP and Nitrogen Physisorption

X-ray powder diffraction, ICP, and BET were performed as described previously\cite{217}. For XRD the reference diffractograms were taken from the Inorganic Crystal Structure Database (ICSD)\cite{65} with the following collection codes for the phases: quartz (16331), CaMoO\textsubscript{4} (417513), Ca\textsubscript{2}(OH)(PO\textsubscript{4})\textsubscript{2} (26204), SrMoO\textsubscript{4} (239418), Sr(OH)\textsubscript{2} (15167), Sr\textsubscript{0.5}P\textsubscript{2}O\textsubscript{7} (59395), and β-Sr\textsubscript{2}P\textsubscript{2}O\textsubscript{7} (14313).

Scanning Electron Microscopy and Scanning Transmission Electron Microscopy

The Scanning Transmission Electron Microscopy (STEM) was performed on a FEI\textsuperscript{TM} Talos microscope, operated at 200 kV. The samples were ground to fine powder and dispersed on a Cu grid covered with continuous carbon using ethanol. EDX maps were acquired over a period of 10 min per map with a probe current of 700 pA and HAADF-STEM imaging was performed with a nominal magnification of 28,500x to 1,800,000x. For quantification of the element compositions the Cliff-Lorimer method was used. EDX signals from C, Fe, Co, Cu, Zr, and Pb were included in the spectrum and deconvoluted with fixed concentrations of zero as they were treated as system peaks arising from the microscope interior and sample holder grid. The sample areas were not beam stable for longer time, limiting the number of magnifications at which element maps and HAADF-STEM pictures could be properly taken (see Supporting Information). Particle size distributions were analyzed on recorded images not previously exposed to the electron beam.

X-ray Absorption Spectroscopy

The measurements were performed \textit{ex situ} on the MAX IV (Lund, Sweden) Balder beamline, measuring from 19.8–21.0 keV for the Mo k-edge. The samples were all prepared as pellets with cellulose as binder. The pellets were pressed with the aim of 87\% absorbance at 20.050 keV (i.e. above the absorption edge) if enough sample was available. In case of limited sample amount, all available sample was pressed. Fresh samples were pressed as 13 mm pellets after grinding together with cellulose. Spent samples were prepared as 5 mm pellets in paper inserts for the 13 mm pellet press. XAS data processing was performed using Athena from the Demeter package (version 0.9.26)\cite{66}. The monochromator was calibrated against a Mo foil and no further energy calibration was performed in the data analysis. Four to eight scans of each sample were merged as raw \( \mu(E) \). For the normalization and background removal the following parameters were used: \( E_0 \) was set to the 2\textsuperscript{nd} derivative zero crossing, Pre-edge range: \(-180 \text{ to } -90 \text{ eV}, \text{ normalization range: } 20 \to 30 \text{ eV} \) relative to the sample \( E_0 \). \( E_p \) of the standards were fitted to the sample and weights forced to sum to 1. For the EXAFS fitting the data were imported into Artemis. The ICSD collection codes: CaMoO\textsubscript{4} (194078), MoO\textsubscript{3} (180590) and SrMoO\textsubscript{4} (239418) were used to generate the paths by first running on pure CaHAP and the 5, 10 and 15 wt% MoO\textsubscript{3}/CaHAP samples using a Panalytical Empyrean Series 3 Diffractometer equipped with an Ag K\textsubscript{α} source with K\textsubscript{α1}: λ = 0.5594 Å and K\textsubscript{α2} λ = 0.5637 Å. Total scattering data from each sample was measured in a spinning 0.8 mm diameter borosilicate sample holder grid. The sample areas were not beam stable for longer time, limiting the number of magnifications at which element maps and HAADF-STEM pictures could be properly taken (see Supporting Information). Particle size distributions were analyzed on recorded images not previously exposed to the electron beam.

X-ray Pair Distribution Function Analysis

The total scattering data was measured on pure CaHAP and the 5, 10 and 15 wt% MoO\textsubscript{3}/CaHAP samples using a Panalytical Empyrean Series 3 Diffractometer equipped with an Ag K\textsubscript{α} source with K\textsubscript{α1}: λ = 0.5594 Å and K\textsubscript{α2} λ = 0.5637 Å. Total scattering data from each sample was measured in a spinning 0.8 mm diameter borosilicate capillary in the Q-range 0.63–18.34 ˚A\(^{-1}\). Scattering data measured from an empty 0.8 mm diameter borosilicate capillary was used as background signal. Background subtraction, normalization and Fourier transform to obtain the PDFs was done using PDFgetX3\cite{67}. Modelling and calculation of PDFs were done using PDFgui.\cite{68} The crystal structures used for fitting were taken from ICSD with the
The drying of the sample was as for the CO\textsubscript{2}TPD. CO\textsubscript{2}TPD measurements were performed in the same setup as the activity measurements with the addition of a Pfeiffer Vacuum OMNIStar\textsuperscript{TM} mass spectrometer (MS) at the effluent line sampling before the GC as described in\textsuperscript{[26]}. For the measurements, 200 mg of sample was held in place between two quartz wool plugs in the 4 mm inner diameter quartz U-shaped reactor.

**CO\textsubscript{2}TPD**

The samples were heated to 450°C with 10°C/min and dried for 2 h in 150 NmL/min 10 vol.% O\textsubscript{2} in N\textsubscript{2}. The oven was cooled to 80°C, where the reactor was bypassed and the MS calibrated with 5/145, 10/140, and 15/135 vol/vol ratios of CO\textsubscript{2} (Air Liquid N45) and N\textsubscript{2} summing to 150 NmL/min for 7 min each. CO\textsubscript{2} was adsorbed from a flow of 5 NmL/min CO\textsubscript{2} in 145 NmL/min N\textsubscript{2} for 9 min. Non-adsorbed CO\textsubscript{2} was flushed by 150 NmL/min N\textsubscript{2} for 300 min. The temperature was lowered to 70°C to obtain a better baseline. The desorption was performed at 150 NmL/min of N\textsubscript{2} with a ramp of 10°C/min until 600°C. Subtraction of the baseline, peak fitting and integration were performed in the Fityk software\textsuperscript{[26]} using Voigt functions fitting peak area. For the CO\textsubscript{2}-TPD measurements the MS was tracking single ions: N\textsubscript{2} (m/z = 28), O\textsubscript{2} (m/z = 32) and H\textsubscript{2}O (m/z = 18) on the faraday detector and CO\textsubscript{2} (m/z = 44) on the SEM detector. The heat tracing of the steel tubing was 150°C to make the CO\textsubscript{2} adsorb less to the tube walls.

**NH\textsubscript{3}-TPD**

The drying of the sample was as for the CO\textsubscript{2}-TPD. After drying the oven was cooled to 100°C after which the reactor was bypassed and a one point calibration measurement for the MS was performed with a 1.00 mol% NH\textsubscript{3} in N\textsubscript{2} certified gas mixture (BOC) for 15 min at 150 NmL/min, followed by adsorption for 15 min with the same flow. Non-adsorbed NH\textsubscript{3} was flushed with 200 NmL/min N\textsubscript{2} for 380 min. The temperature in the reactor was lowered by 10°C to have a better baseline. The desorption was performed at 150 NmL/min of N\textsubscript{2} with a ramp of 10°C/min until 600°C. For the NH\textsubscript{3}-TPD measurements the MS was tracking single ions N\textsubscript{2} (m/z = 28), O\textsubscript{2} (m/z = 32) and H\textsubscript{2}O (m/z = 18) on the faraday detector and NH\textsubscript{3} (m/z = 17) on the SEM detector. The heat tracing of the steel tubing was set to 180°C to make the NH\textsubscript{3} adsorb less to the tube walls. For the data treatment the ratio between the responses on the MS for m/z = 17 and m/z = 18 have been used to subtract the water contribution to m/z = 17. Quantification of the ammonia desorption by integration was performed in the Origin software.

**H\textsubscript{2}-TPR**

For the TPR experiments a 5.00 mol% certified H\textsubscript{2} in N\textsubscript{2} gas bottle (AGA) was used. The reduction was performed with a flow of 100 NmL/min and a ramp of 10°C/min until 1000°C. The MS was tracking single ions H\textsubscript{2} (m/z = 2) and H\textsubscript{2}O (m/z = 18). The highest measured MS response was used as the calibration for the 5 mol% H\textsubscript{2} MS response. H\textsubscript{2} consumption was found by integration using the Origin software.

2. Results and Discussion

2.1. Catalytic Activity, Selectivity and Stability Measurements

Catalytic activity and selectivity were measured in a lab-scale, fixed bed reactor setup for all the molybdenum oxide impregnated catalysts. Methanol conversion, formaldehyde selectivity and first-order reaction rate constants are shown in Figure 1.

The 10 and 15 wt% MoO\textsubscript{3}/CaHAP samples were the most active of the supported catalysts on mass basis (Figure 1a and c), with the 15 wt% MoO\textsubscript{3}/CaHAP obtaining the highest selectivity towards formaldehyde, >96% at all temperatures, but all the catalysts showed corrected selectivities above 90% (Figure 1b) at all temperatures. The CaHAP samples obtained a better selectivity with a lower nominal MoO\textsubscript{3} loading than the SrHAP samples (Figure 1b), even though the surface area of the SrHAP was lower than the CaHAP (see Section 3.2.1), and thus should require less molybdenum oxide to cover the surface.

For reference, the catalytic activity of the bare supports for both methanol and formaldehyde oxidation was measured in the same setup (see SI for experimental description and data in Figure S2). This showed that CaHAP had a higher tendency than SrHAP towards oxidation of formaldehyde, possibly due to its higher surface area, but overall both the methanol and formaldehyde oxidation activities of both supports were low, which is important for achieving catalysts with high selectivity.

The first order rate constants based on catalyst mass for the MoO\textsubscript{3}/CaHAP catalysts were comparable to the industrial FeMo catalyst at 250 and 300°C and slightly higher at 350 and 400°C (Figure 1c), showing that the catalytic activity of these catalysts was high enough to be of industrial interest. The mass based activity of the SrHAP based catalysts were lower than the FeMo catalyst. The first order rate constants based on BET surface area generally increased with increasing MoO\textsubscript{3} content until reaching a maximum value, with only minor differences between the 10 and 15 wt% MoO\textsubscript{3}/CaHAP and the 20 wt% MoO\textsubscript{3}/SrHAP catalysts at 300 to 400°C (Figure 1d). The BET surface area normalized rate constants at 400°C were 0.8 to 1.6·10\textsuperscript{-3} L/(m\textsuperscript{2}·s) (Figure 1d and Table S1) for the 5–15 wt% MoO\textsubscript{3}/CaHAP and 10–20 wt% MoO\textsubscript{3}/SrHAP catalysts, similar to the activity achieved for bulk alkali earth metal molybdates with excess Mo.\textsuperscript{[26]} It should be noted that at 400°C the CaHAP catalysts showed >80% conversion, resulting in underestimation of the rate-constant, but generally they followed the Arrhenius expression (Figure S3 and Table S2). The surface area normalized rate constant for the industrial FeMo catalyst was significantly higher than for the HAP based catalysts, mainly due to the order of magnitude lower the BET surface area of this catalyst (see Section 3.2.1). However, for industrial application this has low importance since it is the catalytic activity per catalyst mass or catalyst volume that is relevant for reactor design.

Regarding the specific selectivities (Figure S4 and Table S1) the SrHAP samples showed lower DME selectivity compared to the CaHAP catalysts. DME forms on acidic sites, so this is in agreement with the NH\textsubscript{3}-TPD showing a very low number of...
acidic sites on the SrHAP samples (see Section 3.2.6). DMM was the most significant byproduct for the SrHAP samples at all temperatures, but for the CaHAP catalysts significant amounts of DMM were only observed at 250–350 °C. DMM is known to be a reversibly formed byproduct and as the conversion was >80% at 400 °C for the CaHAP samples, DMM formed near the inlet of the reactor rehydrated and was oxidized down through the reactor.

As the main industrial problem in selective oxidation of methanol to formaldehyde is the evaporation of Mo and resulting low stability of the industrial FeMo catalyst, the 10 wt % MoO3/CaHAP and 10 wt% MoO3/SrHAP samples were investigated for up 600 h on stream at 350 °C with comparison to the industrial FeMo catalyst measured at the same conditions (Figure 2).

Both the 10 wt% MoO3/CaHAP and 10 wt% MoO3/SrHAP showed significantly higher stability in terms of activity compared to the industrial FeMo catalyst, which lost 86% of its initial activity within the first 62 hours on stream (62 NL/s/kgcat to 9 NL/s/kgcat) but then reactivated and reached 11 NL/s/kgcat after 100 h on stream and would keep reactivating with further time on stream, as we have previously reported.24,26 The 10 wt % MoO3/CaHAP and 10 wt% MoO3/SrHAP monotonically deactivated and lost 80% (108 NL/s/kgcat to 34 NL/s/kgcat) after 408 h and 73% after 600 h (22 NL/s/kgcat to 6 NL/s/kgcat) respectively. The 10 wt% MoO3/SrHAP lost 66% of the activity after 408 h on stream. Thus the 10 wt% MoO3/CaHAP and especially the 10 wt% MoO3/SrHAP were highly stable compared to the FeMo reference catalyst, as the time on stream for comparable deactivation was much longer for the HAP based catalysts.

Both HAP based catalysts maintained high formaldehyde selectivity throughout the experiments with the 10 wt% MoO3/CaHAP going from initially 97% to 92% after 408 h on stream, where the selectivity of the 10 wt% MoO3/SrHAP evolved in
parallel, starting a little lower at 95% and ending at 90% after 600 h. The FeMo reference catalyst had a corrected selectivity starting at above 99% and stayed above 98% during the 100 h on stream.

For comparison, the 15 wt% MoO$_3$/SrHAP catalyst was measured at identical conditions for 100 h and a comparison of the first 100 h on stream for the four catalysts is shown in the SI Figure S5. The 15 wt% MoO$_3$/SrHAP deactivated faster than the 10 wt% MoO$_3$/SrHAP catalyst and the similar activity and selectivity of these two samples after 100 h indicate that they are essentially similar at this point, likely due to a higher rate of Mo volatilization with increasing Mo content.

The volatilization of Mo and resulting catalyst deactivation is highly diffusion limited. The deactivation observed within about 100 h on stream for 150 to 250 $\mu$m sieve fraction catalyst particles is comparable to the deactivation of industrial sized catalyst pellets during their full lifetime.$^{[70,71]}$

### 2.2. Characterization

#### 2.2.1. X-ray Powder Diffraction, ICP and Nitrogen Physisorption

The HAP supports, all the fresh samples and spent samples from time on stream experiments at 350 °C (see Section 3.1) were investigated by XRD (Figure 3, Table 1 and SI Figures S6–S7 and Table S3). The CaHAP support was found to be phase pure by XRD (decreasing the calcination temperature from 600 to 400 °C also formed phase pure CaHAP, see Table S3), whereas the SrHAP support consisted of SrHAP (47.5 wt%), $\beta$-Sr$_2$(P$_2$O$_7$) (47.6 wt%) and SrO (5.0 wt%). After the impregnation with AHM and calcination calcium/strontium molybdate was detected in increasing amounts with increasing Mo loading. Crystalline $\alpha$-MoO$_3$ was not detected, while this is the main form of excess Mo in the FeMo catalyst. For the SrHAP samples, an increasing amount of $\beta$-Sr$_2$(P$_2$O$_7$) was measured with increasing Mo loading. The increase in $\beta$-Sr$_2$(P$_2$O$_7$) was due to the Sr-apatite phase.

#### Table 1. Specific surface areas from BET, phase composition and crystallite size from XRD Rietveld refinement for the supports, fresh and spent catalysts samples (25 mg, catalyst 350 °C in 150 NmL/min, 5 vol.% MeOH, 10 vol.% O$_2$, 85 vol.% N$_2$). \( M = \text{Ca or Sr.} \)

| Loading [wt %] | TOS [h] | SSA [m$^2$/g] | MHAP [wt %] | D[Å] | MMoO$_4$ [wt %] | D[Å] | $\beta$-Sr$_2$(P$_2$O$_7$) [wt %] | D[Å] | Sr(OH)$_2$ [wt %] | D[Å] | SrO [wt %] |
|----------------|--------|-------------|-------------|------|----------------|------|---------------------------|------|----------------|------|------------|
| Ca 0 5 10 408 15 | 0 0 0 0 | 52.6 48.8 46.1 40.6 | 100 95.6 91.9 96.9 | 182 182 184 191 | – – 8.1 3.1 | – – 236 170 | – – – – | – – | – – | – – |
| Sr 0 0 0 0 | 32.7 26.8 26.6 26 | 47.5 41.5 28.0 30.5 | 200$^{[1]}$ 200$^{[1]}$ 200$^{[1]}$ 200$^{[1]}$ | – – 14.5 11.9 | – – 218 204 | – – 57.3 57.6 | – – | 300$^{[1]}$ 300$^{[1]}$ 300$^{[1]}$ 300$^{[1]}$ | – – | 0.2 0.2 0.2 0.2 |
| 15 | 0 0 0 0 | 30.5 26.5 26.7 26.7 | 200$^{[1]}$ 200$^{[1]}$ 200$^{[1]}$ 200$^{[1]}$ | 19 11.2 10.8 10.8 | – – 216 206 | – – 57.6 57.9 | – – | 300$^{[1]}$ 300$^{[1]}$ 300$^{[1]}$ 300$^{[1]}$ | – – | 0.2 0.2 0.2 0.2 |
| 10 | 0 0 0 0 | 26.8 26.6 26.6 26 | 41.5 28.0 28.0 30.5 | 200$^{[1]}$ 200$^{[1]}$ 200$^{[1]}$ 200$^{[1]}$ | 11.4 14.5 14.5 11.9 | – – 300 204 | – – 57.6 57.9 | – – | 300$^{[1]}$ 300$^{[1]}$ 300$^{[1]}$ 300$^{[1]}$ | – – | 0.2 0.2 0.2 0.2 |
| 15 | 0 0 0 0 | 11.5 11.5 11.5 11.5 | 189 189 189 189 | 275 275 275 275 | 17.8 17.8 17.8 17.8 | – – 94 94 | – – 70.7 70.7 | – – | 294 294 294 294 | – – | – – | – – |
| 20 | 0 0 0 0 | 14.7 14.7 14.7 14.7 | 184 184 184 184 | 283 283 283 283 | 13.3 13.3 13.3 13.3 | – – 71.9 71.9 | – – 57.6 57.6 | – – | 280 280 280 280 | – – | – – | – – |

[a] Quantification uncertain, one peak not accounted for. This peak was not observed in any other sample, [b] Fixed during the Rietveld refinement.
(Sr$_5$(OH)(PO$_4$)$_3$) reacting with molybdenum oxide to form SnMoO$_4$ [Reaction (6), Eq. (6)].
This was also expected for the CaHAP samples, but was not detected by XRD, possibly because the phosphates formed by reaction between molybdenum oxide and CaHAP were amorphous.

It was indicated by XRD that molybdenum evaporated from the samples during time on stream at 350 °C, as the (Ca/Sr)MoO₄ content decreased from 8.1 wt% to 4.2 wt% after 100 h on stream, and further to 3.1 wt% after 408 h on stream for the 10 wt% MoO₃/CaHAP catalyst. For the 10 wt% MoO₃/SrHAP it decreased from 14.5 wt% to 11.9 wt%, 11.2 wt% and finally 10.8 wt% after 100 h, 250 h and 600 h, respectively. For the 15 wt% MoO₃/SrHAP catalyst the SrMoO₄ content decreased from 17.8 wt% to 13.3 wt% within 100 h. Hence, the volatilization of molybdenum was fastest for the first 100 h on stream.

The crystallite sizes of the (Ca/Sr)MoO₃ also generally decreased with time on stream, as the (Ca/Sr)MoO₃ content decreased, with the exception of the 15 wt% MoO₃/SrHAP, which showed a slightly increasing crystallite size from Rietveld analysis. The decrease in (Ca/Sr)MoO₃ content and crystallite size was due to evaporation of Mo from the SrMoO₄ and CaMoO₄. This was in contrast to our previous study on bulk (Ca/Sr)MoO₃, where only excess α-MoO₃ was found to evaporate. The cause of (Ca/Sr)MoO₃ decrease by Mo volatilization is likely that the reaction between molybdenum oxide and (Ca/Sr)HAP (Reaction (6)) is reversible and the molybdenum oxide is volatile under methanol vapors.

The rate of Mo volatilization was however much lower than for the FeMo catalysts, as the average rates of volatilization of Mo over the first 100 h on stream, estimated from XRD data, were 5·10⁻⁸ molMo⁺/gcat/s for the 10 wt% MoO₃/CaHAP and 3·10⁻⁹ molMo⁺/gcat/s for the 10 wt% MoO₃/SrHAP catalysts, in contrast to 7·10⁻⁷ molMo⁺/gcat/s for a FeMo catalyst measured in a previous study. i.e. the rate of Mo volatilization was ~14 to 23 times higher for the FeMo catalyst compared to the HAP based catalysts. The FeMo (Mo/Fe = 2:0) catalyst was measured at 385 to 395 °C, compared to 350 °C here, but with similar gas composition and space velocity. This temperature difference is expected to increase the rate of Mo volatilization from FeMo by less than 9%, hence this temperature difference cannot explain the order of magnitude difference observed.

The surface areas of the catalysts and supports were measured by nitrogen physisorption using the BET method (Table 1). The surface area of the CaHAP samples were higher than of the SrHAP samples and decreased with increasing MoO₃ loading, as expected from the XRD results. This was believed to stem from restructuring when the (Ca/Sr)MoO₃ phases were formed.

The ICP elemental analysis showed that the M/P ratio was 1.55 for the CaHAP sample, in contrast to XRD giving phase pure hydroxyapatite, which has a Ca/P ratio of 1.67. The SrHAP had a Sr/P ratio of 1.27 according to ICP, which was also lower than the ratio of Sr/P = 1.43 determined by XRD, considering the phase distribution by Rietveld refinement. Thus, in both cases the ICP measured a lower M/P ratio than XRD, possibly because the hydroxyapatite can be quite understoichiometric and still retain the crystal structure. The surface area of CaHAP prepared at pH = 10 by Hill et al. and calcined at the same temperature as in this study (600 °C) was only 30 m²/g, about 40% lower than obtained here. The Ca/P ratio determined by ICP was 1.66, but the surface was found to be calcium deficient (Ca/P = 1.35 by XPS). This was also found by Tanaka et al. However, the surface composition has also been found to depend on the orientation of the crystal planes, such that surface Ca enrichment is also possible.

### 2.2.2. Scanning Electron Microscopy

All fresh samples were investigated by SEM. For brevity, the SEM images and EDX results for the 10 wt% MoO₃/CaHAP (Figure 4) and 10 wt% MoO₃/SrHAP (Figure 5) are discussed in the following, while SEM images for the other samples and the pure supports can be found in the SI Figures S8–S16, as there were many similarities and general trends. The images showed that the apatite was the large dark grey particles with a porous, open surface structure, in agreement with SEM images by Santos et al. on hydroxyapatite. With increasing Mo loading an increasing formation of white (higher contrast) particles with a size of < 1 μm on the apatite particle surface was observed. This was observed for both the CaHAP and SrHAP samples and can be seen in Figure 4 and Figure 5. As the number of electrons reflected is proportional with $Z^2$ ($Z$ = core charge/element number), molybdenum rich areas will be lighter than other parts of the samples. EDX analysis showed that the white particles were molybdenum rich and the ratio of P to Ca/Sr was found to be comparably low. This showed, supported by the XRD results, that these particles were CaMoO₄ and SrMoO₄ respectively. The SEM images (Figures S8–S16) showed that the number concentration of these particles increased drastically with increasing Mo loading, whereas the size of the particles was similar for all samples.

The nominal MoO₃ content from SEM-EDX on such a particle was 38.0 wt%–42.6 wt% on the 10 wt% MoO₃/CaHAP (measurement points 1 to 5, 7 and 8 in Figure 4) and was approximately the same for all prepared catalysts samples irrespective of the overall MoO₃ loading and support. In comparison, pure CaMoO₄ has a nominal MoO₃ content of 71 wt%.

Mo was measured even though the electron beam only focused on the support (measurement points 11 and 12 in Figure 4). This could be due to the electrons penetrating 1–2 μm, thus Mo rich species could be present just below the surface of the support or it could be a layer of MoO₃ on the surface, not visible as a different structure. Averaging over a larger area (area 6), resulted in a MoO₃ loading of 29.4 wt%, as it included support not covered in CaMoO₄ particles. This is much higher than the nominal MoO₃ loading. This further showed that the impregnation formed Mo rich areas at the particle surface, and that the Mo concentration through the particle must be lower than the nominal loading, depending on the thickness of the layer of CaMoO₄ particles. However, measurements directly on the support surface (measurement points 9–12) were close to the average nominal loading of MoO₃ of 10 wt%, indicating that the bulk loading was close to the nominal loading. The MoO₃ loading could be lower than...
determined by EDX, as oxygen will be under-estimated, because the soft X-rays emitted by oxygen can have a significant absorption by the sample within the penetration depths of the electrons, thus over-estimating all other elements.

The images of the fresh 10 wt% MoO$_3$/SrHAP (Figure 5) sample showed the same trends as the 10 wt% MoO$_3$/CaHAP (Figure 4). However, the particles of SrMoO$_4$ were less distinguishable and seemed to be sintered together. The nominal concentration of MoO$_3$ measured was in this case 27.3 wt%–38.0 wt% on the Mo-rich particles.

2.2.3. Scanning Transmission Electron Microscopy

The 10 wt% MoO$_3$/CaHAP catalyst was investigated by STEM using the fresh catalyst and a spent sample (408 h at 350 °C), to obtain a better spatially resolved mapping of the elements compared to SEM. The intensity of the HAADF-STEM images is roughly proportional to $Z^2$ and the thickness of the sample.

For the fresh 10 wt% MoO$_3$/CaHAP sample (Figure 6a-c and Figures S17–S19) two different phases/structures were seen. One open and more porous agglomerate structure, which was the hydroxypatite support (marked with A in Figure 6a and c), and on top of this phase more dense/bright particles about 0.5 μm in size, believed to be calcium molybdate (CaMoO$_4$) (marked with B in Figure 4a and c). The average Ca/P ratios were 1.99, 2.28 and 2.87 respectively in Figure 6a–c, while the MoO$_3$ content was 5.1, 27.3 and 45.9 wt%, as determined from the summed EDX spectrum of the whole image area. The bright contrasted particles in Figure 6c had 56.4 wt% MoO$_3$ and the surrounding area only 5.9 wt% MoO$_3$. Thus, the bright particles were molybdenum rich, as expected for CaMoO$_4$ and also observed with SEM. In Figure 6d and Figure S20, it is seen that the distinction between the Mo-rich zone (box 1) and the rest was less well defined. However, by the EDX mapping the Ca/P ratio was 1.85 when averaging the full image area (Figure 6d), 1.84 at the bright spot (box 1) and 1.87 on the open structure (box 2), i.e. very similar. More importantly, the measured MoO$_3$ content was 4.8 wt% when averaging the full image area, 12.3 wt% at the bright box (box 1), and 3.0 wt% on the open structure (box 2), Figure 4d and Figure S20. Thus, molybdenum was measured outside the Mo rich clusters as well, which was difficult to determine from SEM due to the thicker sample and
large electron penetration depth (1–2 μm) that may cause the detector to pick up X-rays from phases below the surface.

The measurement of molybdenum on the surface of the support was investigated further by higher magnifications of the support areas (Figure 6e-f and Figures S21–S23). The surface was speckled with brighter spots of about 1.0 nm in mean diameter (Figure S24 and Table S4), and the Mo content in Figure 6e was 7.9 wt%. This gave evidence to the molybdenum being dispersed all over the support surface, likely as either amorphous MoO₃ or CaMoO₄. The small Mo-rich particles vary in size over Figure 6e-f in the interval from 0.6 nm to 2.5 nm. The samples did show some beam instability and care was taken not to damage or alter the sample in the microscope (see Figure S25).

The spent 10 wt% MoO₃/CaHAP sample after 408 h on stream at 350 °C appeared very similar to the fresh sample (Figure 7a–c and Figures S26–S33), with Mo rich particles on top of the porous support. The particles in Figure 7a–c had an overall MoO₃ content of 5.6 wt%, 13.0 wt% and 19.7 wt% respectively, while the bright Mo rich particles in Figure 7c had 57.0 wt% MoO₃ and the surrounding support area 3.0 wt% MoO₃. Thus, after 408 h on stream there were still Mo-species on the support surface. One particle with much lower MoO₃ content of 0.9 wt% was found (Figure 7d and Figure S32), but as can be seen from Figure 7e and Figure S33 molybdenum was still present on the surface as clusters/particles of sizes 0.6-2.5 nm with an average size of 1.0 nm, thus similar sizes as the fresh sample. A small, not beam stable, bright crystalline region was occasionally found by STEM on the spent 10 wt% MoO₃/CaHAP with lattice spacing of ~0.8 nm (Figure 7f). The brightness implied a molybdenum rich phase. From ICSD suggestions could be β-MoO₃ (ICSD Coll. Code 202324: a = 7.4 Å, b = 7.5 Å, c = 7.7 Å; Coll. Code 644068: a = 7.4 Å, b = 7.4 Å, c = 7.7 Å) or MoO₂ (Coll. Code 243549: a = 9.7 Å, b = 8.4 Å, 4.7 Å), β-MoO₃ was previously observed by Raman spectroscopy on a FeMo catalyst with initial Mo/Fe ratio of 2.01 after 250 h on stream and by both Raman and XRD after 600 h on stream. β-MoO₃ has also been found by Raman spectroscopy on MoO₃/SiO₂ samples after methanol oxidation and after thermal treatments at 350 °C for molybdophosphoric acid catalysts.

Overall, STEM was in agreement with XRD and SEM that the 10 wt% MoO₃/CaHAP catalyst consisted of CaHAP and <1 μm sized CaMoO₄ particles. Additionally, STEM showed molybdenum oxide dispersed over the CaHAP surface for both the fresh
and spent catalyst with approximately same cluster size of ~1 nm. Since the surface molybdenum oxide was expected to form volatile compounds with methanol and the CaMoO$_4$ to be stable under methanol vapors but decreased from 8.1 to 3.1 wt.% according to XRD, the CaMoO$_4$ appeared to act as a reservoir replenishing Mo lost by volatilization.

### 2.2.4. X-ray Absorption Spectroscopy

XAS measurements were conducted on fresh and spent samples as well as standards of AHM, MoO$_3$, MoO$_2$, CaMoO$_4$, SrMoO$_4$ and 1 wt% MoO$_3$/α-Al$_2$O$_3$ as model for supported MoO$_x$. No crystalline α-MoO$_3$ was detected by XRD for the 1 wt% MoO$_3$/α-Al$_2$O$_3$ standard, which had SSA = 9.3 m$^2$/g.

Using the measured standards, linear combination fitting (LCF) was performed in the XANES region for the MoO$_3$/CaHAP samples (Figure 8 and Table 2) and the MoO$_3$/SrHAP samples.

### Table 2. XANES linear combination fitting using MoO$_x$, CaMoO$_4$, and SrMoO$_4$ standards.

| Sample            | TOS     | Supported MoO$_x$ | Phase   | SrMoO$_4$ |
|-------------------|---------|-------------------|---------|-----------|
|                   | [h]     | [% of total Mo]   | CaMoO$_4$ | [% of total Mo] |
| 5 wt% MoO$_3$/CaHAP| 0       | 72                | 28       |
| 10 wt% MoO$_3$/CaHAP| 0      | 60                | 40       |
| 15 wt% MoO$_3$/CaHAP| 100    | 66                | 40       |
|                   | 408     | 60                | 43       |
| 5 wt% MoO$_3$/SrHAP| 0       | 57                | 78       |
| 10 wt% MoO$_3$/SrHAP| 0      | 22                | 80       |
| 15 wt% MoO$_3$/SrHAP| 100    | 28                | 72       |
|                   | 250     | 29                | 71       |
|                   | 600     | 28                | 72       |
|                   | 100     | 25                | 72       |
|                   | 0       | 18                | 82       |
|                   | 100     | 25                | 75       |
The XANES region was found to be fitted best by linear combinations of CaMoO$_4$/SrMoO$_4$ and supported MoO$_x$. Crystalline MoO$_2$, α-MoO$_3$, and AHM were also investigated as standards, both instead of supported MoO$_x$ and as a third standard. MoO$_2$ and AHM did not fit the data. Fitting with crystalline α-MoO$_3$ was possible, but the quality of the fits were much lower than for the supported MoO$_x$. In addition, principal component analysis suggested the catalyst samples should be fitted with only two components. Hence, the XANES spectra and fits clearly showed that (Ca/Sr)MoO$_4$ was present, in agreement with XRD, but also that (Ca/Sr)MoO$_4$ were not the only molybdenum species, despite no other molybdenum phases were detected by XRD. Hence, these species were like surface MoO$_x$ because the 1 wt% MoO$_3$/$α$-Al$_2$O$_3$ standard gave good fits for all the investigated samples (Figure 8 and Figure 9) and STEM showed Mo oxide clusters on the CaHAP surface. The molybdenum was fully oxidized, i.e. in oxidation state VI. The fits showed a relatively larger ratio of SrMoO$_4$ to MoO$_x$ species in the MoO$_3$/SrHAP samples compared to CaMoO$_4$ to MoO$_x$ ratio in the MoO$_3$/CaHAP samples (Table 3). This was in agreement with the higher surface area of the CaHAP samples compared to the SrHAP samples, giving the possibility for a larger amount of MoO$_x$ surface species and in agreement with the lower amount of Mo detected as CaMoO$_4$ compared to SmoO$_4$ by XRD. The differences in the XANES spectra for the 10 wt% MoO$_3$/CaHAP samples after exposure to reaction conditions were statistically insignificant, as the LCFs were approximately the same after 0 h, 100 h and 408 h on stream (Table 3). For the 10 wt% MoO$_3$/SrHAP and 15 wt% MoO$_3$/SrHAP an increase in the relative amount of Mo detected as supported MoO$_x$ after 100 h was observed, in agreement with the XRD results showing decreasing amounts of SrMoO$_4$. No further changes were observed after 250 and 600 h for the 10 wt% MoO$_3$/SrHAP. A decreasing relative amount of supported MoO$_x$ was seen with increasing nominal MoO$_3$ loading, in agreement with the decreasing surface area and the increasing amount of (Ca/Sr)MoO$_4$ measured by XRD.

Fourier transformed EXAFS spectra (k$^3$ weight) and fits (in R-space) for the fresh and spent catalyst samples and references are shown in Figure 10 and Figure S34. For the catalysts, the amplitude reduction factor was fitted to the CaMoO$_4$, SrMoO$_4$ and α-MoO$_3$ standards. The EXAFS fits were performed with 4 paths, 3 from CaMoO$_4$/SrMoO$_4$ and 1 from α-MoO$_3$ with fixed coordination numbers (Table 3 and Table 4). Despite that crystalline α-MoO$_3$ was not detected by XRD and XANES, α-MoO$_3$ was the best available model for the MoO$_x$ species detected by XANES and STEM. In general, good fits were achieved for all the samples, though, the quality of the data for the spent samples was generally not as good as for the fresh samples, because much lower amount of sample than optimal was available for pressing pellets. This was especially visible for the fits of 10 wt% MoO$_3$/CaHAP after 408 h, 10 wt% MoO$_3$/SrHAP after 600 h and 15 wt% MoO$_3$/SrHAP after 100 h in Figure 10d, j and l. From the
difference curves, it was observed that a smaller peak between 2 Å and 3 Å was in general not fitted but fitting an additional Mo–O path near this distance did not improve the fits.

For the CaHAP samples no significant differences in the path lengths were observed. As the EXAFS fits were performed with constant coordination numbers, changes in the relative amounts of the two phases CaMoO$_4$ and MoO$_3$ are reflected by the amplitude reduction factor $\sigma^2$, which decreases for paths corresponding to the phase that increases in relative amount. For the Mo–O$_{1.1}$ and Mo–Ca$_{1.1}$ paths (CaMoO$_4$) the $\sigma^2$ decreased with increasing Mo loading for the fresh samples but increased with time on stream for Mo–O$_{1.1}$. The $\sigma^2$ for the Mo–Mo$_{1.1}$ path

Figure 8. XANES linear combination fitting, performed from 19985 eV to 20045 eV, for MoO$_3$/CaHAP samples. (a) Fitting standards, (b) fresh 5 wt% MoO$_3$/CaHAP, (c) fresh 10 wt% MoO$_3$/CaHAP, (d) spent 10 wt% MoO$_3$/CaHAP after 100 h, (e) after 408 h and (f) fresh 15 wt% MoO$_3$/CaHAP.
Figure 9. XANES linear combination fitting, performed from 19985 eV to 20045 eV, for MoO$_3$/SrHAP samples. (a) Fitting standards, (b) fresh 5 wt% MoO$_3$/SrHAP, (c) fresh 10 wt% MoO$_3$/SrHAP, (d) spent 10 wt% MoO$_3$/SrHAP after 100 h, (e) after 250 h, (f) after 600 h, (g) fresh 15 wt% MoO$_3$/SrHAP, (h) spent 15 wt% MoO$_3$/SrHAP after 100 h.
(MoO₃) increased with increasing Mo loading but was almost constant with TOS. These observations were in agreement with a larger fraction of Mo present as CaMoO₄ with increasing loading, and a decreasing fraction of CaMoO₂, as observed by XRD.

The obtained path lengths for the 10 wt% MoO₃/SrHAP (Table 4) were close to CaHAP samples, but with the Mo–Mo paths being 0.08–0.1 Å longer. The fixed coordination numbers were slightly different for the SrHAP samples, in order to obtain good fits. Overall no trends in the structural parameters were seen, but the fits confirmed the observation that the samples consisted of both SrMoO₄ and MoO₃ species, both before and after exposure to reaction conditions.

The EXAFS spectrum of the 1 wt% MoO₃/γ-Al₂O₃ XANES LCF standard sample was also fitted with paths from the MoO₃ model, with free CN for all the paths. This gave a good fit for three of the four main peaks in the Fourier transformed spectrum (Figure S34). All paths showed coordination numbers between 1 and 2, giving good evidence to the Mo-oxide being supported MoO₃. Combined with the fact that no crystalline MoO₃ was detected by XRD, this sample was reasonable to use as XANES LCF fitting standard for supported MoO₃ (Figure S34d and Table S5). It was not possible to fit the peak at 2.3 Å, neither with an additional Mo–O, Mo–Al or Mo–Mo path.

In general the EXAFS fitting was in agreement with the XANES LCF and STEM, that molybdenum was in oxidation state 6+.

### Table 3. Structural parameters obtained from EXAFS fitting at the Mo K-edge for the fresh and spent MoO₃/CaHAP samples. The coordination number (CN) was fixed during fitting.

| Phase   | Path | TOS = 0 h⁽¹⁾ | TOS = 100 h⁽¹⁾ | TOS = 408 h⁽¹⁾ |
|---------|------|--------------|----------------|---------------|
|         |      | R [Å]        | CN             | α² [Å²]       | R [Å]        | CN             | α² [Å²]       | R [Å]        | CN             | α² [Å²]       |
| CaMoO₄  | Mo–O₁,₁ | 1.76          | 3              | 0.0027       | 1.76          | 3              | 0.0031       | 1.78          | 3              | 0.0033       |
|         | Mo–Ca₁₁ | 3.78          | 3              | 0.0144       | 3.76          | 3              | 0.0193       | 3.80          | 3              | 0.0156       |
|         | Mo–Mo₁₁ | 3.98          | 3              | 0.0182       | 4.05          | 3              | 0.0229       | –             | –              | –            |
| MoO₃    | Mo–Mo₁₁ | 3.40          | 1              | 0.0089       | 3.42          | 1              | 0.0091       | 3.41          | 1              | 0.0085       |

[a] ΔEₘ = −0.27 and χ₂⁺ = 21, [b] ΔEₘ = −0.10 and χ₂⁺ = 4, [c] kₓₚₓ = 12, ΔEₘ = 2.16 and χ₂⁺ = 3, [d] ΔEₘ = −0.27 and χ₂⁺ = 68, [e] ΔEₘ = −0.53 and χ₂⁺ = 40.

### Table 4. Structural parameters obtained from EXAFS fitting at the Mo K-edge for the fresh and spent MoO₃/SrHAP samples. The coordination number (CN) was fixed during fitting.

| Phase   | Path | TOS = 0 h⁽¹⁾ | TOS = 100 h⁽¹⁾ | TOS = 250 h⁽¹⁾ |
|---------|------|--------------|----------------|---------------|
|         |      | R [Å]        | CN             | α² [Å²]       | R [Å]        | CN             | α² [Å²]       | R [Å]        | CN             | α² [Å²]       |
| SrMoO₄  | Mo–O₁,₁ | 1.78          | 4              | 0.0022       | 1.74          | 4              | 0.0013       | 1.78          | 4              | 0.0022       |
|         | Mo–Sr₁₁ | 3.77          | 2              | 0.0109       | 3.92          | 2              | 0.0138       | 3.74          | 2              | 0.0060       |
|         | Mo–Mo₁₁ | 4.07          | 2              | 0.0071       | 4.04          | 2              | 0.0018       | 4.11          | 2              | 0.0077       |
| MoO₃    | Mo–Mo₁₁ | 3.48          | 1              | 0.0103       | 3.38          | 1              | 0.0209       | 3.48          | 1              | 0.0066       |

[a] ΔEₘ = 1.26 and χ₂⁺ = 23, [b] ΔEₘ = −6.64 and χ₂⁺ = 12, [c] ΔEₘ = 1.0 and χ₂⁺ = 9, [d] kₓₚₓ = 12, ΔEₘ = 1.35 and χ₂⁺ = 32, [e] ΔEₘ = 1.51 and χ₂⁺ = 9, [f] kₓₚₓ = 12, ΔEₘ = 1.81 and χ₂⁺ = 26, [g] ΔEₘ = 0.97 and χ₂⁺ = 4.
VI and present as crystalline (Ca/Sr)MoO$_4$, as also detected by XRD, and surface/amorphous MoO$_x$ species, both before and after exposure to reaction conditions.

2.2.5. X-ray Pair Distribution Function (PDF) Analysis

PDF analysis was carried out on the 5, 10 and 15 wt% MoO$_3$/CaHAP samples as well as the pure HAP support. As shown in Figure S35, the PDF of the pure HAP was described well by a
bulk HAP model over the entire r-range (for refined parameters see Tables S6). The crystalline phases found from the XRD analysis, HAP and CaMoO₄, modeled the long-range part of the PDFs from the MoO₃/CaHAP catalysts well, as seen in Figure 11(a), showing the fit of HAP and CaMoO₄ to the PDF obtained from the 15 wt% MoO₃/CaHAP (for refined parameters see Tables S7 and S8). However, the model did not fit the local structure, and discrepancies were seen in the first 6 Å of the PDF. This was also the case for the 5 and 10 wt% MoO₃/CaHAP samples (Figures S36 and S37, Tables S9 to S12). The difference curves between the observed PDFs and PDF fits for the three samples are shown in Figure 11(b), showing the discrepancies between observation and fits at low r values. All of them showed roughly the same peaks: a large peak around 1.5 Å, a peak (which appeared as a shoulder in the 15 wt% MoO₃/CaHAP sample) at 2 Å, a peak around 2.6 Å, a peak at approximately 3.2 Å and for the 10 wt% and 15 wt% samples a peak at 3.8 Å.

In Figure 11(c) and (d), the difference curve for the 15 wt% sample is compared to a number of PDFs from structures containing combinations of Mo, Ca, P, and O. The positions of the peaks in the difference curve were marked with vertical lines, while the peaks in the calculated PDFs are labelled with the atom pairs giving rise to the peaks.

From the comparison, the individual peaks could be assigned to certain interatomic distances. The first peak at 1.5 Å likely originated from P–O pairs as both the Ca–O and Mo–O bond distances are too long at 2.4 Å and 1.7–2.0 Å respectively. The second peak at 2 Å agreed well with a Mo–O distance. The Mo–O distance in MoO₂ is 2.0 Å, but it is unlikely that molybdenum was reduced during the sample preparation (calcination at 500 °C in air) and XAS showed molybdenum was in oxidation state VI. Mo–O distances of 2 Å are also observed in MoO₃, but the majority of Mo–O distances in MoO₃ are shorter. However, in compounds containing Mo and phosphate ions it is common to have a Mo–O distance of 2 Å, even for fully

Figure 11. (a) Fit of HAP and CaMoO₄ to the PDF obtained from the 15 wt% MoO₃/CaHAP plotted from 1–15 Å and 15–75 Å. (b) The difference curves from fitting HAP and CaMoO₄ to the PDFs from the 5, 10 and 15 wt% MoO₃/CaHAP samples. (c) and (d) Comparison of the difference curve from the fit in (a) (enlarged 3 times) to the PDFs from a number of structures containing a combination of Ca, Mo, P and O. The vertical lines indicate the positions of the peaks observed in the difference curve. The labels indicate which atom pair gives rise to the peaks in the calculated PDFs. The molybdophosphate PDF was calculated from the structure reported by Tan et al.[77]
oxidized Mo, for example seen in the molybdophosphate in Figure 11(c). This indicated that the molybdate ions in the structure were bound to phosphate, which also explained the formation of CaMoO₄ when molybdenum oxide reacted with HAP. It was not possible to index the peak at 2.6 Å as it is not a common interatomic distance in phases containing Mo(VI), Ca, O and P. The peak at 3.2 Å could either be assigned to a Mo–P pair or Mo–Mo pair between two edge-sharing [MoO₄] octahedra. It also agreed with a Ca–P distance, as for example in Ca₃(PO₄)₂ or HAP, but this would require the presence of a Ca–O peak at 2.4 Å, which was not observed. The final peak at 3.8 Å may be assigned to the Mo–Mo distance between two corner-sharing [MoO₄] octahedra or [MoO₄] tetrahedra, for example in molybdophosphate or CaMoO₄.

Thus, from PDF analysis, the molybdate species detected by STEM and XAS, besides the crystalline CaMoO₄, seemed to consist of [MoO₄]₃ octahedra, connected through at least corner-sharing, but possibly also edge-sharing. This is consistent with amorphous, disordered MoO₃ surface species as the atomic order did not go beyond more than 2–3 octahedra, which were likely also connected to [PO₄]₃⁻ groups. The MoO₃ species were not isolated oligomolybdate/polyoxometalate species, for example heptamolybdate, as the peak at 3.2 Å would have been much more pronounced and structural order would extend to higher r values in the PDF as shown on Figure S38 and AHM did not fit the XANES spectra.

2.2.6. Temperature Programmed Desorption and Reduction

All samples, the industrial FeMo reference catalyst and bulk MoO₃, were investigated by NH₃-TPD, CO₂-TPD and H₂-TPR to determine the acidity, basicity and reducibility of the samples. The acidity of all the CaHAP samples (Figure 12a) were higher than for the SrHAP samples (Figure 12b). For the CaHAP samples the addition of MoO₃ decreased the number of acidic sites, since the area under the ammonia desorption peak decreased, while the peak appeared at approximately the same temperature, in good agreement with CaHAP having only weak acid sites, desorbing pyridine already at 100 °C, as reported by Hill et al.[22] The nature of the acidity of CaHAP could be both Lewis[72,74] and Brønsted type.[13,24] The opposite was observed for the SrHAP samples, where the area under the ammonia desorption peak generally increased with the addition of MoO₃, with the exception of the 15 wt% MoO₃/SrHAP sample, which was less acidic than the 10 wt% MoO₃/SrHAP.

The CO₂-TPD, showed that the SrHAP had a larger number of basic sites than CaHAP (Figure S39a and b). The CO₂ desorption profile was deconvoluted into three distinct sites, but the overall desorption peak shape, peak temperatures and fits were very similar, with peaks at 120 °C and 160 °C and a shoulder at 200 °C. The major differences were the size of the shoulder/peak 3 at 200 °C and an additional peak 4 for the SrHAP support (Figure S39b). The addition of MoO₃ seemed to cover almost all the basic sites on the CaHAP, even with 5 wt% MoO₃ the maximum peak height decreased by two orders of magnitude (Figure S39a, c, e, g), whereas on the SrHAP the peak height only decreased by one order of magnitude and the overall peak shape stayed similar even with the addition of 15 wt% MoO₃ (Figure S39b, d, f, h). The calculated number of basic and acidic sites from the TPD experiments are summarized in Table 5. The surface density of basic sites was ~1·10⁻⁹ μmol CO₂/m² for the 5–15 wt% MoO₃/CaHAP and ~5·10⁻¹ μmol CO₂/m² for the 5–20 wt% MoO₃/SrHAP. In comparison, the industrial FeMo sample had 1.0·10⁻⁹ μmol CO₂/m² (Figure S40).

Advantageously, none of the samples had a high number or strength of basic nor acidic sites, in agreement with Hill et al.[22] who found CaHAP to be both less basic and less acidic than MgO and ZrO₂ showing only weak sites. Comparing surface density of both acidic and basic sites, the 10 and 15 wt% MoO₃/CaHAP samples most closely resembled the FeMo (Figure S41).

The catalyst samples, the two apatite supports and bulk MoO₃ (Sigma-Aldrich), calcium molybdate (Mo/Ca = 1.0) and strontium molybdate (Mo/Sr = 1.20) prepared in a previous

Figure 12. NH₃-TPD profiles for (a) CaHAP samples and (b) SrHAP samples.
work\textsuperscript{[20]} were subjected to H\textsubscript{2}-TPR (Figure 13). Bulk MoO\textsubscript{3} had two large distinguishable reduction peaks, where the low temperature reduction at 692°C stemmed from the reduction of Mo(VI) to Mo(IV) and the high temperature peak at 875°C corresponded to the reduction of Mo(IV) to Mo(0), as the hydrogen consumption related to the high temperature peak was about twice as high as for the low temperature peak. The pure apatite supports showed low reducibility, as expected. The CaMoO\textsubscript{3} reference only reduced at very high temperatures (Figure 13a). In contrast, the SrMoO\textsubscript{3} with Mo/Sr = 1.20 reduced at lower temperatures, with two separate reduction peaks, however, this was most likely reduction of the excess MoO\textsubscript{3} and not a reduction of the SrMoO\textsubscript{3}. In general, an increase in the MoO\textsubscript{3} content gave an increase in total H\textsubscript{2} consumption during the TPR (Figure 13). There was a significant difference in the reduction behavior of molybdenum oxide supported on CaHAP and SrHAP respectively. The CaHAP samples (Figure 13a) had no well-defined peaks but reduced over a broad temperature range with a number of small reduction peaks of approximately equal size. This could be an indication of the presence of different Mo species with different reduction behaviors. The SrHAP samples showed two distinct reduction peaks, which became larger with increasing nominal MoO\textsubscript{3} loading. Interestingly, the peak at 750–780°C became larger relative to the peak at 845–857°C with increasing loading. This indicate two different Mo species. The 750–780°C peak was also observed for the SrMoO\textsubscript{3} sample, while the 845–857°C peak was not. Together with the XRD and XAS results of increasing amounts of SrMoO\textsubscript{3} with increasing Mo loading this peak likely corresponded to this phase, while the 845–857°C peak likely originated from the surface molybdate species.

![Figure 13. H\textsubscript{2}-TPR profiles for (a) CaHAP samples and (b) SrHAP samples as well as MoO\textsubscript{3} and the respective molybdates for comparison.\textsuperscript{[20]} 200 mg of sample was used, with the exception of MoO\textsubscript{3} (25 mg).](image-url)

| Sample       | Total Basicity | Total Acidity | Total Reducibility |
|--------------|----------------|---------------|--------------------|
| MoO\textsubscript{3}  | 1.5 \times 10^{-1} | 6.9 \times 10^{-2} | 0.0               | 0.0          | 2.13 \times 10^{-2} | 2.89            |
| FeMo         | 4.1 \times 10^{-2} | 1.0 \times 10^{-2} | 4.9 \times 10^{-1} | 8.9 \times 10^{-1} | –             | –              |
| CaMoO\textsubscript{3} (Mo/Ca = 1:0)\textsuperscript{[20]} | 2.7 \times 10^{-1} | 7.8 \times 10^{-2} | –                 | –            | 5.64 \times 10^{-2} | 1.13            |
| CaHAP        | 2.0 \times 10^{-2} | 3.7 \times 10^{-2} | 4.9 \times 10^{-1} | 9.4 \times 10^{-1} | 4.70 \times 10^{-1} | 4.70 \times 10^{-1} |
| 5 wt% MoO\textsubscript{3}/CaHAP | 7.3 \times 10^{-3} | 1.5 \times 10^{-3} | 3.7 \times 10^{-1} | 7.5 \times 10^{-1} | 2.78 \times 10^{-1} | 6.73\textsuperscript{d} |
| 10 wt% MoO\textsubscript{3}/CaHAP | 4.0 \times 10^{-2} | 8.7 \times 10^{-4} | 3.2 \times 10^{-1} | 7.0 \times 10^{-1} | 2.72 \times 10^{-1} | 3.30\textsuperscript{d} |
| 15 wt% MoO\textsubscript{3}/CaHAP | 4.3 \times 10^{-2} | 1.1 \times 10^{-3} | 2.9 \times 10^{-1} | 7.1 \times 10^{-1} | 3.86 \times 10^{-1} | 3.32\textsuperscript{d} |
| SrMoO\textsubscript{3} (Mo/Sr = 1.20)\textsuperscript{[20]} | 2.9 \times 10^{-4} | 9.4 \times 10^{-3} | –                 | –            | 5.12 \times 10^{-1} | 1.18            |
| SrHAP        | 2.8 \times 10^{-1} | 7.1 \times 10^{-2} | 5.0 \times 10^{-1} | 1.6 \times 10^{-2} | 2.12 \times 10^{-2} | 2.10\textsuperscript{d} |
| 5 wt% MoO\textsubscript{3}/SrHAP | 1.4 \times 10^{-1} | 5.1 \times 10^{-3} | 1.6 \times 10^{-1} | 5.9 \times 10^{-2} | 1.22 \times 10^{-2} | 5.05\textsuperscript{d} |
| 10 wt% MoO\textsubscript{3}/SrHAP | 1.0 \times 10^{-1} | 3.9 \times 10^{-3} | 2.8 \times 10^{-1} | 1.0 \times 10^{-1} | 3.97 \times 10^{-1} | 5.05\textsuperscript{d} |
| 15 wt% MoO\textsubscript{3}/SrHAP | 1.6 \times 10^{-1} | 6.0 \times 10^{-3} | 2.5 \times 10^{-1} | 9.4 \times 10^{-2} | 5.04 \times 10^{-1} | 4.42\textsuperscript{d} |
| 20 wt% MoO\textsubscript{3}/SrHAP | 6.2 \times 10^{-2} | 3.7 \times 10^{-3} | 3.1 \times 10^{-1} | 1.9 \times 10^{-1} | 5.49 \times 10^{-1} | 3.66\textsuperscript{d} |

[a] H\textsubscript{2} consumption of the pure support was subtracted.
The total H₂ consumption during the TPR and the reduction peak temperatures observed in Figure 13 are summarized in Table 5 together with the H₂ consumption per moles of Mo. The CaHAP samples in general had the first reduction peak at a lower temperature than the SrHAP samples, and if comparing the onset of the reduction the difference became larger as the reduction profile for the SrHAP samples were sharper. Interestingly, all samples (with the exception of the supports) reduced more easily than bulk MoO₃ (this was also the case for 6.2 wt% MoO₃/α-Al₂O₃ and the FeMo industrial catalyst (Figure S42)). This may in part be due to the larger amount of MoO3 in the reactor when loading pure MoO3 as an increase in sample amount has been shown to increase the measured reduction temperature, though only 25 mg MoO₃ was loaded in comparison to 200 mg supported catalyst samples.

For all the samples the reduction happened at temperatures above reaction conditions for methanol oxidation. However, the reduction temperature has previously been observed to be significantly lower with methanol compared to hydrogen. It is of interest to note that the H₂ consumption per mol Mo in the supported samples was measured to be higher than 3, indicating an effect of the impregnation on the reducibility of the support.

2.3. Discussion

A surface layer of MoO₃ on the support has been found to be the active species for the selective oxidation of methanol to formaldehyde in FeMo catalysts. In this study we found finely dispersed molybdenum oxide on the surface of the 10 wt% MoO₃/CaHAP sample by STEM, which was believed to be amorphous MoO₃. XANES LCF analysis and EXAFS fitting also showed the presence of MoO₃ surface species with Mo in oxidation state VI. This was further substantiated by the PDF analysis, which showed that in the MoO₃/CaHAP samples, Mo was present as [MoO₃]₆-octahedra, in addition to the crystalline CaMoO₄. The [MoO₄]₆-octahedra were likely connected through corner- and maybe edge-sharing in groups of 2–3 octahedra. Additionally, there were indications from PDF that the [MoO₄]₆-octahedra may be bonded to phosphate groups at the support surface. Raman spectroscopy was attempted on the samples, as this method is often used to detect surface molybdate species, but only an intense fluorescence background signal was measurable.

A previous study of alkali earth metal molybdates from our group, showed that stoichiometric CaMoO₄ was stable under MeOH vapors, but catalytically not very active nor selective. This is in contrast to the MoO₃/CaHAP catalysts investigated in this work. CaMoO₄ was found by XRD, XANES, EXAFS and PDF on the MoO₃/CaHAP, however, this cannot be the active phase as the activity and selectivity of the MoO₃/CaHAP catalysts were much higher than pure CaMoO₄. Furthermore, excess MoO₃ on CaMoO₄ was found to quickly evaporate. Thus, the high activity, stability and selectivity of the HAP based catalyst must be related to the MoO₃ on the support surface.
SrHAP catalysts compared to the FeMo catalyst can be tolerated, e.g. by only using these more stable catalysts at the inlet of the reactor, where methanol concentration is high and temperature moderate. Alternatively, if the MoO$_3$/(Ca/Sr)HAP catalysts can be prepared or promoted to better selectivity than reported here, e.g. by adjusting pH during the co-precipitation to tune the resulting apatite surface basicity, they may be used throughout the whole reactor.

Analogous Mg and Ba based HAP catalysts were also attempted, but neither formed the apatite structure when precipitating and calcining as for Ca- and SrHAP. The XRD, BET and catalytic activity and selectivity results of these investigations are briefly summarized in the SI Section 4, Figures S43 to S46 and Tables S13 to S16.

3. Conclusion

The aim of this study was to find more stable and still active and selective catalysts of selective oxidation of methanol to formaldehyde. To reach this aim, molybdenum oxide supported on hydroxyapatite and the Sr analogue were synthesized and evaluated. The synthesis was confirmed by XRD to yield the desired hydroxyapatites and showed further the formation of CaMoO$_4$ and SrMoO$_4$ after the impregnation with AHM and calcination. A surface layer of MoO$_3$, consisting of distorted (MoO$_6$)$_4$-octahedra with corner and maybe edge sharing to an order of 2–3 octahedra was found on the surface of the 10 wt% MoO$_3$/CaHAP sample. This was substantiated by the XANES LCF analysis, STEM images and X-ray scattering with PDF analysis. This surface layer was found to be the active phase, with CaMoO$_4$/SrMoO$_4$ acting as tightly binding molybdenum reservoirs replenishing surface molybdate that evaporates under methanol vapors. The phosphate in the hydroxyapatite was proposed to increase the selectivity towards formaldehyde, by inhibiting over-oxidation compared to bulk CaMoO$_4$ and SrMoO$_4$. The HAP based catalysts showed impressive stability during long time on stream at harsh conditions (350 °C and 5 vol.% MeOH in the feed), as the 10 wt% MoO$_3$/CaHAP lost 80% activity after 408 h and the 10 wt% MoO$_3$/SrHAP lost 73% after 600 h, in comparison to an industrial FeMo reference catalyst which lost 86% within only 62 h. The catalysts also retained good selectivity towards formaldehyde (above 90%) and, importantly, the amount of Mo evaporating was much lower than for the FeMo catalyst, potentially reducing the temporal increase in pressure observed in industrial reactors due to Mo migration. Overall, this class of catalysts could fulfill the aim of more stable catalysts for selective oxidation of methanol.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Formox process · selective oxidation · hydroxyapatite · formaldehyde · methanol

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