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Modeling of the Molybdenum Loss in Iron Molybdate Catalyst Pellets for Selective Oxidation of Methanol to Formaldehyde†

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Abstract

The loss of molybdenum from industrial iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) catalyst pellets with an excess of molybdenum oxide was studied during selective oxidation of methanol to formaldehyde for up to about 10 days on stream at varying reaction conditions ($\text{MeOH} = 1.6\text{-}4.5\%$, $\text{O}_2 = 2.5\text{-}10\%$, $\text{H}_2\text{O} = 0\text{-}10.2\%$ in N_2 and temperature = 250, 300 and 350 °C). The changing morphology and the local elemental composition in the pellets were followed for increasing time on stream. Molybdenum was shown to volatilize, leaving a depleted zone starting at the pellet surface and moving inwards with time. For temperatures ≤ 300 °C only volatilization of the excess MoO_3 phase was observed. Increasing concentration of MeOH and temperature enhanced the rate of volatilization, the oxygen concentration had negligible effect, while increasing the H_2O concentration decreased the volatilization rate. At 350 °C ($\text{MeOH} = 4.5\%$, $\text{O}_2 = 10\%$, $\text{H}_2\text{O} = 0\%$ in N_2) Mo in the $\text{Fe}_2(\text{MoO}_4)_3$ phase was furthermore volatilized leading to the formation of the reduced ferrous molybdate (FeMoO_4). A dynamic 1D mathematical model for a single pellet, in which methanol oxidation to formaldehyde and simultaneous volatilization of free MoO_3 takes place, was developed. The model parameters were fitted using experimental data of the pellet weight loss while the evolution of the MoO_3 depletion layer thickness was used to validate the model. The model describes the data well and additionally predicts that deposition of MoO_3 behind the depletion layer front occurs under certain conditions, leading to a MoO_3 deposition layer, which was verified by scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS). Simulations with the model show that the overall loss of molybdenum is significantly slower for large pellets compared to small pellets, which is a key parameter for the success of the industrial process.

Contents

Abstract	2
Contents	3
1 Introduction.....	5
2 Experimental.....	7
2.1 Single pellet Mo loss measurements.....	7
2.2 Scanning Electron Microscopy.....	8
2.3 X-ray micro computed tomography	9
3 Results and discussion	10
3.1 SEM images.....	10
3.2 Mass loss of excess MoO ₃ at increasing TOS.....	14
3.2.1 Effect of MeOH	14
3.2.2 Effect of temperature	14
3.2.3 Effect of H ₂ O	15
3.2.4 Effect of oxygen	15
3.3 X-ray micro computed tomography	18
4 Model.....	19
4.1 Concentration profiles.....	21
4.1.1 Species mass balances.....	21
4.1.2 Rate of formation	21
4.2 Boundary and initial conditions.....	24
4.3 Diffusivity.....	24
4.4 Solution procedure	25
4.4.1 Estimation of pellet mass loss	26
4.5 Fitting procedure	26
4.6 Model predictions	29
4.6.1 Excess MoO ₃ profile.....	29
4.6.2 MeOH, Mo(g), H ₂ O and porosity profiles	30
4.6.3 Loss of excess MoO ₃	32
5 Discussion	34

5.1	Effect of catalyst pellet size	34
6	Conclusion	36
7	Acknowledgments	37
8	Supplementary data	37
9	References	37

Nomenclature			n_A	Reaction order of component A	-
			r	Distance in pellet	[m]
a_A	Activity of component A	-	r_A	Reaction rate of component A	[mol/m ³ _{Pellet} /s]
$D_{e,A}$	Effective diffusion coefficient of component A	[m ² /s]	R_h	Radius of hole in pellet	[m]
C_A	Concentration of component A	[mol/m ³]	R_p	Radius of pellet	[m]
C_A^0	Dimensionless concentration of component A	-	t	time	[s]
C_A^b	Bulk concentration of component A	[mol/m ³]	T	temperature	[K]
k_A	Rate constant of reaction A and pre-exponential factor of adsorption of component A	[s ⁻¹]	z	Dimensionless distance in pellet	-
K	Constant	-	ρ_A	Density of component A	[kg/m ³]
M_A	Molar mass of component A	[g/mol]	ε	Porosity of pellet	-

1 Introduction

Formaldehyde (CH₂O) is synthesized industrially by selective oxidation of methanol over an iron molybdate catalyst with excess molybdenum oxide according to (1)[1]:

The reaction is carried out in a multitubular reactor (tube length = 1 to 2 m) with stoichiometric excess of oxygen (MeOH $\approx$ 8-10 %, H₂O = 4-8 %, O₂ $\approx$ 10 % in N₂) at near atmospheric pressure with complete methanol conversion in a single pass giving a formaldehyde yield around 88-92 %, known as the Formox process [2]. The feed gas is introduced to the catalytic bed at 200-250 °C and due to the exothermic reaction a hotspot of 350-400 °C is formed in the reactor [3].

Molybdenum forms volatile species with methanol under the reaction conditions, which can deplete the catalyst pellets of Mo and leave behind molybdenum poor zones in the catalyst bed [4], [5]. The Mo depleted zones become rich in iron oxide sites, which are less selective towards formaldehyde, forming more CO and potentially CO₂ [6]–[10]. To counter the loss of Mo, excess MoO₃ is added to the commercial catalyst, thus containing Fe₂(MoO₄)₃ and MoO₃ as two distinct crystalline phases [7].

In the industrial reactor the volatilization of Mo occurs mainly in the initial part of the reactor, while the volatile Mo species decompose downstream in the reactor after the hotspot. The decomposed volatile Mo species deposits as needle like crystals in the void space between the catalyst pellets [3-11], which blocks the reactor and leads to increased pressure drop.

Ivanov and Dimitrov [12] performed experiments on single, industrial like reactor tubes for 15 months in the temperature range 200-340 °C (MeOH = 6.2 %, O₂ = 11 % in N₂). Their data show that the catalyst pellets placed

$\frac{1}{4}$ into the bed (temperature = 225-245 °C) were subjected to loss of Mo from the pellet surface. However, the pellet core was not affected. Furthermore, at high temperatures ($T > 300$ °C), they observed a reddish-brown coloration of the pellet surface due to formation of FeMoO_4 and Fe_2O_3 . Formation of FeMoO_4 and Fe_2O_3 is also observed elsewhere [3,13–17].

Anderson et al. [5] studied catalyst pellets extracted from an industrial plant after half and full lifetime and likewise observed the formation of FeMoO_4 and Fe_2O_3 . Furthermore, they quantified the amount of Mo in the catalyst pellets throughout the bed. After half and full process life time approximately the first $\frac{1}{4}$ and $\frac{1}{3}$ of the catalyst bed was depleted for Mo, respectively. Moreover, it was observed that Mo depleted pellets were subject to increased pore volume and decreased activity. The deposition of Mo downstream in the reactor predominantly occurred in the void space between the pellets after the hotspot, which is also observed elsewhere [3].

The Mo transport and downstream deposition leads to increased pressure drop over the reactor, which is one main reason for the rather short life time of only 1-2 years, after which the catalyst load must be replaced [5]. Another reason for replacement of the catalyst is loss of selectivity, which is also related to Mo depletion [14].

Popov et al. [4] studied the Mo volatilization from an iron molybdate catalyst under varying reaction conditions. They concluded that the rate of volatilization is mainly affected by the methanol concentration and suggested the formation of the volatile compounds $\text{MoO}_2(\text{OCH}_3)_2$, $\text{MoO}_2(\text{OH})(\text{OCH}_3)$, $\text{MoO}_2(\text{OCH}_3)$ and $\text{MoO}_2(\text{OH})$. They observed that the volatile Mo species condensed as a blue film on the reactor tube inner surface at the reactor outlet. Smith et al. [18] observed likewise a blue Mo-rich film during their experiments with single MoO_3 crystals under continuous flow of a MeOH-air mixture. Using XRD they concluded that the film layer consisted of $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$ and suggested two pathways for its formation. In the first pathway MeOH forms surface methoxy and hydroxyl groups upon adsorption on the MoO_3 surface and a molybdenum oxide

hydroxide molecule desorbs into the gas phase. The desorbed molecule then reacts with methanol in the gas phase forming $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$. In the second pathway surface molybdenum methoxides desorb directly as the observed molybdenum oxide-methoxide. The authors suggested that the second pathway was the most plausible [18] and this was also suggested by Ivanov and Dimitrov [12] and follows:

The volatilization of Mo and deposition downstream in the reactor leading to pressure drop buildup is a major unsolved issue of the iron molybdate catalysts. In our laboratories the volatilization has been studied at well-defined conditions for small catalyst particles (150-250 μm) [17], revealing that all excess MoO_3 volatilizes rapidly (TOS $\approx$ 10 h, MeOH = $\sim$ 5 %, O_2 = 10 % in N_2 at catalyst temp = 384-398 $^\circ\text{C}$) which is much faster than observed in industry. The results thus indicate that the rate of volatilization is strongly dependent on the catalyst particle size. In this work, the rate of volatilization of Mo from industrial catalyst pellets has been studied as a function of well-defined operating conditions and a single pellet model that take the relevant phenomena into account has, for the first time, been developed.

2 Experimental

2.1 Single pellet Mo loss measurements

The industrial iron molybdate catalyst pellets had a molar ratio of Mo to Fe of 2.4. The pellets were shaped as a cylinder with a hole in the middle (OD = 4.55 mm, hole diameter = 1.70 mm and length = 4 mm). A pellet was slid onto a thermocouple (OD = 1.5 mm) and centered in a tubular flow reactor (ID = 6.5 mm). A photo of the reactor and pellet can be seen in Figure S1. Three identical reactors containing one pellet each were placed in a three zone electrically heated furnace and operated in parallel. The feed gas was equally distributed between

the reactors using rotameters and needle valves. The feed gas composition was varied in the individual experiments between 1.6-4.5 vol.% MeOH, 2.5-10 vol.% O₂ and 0-10.2 vol.% H₂O in N₂, and was introduced at a total flowrate of 9 L/min (3 L/min per reactor, 1 bar, 273.15 K). N₂ and O₂ were introduced by mass flow controllers (Bronkhorst). Before entering the three reactors, a fraction of the gas was bubbled through two flasks in parallel containing MeOH ($\geq 99.9\%$, Sigma-Aldrich) and demineralized water respectively (0.5-1.1 L/min for MeOH and 0-1 L/min for H₂O). The gas was saturated by MeOH and H₂O respectively and the concentrations were controlled by heating the bubble-flasks (45 °C for MeOH and 72-80 °C for H₂O). The two saturated gas flows were mixed with the remaining gas to a single feed of the desired composition before entering the reactors. The respective thermocouples were placed through the pellets hole measuring the gas temperature just before the pellet (250 $\pm$ 3, 300 $\pm$ 3 and 350 $\pm$ 3 °C). The mass of the pellets was measured before and after the experiments. To ensure precise measurements, the pellets were initially dried at 120 °C and heat-treated at 420 °C after the experiments to ensure full oxidation of the catalyst [19].

2.2 Scanning Electron Microscopy

The Mo depleted catalyst pellets were cast in epoxy polymer and cut through the middle along the radial axis to reveal the cross sectional area of the pellet. The samples were coated with an electron conductive layer of carbon prior to investigation. Scanning Electron Microscopy (SEM) images were acquired in an Environmental SEM, FEI XL30 FEG, at 15 kV using the backscattered electron signal. EDS analyses were acquired in the electron microscope without standards at 15 kV with an EDAX liquid Nitrogen cooled Si(Li) detector and a liquid Nitrogen free Thermo Silicon Drift Detector (SDD).

2.3 X-ray micro computed tomography

X-ray tomograms were obtained using a ZEISS XRadia 410 Versa instrument. The instrument was operated at 140 kV and 10 W using the high energy 2 (HE2) filter and a 4X objective. For measurements of the whole sample 1601 projections with 5 sec exposure time were used, which resulted in a total measurement time of 3:02 h:min. A pixel size of 4.6 μm was obtained using a 2x2 binning. Image reconstruction was performed using the built-in acquisition and reconstruction software package provided by ZEISS.

Visualization, image analysis and phase segmentation were performed using the commercial software Avizo 9.5.0 (FEI). The following procedure was used: Initially the reconstructed volume of the whole catalyst was filtered using a nonlocal means filter which was applied on the individual xy planes with a search window of 21 pixels, a local neighborhood of 5 pixels, a similarity value 0.6 and using an adaptive choice of lambda. The pellet was segmented using the magic wand tool and characterizing the different phases by the following grey scale intensity values (outer air = 0-13658, depleted phase = 13659-27152 and non-depleted phase = 27153-65535). Both phases contained some holes which were not included in the segmentation. In order to fill these non-assigned holes in the volume, the interactive watershed tool provided by the segmentation editor was used. It uses a gradient magnitude image calculated by a quick Canny method, which controls the expansion of the markers used for the watershed expansion. After this step the depleted and non-depleted phases were segmented and the materials statistics module was applied to obtain the volumetric information of the two phases.

3 Results and discussion

3.1 SEM images

The scanning electron microscopy (SEM) images of the pellets cross section coupled with energy-dispersive X-ray spectroscopy (EDS) showed the depletion of Mo with increasing time on stream. In Figure 1 some characteristic samples are shown and more samples are shown in the supporting information (Figures S2 –S7).

For the fresh pellet (Figure 1 (a)) a mainly light grey (Mo/Fe = 2.4 atomic ratio) appearance throughout the pellet was observed with some smaller Mo rich inclusions (white) and voids (black)(Figure S2). For an exposed pellet (Figure 1 (b)) (Conditions: 4.4 % MeOH, 0 % H₂O, 10 % O₂ in N₂, 350 °C and time on stream (TOS) = 70 h) a Mo depleted, dark grey layer at the pellet surface was observed. EDS area scans at the surface region (Figure 2) revealed that the depleted layer had an atomic ratio of approximately Mo/Fe = 1.5, corresponding to pure Fe₂(MoO₄)₃. In the interior of the pellet the composition was unchanged with a Mo/Fe ratio of 2.4. For pellets exposed to 350 °C a zone with increased Mo (Mo/Fe = 2.8) compared to the fresh pellet was observed behind the depleted layer towards the center (Figure 2 (c)). For the pellets exposed to 350 °C and TOS ≥ 160 h (Figure 3), the composition in the depleted layer was approximately Mo/Fe = 1, which indicates that the initial Fe₂(MoO₄)₃ was reduced to the less Mo rich FeMoO₄ phase. Reduction of Fe₂(MoO₄)₃ and formation of FeMoO₄ is also observed elsewhere in the literature [17,20].

Water in the feed gas (10 %) slowed down the development of the depletion layer, and Mo deposition inside the pellet was not observed at ~350 °C (Figure 4).

For the depleted pellet treated with low oxygen concentration (Figure 5)(Conditions: 3.5 % MeOH, 0 % H₂O, 2.5 % O₂ in N₂, 300 °C and TOS = 288 h) white inclusions at the pellet surface region were observed, and shown by EDS to be Mo rich particles (Figure S7). The Mo inclusions were present both in the depletion layer and further

into the pellet. No inclusions were present in the first $\sim 100\ \mu\text{m}$ from the pellet surface. Volatilization of Mo has been observed to increase at lower oxygen concentration in the literature [4]. However, in this study the oxygen concentration in the feed gas was shown to have no effect on the overall mass loss of the pellet (Figure S12). To the authors knowledge the formation of Mo inclusions at low oxygen concentration (2.5 % O_2) has not been observed elsewhere in the literature, and is not fully understood.

Figure 1 – SEM images of the cross section of fresh (a) and depleted (b) pellets (Conditions: 4.5 % MeOH, 0 % H_2O , 10 % O_2 in N_2 , 300 °C and TOS = 71 h). Light grey indicates Mo rich areas, dark grey indicates Mo depleted areas and white indicate Mo rich inclusions.

Figure 2 – SEM images of the cross sectional surface regions of depleted pellets treated at (a) 250 °C, (b) 300 °C and (c) 350 °C. TOS = 71-78 h, 4.4-4.5 % MeOH, 0 % H_2O , 10 % O_2 in N_2 . Mo/Fe: area 1 = 1.6, area 2 = 2.5, area 3 = 2.4, area 4 = 1.5, area 5 = 2.4, area 6 = 1.6, area 7 = 2.8 and area 8 = 2.5.

Figure 3 - SEM image of the cross sectional surface region of a depleted pellet treated at 350 °C for 160 h (Conditions: 4.4 % MeOH, 0 % H₂O, 10 % O₂ in N₂). Mo/Fe: area 1 = 1.1, area 2 = 1.2, area 3 = 3.0 and area 4 = 2.5.

Figure 4 – SEM image of the cross sectional surface region in a depleted pellet treated at 350 °C for 73 h with water added to the gas phase (Conditions: 4.2 % MeOH, 9.3 % H₂O, 10 % O₂ in N₂). Mo/Fe: area 1 = 1.7, area 2 = 2.2 and area 3 = 2.5.

Figure 5 - SEM image of the cross sectional surface region in a depleted pellet treated at 300 °C for 288 h with low oxygen concentration (Conditions: 3.50 % MeOH, 0 % H₂O, 2.5 % O₂ in N₂). Mo/Fe: area 1 = 1.7, area 2 = 1.6, area 3 = 2.5, area 4 = 12.6, area 5 = 8.0 and area 6 = 5.1.

It is widely observed in the literature that Mo in the iron molybdate catalyst can form volatile species with MeOH and be transported away from the catalyst [2, 3, 7], which was also observed in the current work as blue molybdenum deposits at the reactor outlet. The SEM images combined with EDS of the depleted pellets show that the excess MoO₃ present in the catalyst forms volatile Mo species which diffuse through the pellet. At the pellet surface the Mo species leave the pellet and enter the bulk gas phase and is carried out of the reactor. The depletion layer has a rather sharp front, which indicates that the volatilization reaction is equilibrium limited and that the equilibrium is established at the front. The volatile Mo species formed at the front will also diffuse into the pellet. At ~350 °C deposition of excess Mo inside the pellet is observed. As the temperature increases the MeOH concentration through the pellet is decreasing faster due to the higher rate of reaction. The volatile Mo species likely decomposes inside the pellet pores as the MeOH concentration decreases towards the pellet center due to the equilibrium between MeOH and the Mo species according to reaction (2). The formation of FeMoO₄ is only observed at 350 °C, which indicates that Fe₂(MoO₄)₃ is significantly more stable than MoO₃ and that volatilization of Mo only occurs from the MoO₃ phase at moderate temperatures (≤ 300 °C) under the applied reaction conditions.

3.2 Mass loss of excess MoO_3 at increasing TOS

As the pellets underwent Mo depletion they were likewise subject to a corresponding mass loss with increasing time on stream. Figure 6-Figure 8 show the mass loss of the catalyst pellets at increasing TOS at varying temperature, MeOH and water concentrations. The mass loss is converted to the corresponding loss of the excess MoO_3 phase assuming that only this phase forms volatile Mo species. The 95 % confidence interval of the mass loss measurement were calculated to ± 6.9 % (ESI section 3).

All applied reaction conditions showed the same trend in the mass loss rate with increasing TOS. Initially the mass loss was fast, due to the high MeOH concentration at the pellet surface, which quickly volatilizes the excess MoO_3 present there, according to (2). After 10-20 h on stream the rate decreases, due to the effect of decreased MeOH concentration at the developed depletion layer front and diffusion limitations of the formed Mo species out of the pellet. These inhibiting effects increasingly slowed down the rate of depletion with time on stream.

3.2.1 Effect of MeOH

The MeOH concentration strongly affects the mass loss rate of the catalyst pellet (Figure 6). As discussed in the introduction similar results have been observed for Mo volatilization in the literature [4, 18].

3.2.2 Effect of temperature

The volatilization rate of solid MoO_3 in the catalyst with MeOH (2) increases with increasing temperature (Figure 7). However, the rate of reaction for MeOH to formaldehyde will likewise increase, which counteract the rate of volatilization due to the decreasing MeOH concentration inside the pellet. Furthermore, the rate of diffusion of the gaseous species out of the pellet will also increase at increasing temperature. The overall loss of Mo from the pellet is affected by all these contributions and the net effect is an increased rate of Mo loss

from the pellets with increasing temperature at the applied reaction conditions (MeOH = ~ 4.4 %, H₂O = 0 %, O₂ = 10 % in N₂).

3.2.3 Effect of H₂O

An increased H₂O concentration decreases the mass loss rate, which indicates that H₂O inhibits the volatilization reaction (2)(Figure 8). H₂O is likewise known to inhibit the oxidation of MeOH (1) [21], which will increase the MeOH concentration through the pellet and an increased volatilization rate might be expected. However, the mass loss measurements show this is not the case and that H₂O overall inhibits the mass loss of the pellet. This indicates that the volatile Mo species are formed during the catalytic cycle, likely as a low concentration side product.

3.2.4 Effect of oxygen

Varying the oxygen concentration (2.5-10 % O₂, ~2 % MeOH, 0 % H₂O in N₂) had no effect on the mass loss rate of the catalyst pellet (Figure S3). Mo-rich inclusions are observed with SEM at an O₂ concentration of 2.5 % (Figure 5), indicating that Mo is mobilized but retained in the catalyst pellet as Mo-rich inclusions.

Figure 6 – Influence of MeOH concentration on the overall loss of excess MoO₃ in the pellets as a function of TOS. Treated at MeOH = 1.6-4.5 %, H₂O = 0 %, O₂ = 10 % in N₂ at 300 °C. Mo/Fe = 2.4. Flow rate = 3000 mL/min (1 bar, 273.15 K).

Figure 7 – Influence of temperature on the overall loss of excess MoO₃ in the pellets as function of TOS. Treated at MeOH = 4.4-4.5 %, H₂O = 0 %, O₂ = 10 % in N₂ at 250-350°C. Mo/Fe = 2.4. Flow rate = 3000 mL/min (1 bar, 273.15 K). Data point at 350 °C and TOS = 238 h is equal to 50.4 % loss of excess MoO₃.

Figure 8 – Influence of water concentration on the overall loss of excess MoO₃ in the pellets as function of TOS. Treated at MeOH = 4.0-4.5 %, H₂O= 0-10.2 %, O₂ = 10 % in N₂ at 300 °C. Mo/Fe = 2.4. Flow rate = 3000 mL/min (1 bar, 273.15 K).

3.3 X-ray micro computed tomography

For non-destructive information on a whole catalyst pellet and complementary insights to SEM cross section images, X-ray micro computed tomography (μ -CT) was conducted on a depleted pellet (Figure 9) after 64 h on stream at 350 °C, MeOH = 4.4 %, H₂O = 0 % O₂ = 10 % in N₂. This technique revealed the MoO₃ depletion development throughout the entire pellet. Figure 9 shows an image of the entire axial cross section of the depleted pellet. The depletion layer has evolved evenly from the outer surface of the pellet and from the top surface facing towards the reactor inlet. Only a slight depletion has evolved from the inner surface and from the bottom surface facing away from the reactor inlet. During exposure the inner hole of the pellet was blocked by a thermocouple and the downstream end of the pellet was facing a spacer centering the pellet in the reactor (see Figure S1). The blocking of the inner and end surface lead to only slight depletion from these surfaces. Segmentation of the depleted and non-depleted areas of the pellet showed that 20.3 vol.% (10.8 of 53.1 mm³) of the entire pellet were subject to depletion, corresponding to a mass loss of 6.19 % at Mo/Fe = 2.4. The measured mass loss is however slightly lower (5.97 %), since some of the volatilized MoO₃ have moved inside the pellet. The depletion layer thickness in the radial direction was measured to approximately 110 μ m. Images of the cross-section in the radial plane through the pellet (Figure S8) and a movie showing the depletion through the entire pellet can be seen in the ESI.

Figure 9 – X-ray micro computed tomography image of the entire axial cross section in a depleted pellet (Conditions: 4.4 % MeOH, 0 % H₂O, 10 % O₂ in N₂, 350 °C and TOS = 64 h). Dark grey indicates the less X-ray absorbing depleted layer and light grey indicates a higher absorbing non-depleted material, while white indicates areas of strong absorption due to Mo deposition.

4 Model

In this section, the single catalyst pellet model is derived describing the concentration profiles of MeOH, H₂O, solid MoO₃ and volatile Mo-species. Methanol diffuses from the bulk gas phase into the pellet at the surface, where it is primarily oxidized to formaldehyde and water, which diffuses out of the pellet. Furthermore, methanol and solid MoO₃ in the catalyst react to form the volatile Mo-species. The volatile Mo-species can either diffuse inwards or outwards the pellet or it can decompose and depositing solid MoO₃. The volatile Mo-species enters the bulk gas phase at the pellet surface. There is no diffusion of solid MoO₃, however it is removed during volatilization.

The industrial catalyst pellets are cylindrical with a hole in the middle. During experiments the pellets were placed on a thermocouple blocking the hole. Only small amounts of Mo volatilization were observed from the inner surface and the end surface facing away from the reactor inlet (Figure 9). Figure 10 shows a schematic of the cylindrical cross section.

Figure 10 – Schematic of the catalyst pellet system with the cross sectional view of the cylindrical shape of the. The green lines are the pellet surface. The radius of the pellet is R_p and the radius of the hole in the pellet is R_h .

The following assumptions have been made during the derivation and solution of the single catalyst pellet model:

- The volatilization reaction of MoO_3 with MeOH follows the reversible reaction:

- The volatile Mo species is $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$
- Mo in iron molybdate is not volatile.
- No film resistance at the pellet surface.

4.1 Concentration profiles

4.1.1 Species mass balances

The concentration profiles in the pellet can be calculated by setting up a shell mole balance over a small section of the pellet, taking the diffusion in and out of the element into account, and the respective formation and accumulation at the position ($S1^+$). The diffusion can be calculated by Fick's first law of diffusion ($S2^+$ where the diffusion coefficient in the pellet is dependent on the porosity ($S3^+$). Due to the volatilization of Mo in the pellet the porosity is dependent on the time due to the changing concentration of solid Mo ($S4-S5^+$) at a given position. The balance is reduced ($S6-S7^+$) and becomes Equation (3) (Table 1), where r equal to zero is at the center of the cylindrical pellet, R_h is at the inner pellet surface and R_p is at the outer surface. With respect to solid Mo there is no diffusion and the diffusion coefficient is thus equal to zero.

4.1.2 Rate of formation

4.1.2.1 MeOH and H₂O

Bibin and Popov [22] studied the kinetics of selective oxidation of MeOH over iron molybdate catalysts (1) and suggested a rate expression (4), which takes the inhibition by water and MeOH into account. Water is formed during oxidation of MeOH to formaldehyde (5). The selective oxidation reaction is much faster than the volatilization of solid Mo in the catalyst. Only the contribution from the oxidation of MeOH is taken into account with respect to the rate of reaction of MeOH and H₂O.

4.1.2.2 Solid and volatile Mo

MeOH and solid MoO_3 in the catalyst reversibly form a volatile gaseous Mo species. The obtained mass loss data at varying conditions and TOS, reveal that water inhibits the volatilization reaction of Mo. The reaction mechanism is not fully understood and several volatile Mo species have been proposed as discussed above, of which $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$ appears to be the most likely species [4][18]. The rate expression with respect to volatilization of Mo can be described in several ways. Two rate expressions have been tested in the model and fitted to the experimental data. The first expression was a power-law rate expression, with different orders in both the forward reaction between MeOH and solid MoO_3 and backward reaction between $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$ and H_2O (2). This expression was found to overestimate the deposition of Mo inside the pellet at zero H_2O bulk concentration. Both the reaction rates are fast and an equilibrium is approximately reached at the depletion front. However, for zero H_2O at the pellet surface, only the forward reaction will take place, leading to almost instantaneous volatilization of Mo at the pellet surface. According to that model the formed volatile Mo-species will then mistakenly diffuse inside the pellet and decompose where water is present due to the oxidation of MeOH. To better implement the inhibiting effect of water a Langmuir-Hinshelwood type expression is used for the forward reaction and only the concentration of the volatile Mo-species is taken into account for the backward rate. Due to the limited amount of data, a temperature dependency of the water inhibition is not included. The reversible volatilization rate expression with respect to gaseous Mo, Equation (6), and solid Mo, Equation (7), is shown in Table 1. a_{MoO_3} has the value of one when there is solid MoO_3 present and zero when there is not.

Table 1 – Equations for calculation of the concentration profiles in the pellet with respect to MeOH, H₂O, volatile Mo species and solid MoO₃. With respect to MoO₃ the diffusion (D_{e,MoO_3}^0) is zero.

Concentration profile	
$\frac{D_{e,i}^0}{\varepsilon^0} \frac{\partial C_i}{\partial r} \frac{\partial \varepsilon(r)}{\partial r} + \frac{D_{e,i}^0}{\varepsilon^0} \frac{\partial^2 C_i}{\partial r^2} \varepsilon(r)$ $+ \frac{1}{R_h + r} \frac{D_{e,i}^0}{\varepsilon^0} \frac{\partial C_i}{\partial r} \varepsilon(r) + r_i = \frac{\partial C_i}{\partial t} \varepsilon(r)$	(3)
Reaction rate expressions	
$r_{MeOH} = - \frac{k_{MeOH} C_{MeOH}}{1 + k_1 C_{MeOH} + k_2 C_{H_2O}} \rho_{FeMo}$	$\left[\frac{\text{mol}}{m^3 \cdot s} \right]$ (4)
$r_{H_2O} = \frac{k_{MeOH} C_{MeOH}}{1 + k_1 C_{MeOH} + k_2 C_{H_2O}} \rho_{FeMo}$	$\left[\frac{\text{mol}}{m^3 \cdot s} \right]$ (5)
$r_{Mo(g)} = \frac{k^+ a_{MoO_3} C_{MeOH}^{n_{MeOH}}}{1 + K_3 C_{H_2O}} - k^- C_{Mo(g)}^{n_{Mo(g)}}$	$\left[\frac{\text{mol}}{m^3 \cdot s} \right]$ (6)
$r_{MoO_3} = - \frac{k^+ a_{MoO_3} C_{MeOH}^{n_{MeOH}}}{1 + K_3 C_{H_2O}} + k^- C_{Mo(g)}^{n_{Mo(g)}}$	$\left[\frac{\text{mol}}{m^3 \cdot s} \right]$ (7)
Boundary conditions	
$C_i(t, R_p) = C_i^b$	(8)
$\frac{\partial C_i(t, R_h)}{\partial r} = 0$	(9)
Initial conditions for MeOH, H ₂ O and Mo(g)	
$C_i(0, r) = 0$	(10)
Initial condition for MoO ₃	
$C_i(0, r) = C_i^0$	(11)

4.2 Boundary and initial conditions

It is assumed that there is no gas film layer at the catalyst surface and thus the MeOH and H₂O concentrations are equal to the bulk concentrations. Furthermore, it is assumed that there is no gradient at the inner catalyst surface since it is blocked by the thermocouple on which the pellet is hanging. It is assumed that there is no initial concentration of gaseous species in the pellet. The boundary and initial conditions become Equations (8)-(11) in (Table 1).

4.3 Diffusivity

The effective diffusion coefficient of MeOH, $D_{e,MeOH}^0$ (m²/s), at a given temperature, T is estimated by:

$$D_{e,MeOH}^0 = K_1 \left(\frac{T^{K_2}}{T_{Ref}^{K_2}} \right) \quad (12)$$

Where K_1 and K_2 are constants and T_{Ref} is a reference temperature.

The effective diffusion coefficient of the gaseous Mo-species (Mo₂O₅(OCH₃)₂) and water is estimated using Chapman-Enskog theory for diffusion, using the MeOH as reference species:

$$D_{e,i}^0 = D_{e,MeOH}^0 \frac{\sqrt{1/M_{gas} + 1/M_i}}{\sqrt{1/M_{gas} + 1/M_{MeOH}}} \quad (13)$$

Where $D_{e,i}^0$ is the effective diffusion coefficient (m²/s) and M_i is the molar weight (g/mol) of component i .

M_{MeOH} and M_{gas} is the molar weight of MeOH and the entire gas (g/mol) respectively.

4.4 Solution procedure

Before the system of equations was solved, it was made dimensionless (S8-S24). The partial differential equation system was transformed to ordinary differential equations by discretization in the pellet radial dimension using a central finite difference scheme and solved using the method of lines (MoL) with the build-in Matlab solver ODE15s.

The activity of the solid MoO_3 (a_{MoO_3} see equation (6)-(7)) is equal to 1 if there is solid MoO_3 present and 0 if all MoO_3 has volatilized. This step changes makes the system very stiff and difficult to solve numerically. To make the system less stiff the activity is replaced by the following expression:

$$a_{\text{MoO}_3} \approx \frac{K \bar{C}_{\text{MoO}_3}}{1 + K \bar{C}_{\text{MoO}_3}} \text{ for } K \gg \bar{C}_{\text{MoO}_3} \text{ and } K \gg 1 \quad (14)$$

While MoO_3 is present, the expression will be close to zero order behavior. However, when the concentration of MoO_3 approaches 0 the expression will change to first order behavior. By replacing the activity by this expression the system becomes less stiff.

4.4.1 Estimation of pellet mass loss

The model predicts the excess MoO₃ profile through the radial direction of the pellet. The profile is converted to the remaining excess MoO₃ in the pellet, by taking the cylindrical geometry of the radial plane into account as follows:

$$\text{Excess MoO}_3 = \int_{R_h}^{R_p} C_{\text{MoO}_3}(r) \frac{r}{R_p^2 - R_h^2} dr \quad (15)$$

Where $C_{\text{MoO}_3}(r)$ is the predicted concentration of excess MoO₃ at the position r and R_p and R_h are the outer and inner radius respectively of the pellet.

Furthermore, for comparison of the model results with the experimental data, the depletion layer thickness at the top of the pellet was assumed to be equal to the thickness in the radial plane.

4.5 Fitting procedure

The model predicts the profiles through the catalyst pellet of the various species and the total loss of excess MoO₃ from the pellet. The total Mo loss can simply be converted to the corresponding mass loss. The model is fitted towards the measured mass loss data shown in Figure 6-Figure 8 indicating a good fit to the data. The parameters to be fitted in the model are the reaction orders, rate constants of the rate expressions (4)-(7) and the adsorption equilibrium constant (K_3) with respect to water (6)-(7).

The backwards volatilization rate constant (k^-), is fitted using a modified Arrhenius equation as follows:

$$k^{-}(T) = k^{-}(T_{Ref}) \cdot \exp\left(\frac{-E_a^{-}}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{Ref}}\right)\right) \quad (16)$$

Where $k^{-}(T_{Ref})$ is the backwards rate constant at a reference temperature (300 °C). By introducing a reference temperature the correlation between the pre-exponential factor and the activation energy is significantly decreased [23]. Due to the limited amount of data the water equilibrium constant is assumed independent of temperature.

The backwards volatilization rate constant at the reference temperature ($k^{-}(T_{Ref})$), the activation energy (E_a^{-}), the reaction orders and waters adsorption equilibrium constant (K_3) are fitted to the mass loss data using the built-in MATLAB optimization tool `fmincon`. The fitted parameters are used in the built-in MATLAB statistic tool `nlinfit`, which provide the statistics used to calculate the 95 % confidence intervals of the fitted parameters (Table 2), the covariance matrix and the Pearson's correlation coefficients (Table S4 and Table S5). The correlation between the model parameters is low (< 29 %), which indicate that all the parameters are relevant for the model.

The rate constants with respect to the main reaction (k_{MeOH} , k_1 and k_2) were fitted to methanol conversion data not enclosed here. Popov et al. [4] studied the volatilization of Mo from the iron molybdate catalyst, and reported a rate constant of Mo volatilization of $4.4 \times 10^{-3} \text{ s}^{-1}$ at low contact time (< 0.005 s). This value was fixed and used independently of temperature. The backward volatilization rates were fitted independently for the different temperatures towards the mass loss of the pellets. The fitted constants and the forward volatilization rate constant are shown in Table 2. Since the forward volatilization rate constant, k^{+} , is kept constant at all temperatures, the activation energy (E_a^{-}) of the backward rate constant ($k^{-}(T)$) is negative, yielding faster overall volatilization at increased temperature.

Table 2 – Fitted reaction orders and rate constants (95 % confidence intervals) for the single pellet model (Table 1).

Rate constants	
$n_{MeOH} = 1.50 \pm 0.02$	(17)
$n_{Mo(g)} = 1.00 \pm 0.01$	(18)
$K_3 = 64.89 \pm 0.91$	(19)
$k_+ = 4.4 \cdot 10^{-3} \left[s^{-1} \right] [4]$	(20)
$E_a^- = -45.7 \pm 0.7 \left[\frac{kJ}{mol} \right]$	(21)
$k^-(T_{Ref}) = (1.47 \pm 0.018) \cdot 10^6 \left[s^{-1} \right]$	(22)

4.6 Model predictions

4.6.1 Excess MoO_3 profile

Figure 11 shows the model predictions of the radial excess MoO_3 profiles and the measured depletion layer thickness for a representative section of the depleted pellets investigated by SEM-EDS (Figure 2 and Figure 4) and X-ray μ -CT (Figure 9). The model is only fitted towards the mass loss measurements, and so the corresponding prediction of the Mo profiles through the pellets can be used as independent validation of the models capability to predict the Mo depletion behavior. The model predicts the thickness of the depletion layer well and correctly predicts the deposition behavior of MoO_3 inside the pellet at high temperature and no H_2O in the feed (350 °C, MeOH = 4.4 %, H_2O = 0 %, O_2 = 10 % in N_2). With respect to the depleted pellet investigated by μ -CT, the depletion of the entire pellet was estimated to 20.3 vol.% by segmentation, which corresponds to a predicted depletion layer at a distance equal to 0.85. The depletion layer thickness measured with μ -CT is in good agreement with the model prediction (0.86).

Figure 11 – Model prediction of MoO_3 profile (lines) and depletion layer thickness (squares) across the radial direction of the pellet. Pellet distance = 0 is equal to the inner surface and pellet distance = 1 is equal to outer surface. Initial Mo/Fe = 2.4. O_2 = 10 % and N_2 as balance.

4.6.2 MeOH, Mo(g), H₂O and porosity profiles

For the representative section of pellets shown in Figure 11, the MeOH, Mo(g), H₂O and porosity profiles are shown in Figure 12. For all gaseous species the concentration is equal to the feed concentration at the pellet surface (pellet distance = 1) due to the assumption of no gas film resistance. MeOH is converted through the pellet forming formaldehyde along with H₂O. As expected high bulk H₂O concentration (9.3 %) inhibits the MeOH conversion (compare red and green curves at 350 C). The volatile Mo species (Mo(g)) are formed by MeOH and solid excess MoO₃ in the pellet. At the inside of the depletion front the Mo species follows the trend of MeOH. However, outside the front there is no excess MoO₃ to form the Mo species. The concentration of Mo species decreases from a maximum at the front to zero (the imposed bulk concentration) through the depleted layer. Also note that the concentration of the volatile Mo species is 12 orders of magnitude lower than the MeOH concentration. Despite this low value, it is enough to remove significant levels of MoO₃ with time. The porosity increases as the pellet is depleted of excess MoO₃, and likewise decreases when MoO₃ is deposited inside the pellet.

Figure 12 - Model prediction of MeOH, volatile Mo species (Mo(g)), H₂O and the porosity profiles across the radial direction of the pellet. Pellet distance = 0 is equal to the inner surface and pellet distance = 1 is equal to outer surface. Initial Mo/Fe = 2.4. The legend is the same for all figures.

4.6.3 Loss of excess MoO₃

The model is capable of predicting the corresponding loss of excess MoO₃ at varying reaction conditions with time on stream with reasonable accuracy (Figure 6-Figure 8). The equilibrium of the volatilization reaction (2) is shifted towards the volatile Mo species and the loss of excess MoO₃ in the pellet with increasing temperature (Figure 7). At a temperature of 350 °C and TOS above 159 h formation of FeMoO₄ in the depletion layer takes place, which the model does not take into account, hence the underestimation of the excess MoO₃ loss. Water inhibits the forward volatilization reaction which in turn decreases the volatilization rate with increasing water concentration (Figure 6). However, the forward volatilization reaction is enhanced by the MeOH concentration and the rate of volatilization increases with increasing MeOH concentration (Figure 6).

To further verify the model, two additional sets of data were generated (Figure 13 and Figure 14) at varying temperature and other reaction conditions (MeOH = ~2 %, H₂O = 0 % and MeOH = ~4 %, H₂O = ~10 %, both at O₂ = 10 %, in N₂). At low MeOH concentration (1.6-1.7 % MeOH (Figure 13)) the model slightly over predicts the loss of MoO₃. At high H₂O concentration (9.4-10.2 % H₂O (Figure 14)) the model prediction is rather accurate at 250 and 300 °C. However, at 350 °C the model slightly under predicts the loss of MoO₃. The inaccurate prediction at low MeOH concentration indicates that there is an effect in the volatilization of MoO₃ that the model does not account for. Furthermore, the inaccurate predictions at 350 °C indicate that there is likely a temperature dependency of the inhibiting effect of water (K_3) on the volatilization of MoO₃, which is not taken into account in the model due to the limited amount of data. Measuring a larger amount of data and including this temperature effect in the model is expected to improve the accuracy of the model at all temperatures.

Figure 13 - Mass loss of excess MoO_3 in pellets at increasing TOS. Treated at $\text{MeOH} = 1.6\text{-}1.7\%$, $\text{H}_2\text{O} = 0\%$, $\text{O}_2 = 10\%$ in N_2 at 300-350 °C. $\text{Mo/Fe} = 2.4$. Flow rate = 3000 mL/min (1 bar, 273.15 K).

Figure 14 - Mass loss of excess MoO_3 in pellets at increasing TOS. $\text{MeOH} = 3.6\text{-}4.2\%$, $\text{H}_2\text{O} = 9.4\text{-}10.2\%$, $\text{O}_2 = 10\%$ in N_2 at 250-350 °C. $\text{Mo/Fe} = 2.4$. Flow rate = 3000 mL/min (1 bar, 273.15 K).

Figure 15 shows a comparison of the measured and predicted mass loss for the applied reaction conditions.

90 % of the predictions are within 7 % of the measurements, which confirms that the model predictions are in good agreement with the measured data. The two data points in Figure 7 where FeMoO_4 were formed are not included.

Figure 15 – Comparison of predicted vs measured excess MoO_3 in pellet.

5 Discussion

5.1 Effect of catalyst pellet size

As reported by the authors [17], excess MoO_3 volatilizes completely from small catalyst particles within hours (TOS = 10 h, sieve fraction 150-250 nm, initial Mo/Fe = 2). However, in the current work Mo volatilization from catalyst pellets is significantly slower. The significant difference in the overall rate of Mo volatilization is mainly due to the difference in the size between the small particles and the catalyst pellets. For the small catalyst particles the depletion layer only has to develop a small distance to reach the center of the particle and completely volatilize all excess MoO_3 . However, for the larger pellets the depletion layer must develop a larger

distance through the pellet, and the time to completely volatilize all MoO_3 in the pellet will be significantly higher.

To demonstrate the effect of the catalyst pellet size, the model has been used calculate the loss of excess MoO_3 at varying pellet size (MeOH = 5 %, H_2O = 5 % at 300 °C). The pellets size has been scaled with respect to volume keeping the ratio between the dimensions constant (pellet length, inner and outer radius). The loss of excess Mo can be seen in Figure 16. The pellet size affects the overall depletion of Mo and by increasing the pellet volume to 200 % the depletion is decreased from 21.5 to 17.2 % after 400 h on stream (corresponding to a decrease of 20 %).

However, increasing the pellet size might lead to other process challenges, such as difficult packing of the catalyst in the reactor tubes and non-intended high temperatures in the pellet center. Furthermore, the overall process selectivity might be affected, due to higher formaldehyde concentration inside larger pellets leading to increased oxidation of formaldehyde to CO [24].

Figure 16 – Predicted mass loss of excess MoO_3 in pellets at increasing TOS. The ratios of the pellet dimensions are constant (pellet length, inner and outer radius). MeOH = 5 %, H_2O = 5 % at 300°C. Initial Mo/Fe = 2.4.

6 Conclusion

The influence of temperature and concentration of methanol and water on the molybdenum loss from iron molybdate catalyst pellets ($\text{Fe}_2(\text{MoO}_4)_3$ with excess MoO_3 corresponding to a molar Mo/Fe ratio of 2.4) used in the oxidation of methanol to formaldehyde was investigated experimentally. The volatilization and diffusion of molybdenum, leads to a layer depleted of excess MoO_3 evolving from the surface of the catalyst pellet. The rate of depletion is increased by MeOH and temperature, due to the volatilization reaction between MeOH and solid MoO_3 in the catalyst. Water in the gas phase inhibits the volatilization reaction and the rate of depletion. A 1D dynamic single particle model was furthermore developed and compared to experimental data. The model simultaneously calculates the formation of formaldehyde in the pellet, the volatilization of Mo and subsequent transport of the volatile Mo species into and out of the pellet as function of time. The model parameters were fitted to the overall mass loss of the pellets at varying reaction conditions and time on stream, using a feed composition of 1.6-4.5 % MeOH, 0-10.2% H_2O , 10 % O_2 balance N_2 at 250 – 350 °C. The model is capable of describing the molybdenum loss and corresponding depletion layer thickness of a single catalyst pellet. The model shows a significant effect of pellet size on the overall rate of MoO_3 volatilization and the use of pellets in the industrial process is required to dampen the loss of Mo. Incorporation of the single pellet model into a reactor model could be a useful tool to predict the loss of Mo and the associated pressure drop development in a reactor and estimation of process lifetime at varying reaction conditions and is ongoing in our group.

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8 Supplementary data

Detailed model derivation, SEM images and pellet mass loss data with corresponding model predictions.

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