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Review

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Modeling of Molybdenum Transport and Pressure Drop Increase in Fixed Bed Reactors used for Selective Oxidation of Methanol to Formaldehyde using Iron Molybdate Catalysts†

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Abstract

A dynamic model was developed for a single reactor tube, in which methanol oxidation to formaldehyde over an iron molybdate/molybdenum oxide catalyst takes place simultaneously with transport of MoO_3 from the catalyst through the reactor. A previously developed dynamic 1D mathematical model for a single ring-shaped cylindrical catalyst pellet, in which volatilization of MoO_3 takes place, was implemented in the reactor model. Known axial profiles in a pilot scale reactor with respect to MeOH and H_2O concentration and temperature were used as input to the model. MeOH forms volatile Mo-species with solid MoO_3 in the catalyst pellets, which diffuses to the bulk gas phase and is transported through the reactor, leading to MoO_3 depleted pellets. Volatilization of MoO_3 from the pellets occur at the inlet of the reactor. As MeOH is oxidized down the reactor, the volatile Mo-species decomposes via the reverse reaction that formed them. Deposition of MoO_3 downstream in the reactor decreases the void space between the catalyst pellets leading to increased pressure drop. The hydraulic diameter of the catalyst pellets and the porosity of the deposited MoO_3 were fitted to experimental data obtained in a pilot plant unit containing a single reactor tube. Furthermore, the model was

used to simulate a tube under industrial conditions for up to two years (feed composition 8.4 % MeOH, 4 % H₂O, 10 % O₂ in N₂, bed length = 100 cm and a temperature of 190-346 °C). Finally, two cases where catalyst pellets with no excess MoO₃ or shaped as filled cylinders are used in the initial 21 cm of the catalyst bed were simulated. The simulations show that this significantly decreases the rate at which the pressure drop increases. This model is a first step towards a useful tool to predict MoO₃ transport, pressure drop increase and estimation of process life time at varying reaction conditions.

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Nomenclature			n_A	Reaction order of component A	-
			N_A^b	Moles of component A in the bulk gas	[mol]
a_A	Activity of component A	-	P	Pressure	[Pa]
A_p	External catalyst surface area	$[\text{m}^2/\text{m}^3_{\text{reac tor}}]$	Δp_n	Pressure drop	[Pa]
d	Diameter	[m]	Q_A	Volumetric flow rate of component A	$[\text{m}^3/\text{s}]$
$D_{e,A}$	Effective diffusion coefficient of component A	$[\text{m}^2/\text{s}]$	r	Distance in pellet	[m]
D_p	Hydraulic diameter	[m]	r_A	Reaction rate of component A	$[\text{mol}/\text{m}^3_{\text{pellet}}/\text{s}]$
C_A	Concentration of component A	$[\text{mol}/\text{m}^3]$	R	Gas constant	$[\text{Pa} \cdot \text{m}^3/\text{mol}/\text{K}]$
			t	time	[s]
C_A^b	Bulk concentration of component A	$[\text{mol}/\text{m}^3]$	T	temperature	[K]
$C_{A,\text{sat}}$	Equilibrium concentration of component A	$[\text{mol}/\text{m}^3]$	V	Volume	$[\text{m}^3]$
k_A	Rate constant of reaction A and pre-exponential factor of adsorption of component A	$[\text{s}^{-1}]$	ρ_A	Density of component A	$[\text{kg}/\text{m}^3]$
k_g	Mass transfer coefficient	$[\text{m}/\text{s}]$	ε	Porosity	-
K	Constant	-	ϕ_{dil}	Volumetric dilution fraction	-
L	Length	[m]	μ	Dynamic viscosity	$[\text{Pa} \cdot \text{s}]$
M_A	Molar mass of component A	$[\text{g}/\text{mol}]$	v_s	Superficial velocity	$[\text{m}/\text{s}]$
			ψ	Shape factor	-

1. Introduction

Selective oxidation of methanol with air to formaldehyde was performed by von Hoffman over platinum in 1868 [1]. Commercial heterogeneous catalytic processes were developed in the eighteen hundred eighties using copper gauze and with silver catalysts in 1910, due to higher yield. In 1931, Adkins and Peterson [2] discovered the use of iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) as catalyst according to (1.1)[3]:

Nowadays the most common process for formaldehyde production uses the iron molybdate catalyst in a fixed-bed-reactor known as the Formox process [4]. Fresh air, recycle gas and methanol is mixed to a single feed stream ($\text{MeOH} = 8\text{-}10\%$, $\text{H}_2\text{O} = 4\text{-}8\%$, $\text{O}_2 = 10\%$ in N_2) and introduced to the reactor at $150\text{-}200^\circ\text{C}$. The reactor is a multitube heat exchange reactor consisting of thousands of tubes (tube diameter ~ 2 cm and length = $1 - 1.5$ m [4]), with circulating boiling oil on the shell side ($260\text{-}320^\circ\text{C}$ depending on the shell side pressure) to remove excess heat from the reaction [5]. The tubes are loaded with different layers of material. The upper layer consists of inert material, which will further heat the feed gas to $200\text{-}250^\circ\text{C}$ before entering the catalytic bed. The catalytic bed consists of two layers (~ 0.5 m each). The catalyst is diluted ($\sim 50\%$) in the first layer with inert material to avoid thermal runaway. Most of the methanol is converted in this layer and due to the exothermic reaction a hotspot is formed ($350\text{-}400^\circ\text{C}$). In the last, non-diluted catalyst layer the remaining methanol is completely converted. The process is carried out at near atmospheric pressure and the yield is $88\text{-}92\%$ [4].

The iron molybdate catalyst consists of two separate phases of $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 [6]. Molybdenum trioxide forms volatilize species with methanol in the feed gas which depletes the catalyst from MoO_3 [7] under the formation of less selective iron rich sites [8–13]. The following reaction has been suggested in the literature to account for the volatilization of solid MoO_3 in the catalyst under reaction conditions [14, 15]:

To counter the loss of Mo and maintain sufficient selectivity, an excess of MoO_3 is present in the commercial catalyst (molar ratio Mo/Fe $\approx$ 2-3).

In 1980 Burriesci et al. [16] studied spent catalyst pellets at varying positions from an industrial plant, and measured the loss of MoO_3 through the initial ($\sim$ 0.40 m) part of the catalytic bed (total bed length = 0.7 m). The plant was operated at a MeOH feed concentration up to 9 %. They observed that pellets sampled 0.06 – 0.13 m into the bed was subject to loss of approximately half of the initially present MoO_3 (Figure 1 a). As methanol is converted through the reactor the volatile Mo species decompose via the reverse reaction (1.2) forming needlelike crystals of MoO_3 between the catalyst pellets, which is also observed elsewhere [14], [17]–[19] and discussed further later in this section. Samples of the entire mass at 0.19 – 0.40 m were subject to increased MoO_3 content.

In 2006 Andersson et al. [19], similar to Burriesci et al. [16], studied spent pellets from an industrial plant, however pellets were sampled after half and full process life time. Furthermore, over the decades the process design has been optimized to achieve a longer life time, which mainly include dilution of the initial part of the catalytic bed with inert rings to avoid thermal run away and increased MeOH inlet concentration to increase the productivity [20]. In the work of Andersson et al. [19] the initial part of the catalytic bed (total catalytic bed length = 1.03 m) was diluted (dilutant = 55 vol.% at 0-0.50 m in the bed and Mo/Fe = 2.43 in the catalyst pellets), followed by a non-diluted part (with Mo/Fe = 2.29 in the catalyst pellets at 0.50-1.03 m in the bed). The plant was operated at a MeOH feed concentration of 10.2 %. They observed that pellets from the initial, diluted layer over time were subject to complete loss of excess MoO_3 and that the depletion evolved through the bed (Figure 1 b). Their observations deviate from the observations by Burriesci et al. [16] with respect to the pellets placed closest to the inlet, where Burriesci et al. [16] did not observed loss of Mo. Andersson et al.

[19] explained this by the difference in the MeOH inlet concentration. Furthermore, the temperature and H₂O concentration also affects the volatilization of MoO₃ [13], which was not provided in their studies.

Figure 1 – Relative MoO₃ content of catalyst pellets after use in industrial reactors. a: Initial ~40 cm of a catalyst bed (total bed length = 70 cm). Mo/Fe ≈ 2.5. Temperature = 250-400 °C. Adapted from Burriesci *et al.* [16]. b: (total bed length = 103 cm). At 0-50 cm Mo/Fe = 2.4 and at 50-103 cm Mo/Fe = 2.3. Data adapted from Andersson *et al.* [19].

As mentioned above the volatile Mo-species are observed to deposit in the void space between the catalyst pellets downstream in the reactor [14], [16]–[19]. Figure 2 (provided by Haldor Topsøe A/S) shows an image of a spent pellet from a position after the hot spot, where deposition of MoO₃ had occurred. Similar observations have been done by Burriesci *et al.* [16]. The needlelike crystals are seen inside the hole of the pellet and the authors mentioned that crystals on the outer surface probably separated during discharge of the pellets from the reactor. It is furthermore seen that the needlelike crystals form a porous deposit. The increased pressure drop in the industrial reactor is due to the deposition of MoO₃, which decreases the void space between the pellets. The evolving pressure drop is one of the reasons of the relatively short process life time of only 1-2 years.

Figure 2 – Image of an iron molybdate catalyst pellet with deposition of molybdenum oxide on the surface.

In our group, we have experimentally studied and modeled the Mo loss from a single iron molybdate/molybdenum oxide pellet under well-defined reaction conditions [21]. It was observed that the Mo loss was strongly dependent on the MeOH concentration corresponding to a reaction order of 1.5, and was inhibited by H₂O. Moreover, the observations on whole pellets were compared with a those from a previous study on catalyst sieve fractions (150-300 μm) [13], and it was demonstrated that concentration gradients due to diffusion limitations through the catalyst pellet strongly limited the overall volatilization. The developed single particle model was capable of predicting the observations of Mo volatilization at varying reaction conditions (temperature and MeOH, O₂ and H₂O concentrations).

In this work, we present an implementation of our previous single pellet model [21] into a reactor model and show simulation results for the vaporization and downstream deposition of MoO_3 and the development of the pressure drop over time. A study on catalyst modifications to minimize the pressure drop increase is also presented. To the knowledge of the authors, this is the first time that such a model is presented in the open literature.

2. Experimental

2.1. Pressure drop measurements in pilot plant

The industrial catalyst pellets were shaped as a cylinder with a central hole (outer diameter = 4.55 mm, hole diameter = 1.70 mm and length = 4.00 mm) and had a Mo/Fe atomic ratio of 2.6. The pellets were placed in a single tube pilot plant reactor with inner diameter = 21.18 mm, length = 1.5 m and with a 4 mm central thermo-pocket capable of measuring the axial temperature profile along the bed. Before the catalytic part of the bed a layer of inert rings (outer diameter = 4.5 mm, inner diameter = 2.5 mm, length = 4.00 mm and bed height = 0.195 m) were placed to preheat the gas mixture and ensure complete evaporation of methanol (MeOH) and H_2O . The initial part of the catalytic bed (0.44 m) was diluted by inert material (34.4 vol.% catalyst) followed by a non-diluted part (0.51 m), and a bottom layer of 0.1 m inert rings, yielding a total bed length of 1.245 m. The reactor was cooled using fluidized sand on the shell side of the reactor. Fresh air and N_2 were mixed and introduced to an evaporator along with MeOH and H_2O to obtain a feed gas of 8.4 % Methanol, 4 % H_2O and 10 % O_2 in N_2 , which was fed to the reactor at a flowrate of $1.8 \text{ m}^3/\text{h}$ (at 1 bar, 273.15 K). To determine the conversion and selectivity, the gas composition was measured at the outlet of the reactor by a gas chromatograph (GC) (Agilent 7890A). The reactor was pressurized and the outlet pressure was controlled to obtain an inlet pressure of 1.45 bar absolute.

2.2. Model

In this section, the reactor model for a single reactor tube with plug flow of gas (PFR) is derived, describing the transport of Mo and the resulting pressure drop increase. The PFR reactor tube is modeled as a series of CSTR reactors (Figure 3). In the individual CSTR reactor the bulk gas phase conditions are estimated with respect to methanol, temperature and volatile Mo-species. The temperature and methanol profiles through the PFR reactor are obtained from calculations performed by Haldor Topsøe A/S using in-house software. It is further assumed to be constant in the individual CSTR reactor. The concentration of the volatile Mo-species in the bulk gas phase is calculated from the loss of Mo from the catalyst pellets or deposition of MoO_3 in each CSTR reactor volume and the inlet and outlet to/from each reactor. The equilibrium concentration of volatile Mo-species is estimated from the known temperature and MeOH and H_2O concentrations. If the bulk phase in a given CSTR reactor is super-saturated with respect to the volatile Mo-species, it decomposes to MoO_3 in the reactor void space at a rate calculated from the rate of deposition to surfaces by external mass transfer.

Figure 3 – A schematic of the PFR modeled as a series of CSTRs. The temperature and MeOH and H_2O concentrations are known in the individual CSTR from elsewhere. The volatile Mo-species Mo(g) concentration is calculated from the Mo volatilization from the catalyst pellets in the reactor, the inlet and outlet flow, and the rate of deposition.

2.3. Single pellet model

Table 1 shows the equation system of our previously developed dynamic 1D mathematical model of methanol oxidation to formaldehyde and simultaneous volatilization of free MoO₃ in a single catalyst pellet. The model is described in details in [21].

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. Reprinted from [21].

Concentration profile	
$\frac{D_{e,i}^0}{\varepsilon^0} \frac{\partial C_i}{\partial r} \frac{\partial \varepsilon(r)}{\partial r} + \frac{D_{e,i}^0}{\varepsilon^0} \frac{\partial^2 C_i}{\partial r^2} \varepsilon(r) + \frac{1}{R_{hole} + r} \frac{D_{e,i}^0}{\varepsilon^0} \frac{\partial C_i}{\partial r} \varepsilon(r) + r_i = \frac{\partial C_i}{\partial t} \varepsilon(r)$	(2.1)
Reaction rate expressions	
$r_{MeOH} = - \frac{k_{MeOH} C_{MeOH}}{1 + k_1 C_{MeOH} + k_2 C_{H_2O}} \rho_{FeMo}$	$\left[\frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \right]$ (2.2)
$r_{H_2O} = \frac{k_{MeOH} C_{MeOH}}{1 + k_1 C_{MeOH} + k_2 C_{H_2O}} \rho_{FeMo}$	$\left[\frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \right]$ (2.3)
$r_{Mo(g)} = \frac{k^+ a_{MoO_3} C_{MeOH}^{n_{MeOH}}}{1 + K_3 C_{H_2O}} - k^- C_{Mo(g)}^{n_{Mo(g)}}$	$\left[\frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \right]$ (2.4)
$r_{MoO_3} = - \frac{k^+ a_{MoO_3} C_{MeOH}^{n_{MeOH}}}{1 + K_3 C_{H_2O}} + k^- C_{Mo(g)}^{n_{Mo(g)}}$	$\left[\frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \right]$ (2.5)
Boundary conditions	
$C_i(t, R_p) = C_i^b$	(2.6)
$\frac{\partial C_i(t, R_h)}{\partial r} = 0$	(2.7)
Initial conditions for MeOH, H ₂ O and Mo(g)	
$C_i(0, r) = 0$	(2.8)
Initial condition for MoO ₃	
$C_i(0, r) = C_i^0$	(2.9)

2.4. Bulk concentration of volatile Mo-species (Mo(g))

Solid MoO_3 in the catalyst is volatilized according to equation (1.2), and the reaction rate $r_{\text{Mo(g)}}$ locally inside a catalyst particle is given by equation (2.10) [21]:

$$r_{\text{Mo(g)}} = \frac{k^+ a_{\text{MoO}_3} C_{\text{MeOH}}^{n_{\text{MeOH}}}}{1 + K_3 C_{\text{H}_2\text{O}}} - k^- C_{\text{Mo(g)}}^{n_{\text{Mo(g)}}} \quad (2.10)$$

Where k^+ , k^- and K_3 are the rate constants for the forward and backward volatilization reaction and the adsorption equilibrium constant of H_2O respectively. C_i is the concentration of component i with the reaction order n_i . a_{MoO_3} is the activity of solid MoO_3 in the catalyst (1 if there is MoO_3 and zero if there is none. The solution procedure is described in [21]).

At equilibrium, the rate is zero, and the equilibrium concentration of the volatile Mo-species can be calculated as function of the known MeOH and H_2O concentrations as follows (2.11):

$$C_{\text{Mo(g)},\text{sat}} = \left(\frac{k^+ a_{\text{MoO}_3} C_{\text{MeOH}}^{n_{\text{MeOH}}}}{k^- (1 + K_3 C_{\text{H}_2\text{O}})} \right)^{\frac{1}{n_{\text{Mo(g)}}}} \quad (2.11)$$

The reaction rate with respect to selective oxidation of methanol inside the catalyst particle is described in [21].

2.5. Deposition of Mo(g) in reactor void space

If the bulk phase is super-saturated, deposition in the reactor void space will occur. The rate of deposition is governed by the difference in the concentration of volatile Mo-species and the saturation concentration in

each CSTR. The deposition rate is calculated from the mass transfer from the bulk to the catalyst surface. Under this condition, there is no release of Mo(g) from the catalyst pellets, and the rate of deposition is thus given by:

$$r_{Mo,dep} = \frac{dC_{Mo,dep}}{dt} = k_g A_p (C_{Mo(g)} - C_{Mo(g),sat}) \quad (2.12)$$

Where $r_{Mo,dep}$ is the rate of deposition of Mo(g) to Mo(s) (mol/m³ reactor/s), k_g is the mass transfer coefficient (m/s), A_p is the external catalyst surface area per reactor volume (m²/m³ reactor) and $C_{Mo,dep}$ is the concentration of deposited (solid) MoO₃ (mol/m³ reactor).

k_g and A_p are estimated in the ESI (Equations S1-S6).

The void space is decreased as deposition of MoO₃ increasingly occupy some of the void space between the pellets in each CSTR . The respective reactor void space ε can be calculated as follows (2.12):

$$\varepsilon = \varepsilon_0 - \frac{C_{Mo,dep}}{1 - \varepsilon_{dep}} \frac{M_{MoO_3}}{\rho_{MoO_3}} \quad (2.13)$$

Where ε_0 is the initial void space at zero MoO₃ deposition, M_{MoO_3} is molar weight of MoO₃ (g/mol), ρ_{MoO_3} is the density (kg/m³) of MoO₃ respectively, and ε_{dep} is the porosity of the deposited MoO₃.

As seen in Figure 2 the deposited MoO₃ forms needle like crystals with some void space present between the crystals. However, the bulk gas flow through such a zone will be highly limited due to the small pores of these crystals. To account for the inaccessible space between the deposited crystals a “porosity” factor ε_{dep} is taken into account while calculating the development in the reactor void space at increasing deposition. ε_{dep} is

estimated from the pressure drop increase in pilot plant experiments, see Section 3.2, and used to calculate the rate of pressure drop increase in the industrial reactor.

2.6. Transport of Mo(g) through reactor bed

Two regimes can be occurring in the individual CSTR reactor as mentioned in section 2.5. Either the bulk concentration of Mo(g) is under-saturated and volatilization of Mo from the pellets to the bulk concentration is occurring, or the bulk gas is super-saturated and deposition of MoO₃ takes place. For both regimes the concentration of the Mo(g) species is depending on the inlet from the previous reactor and the outlet to the next reactor. If volatilization from the pellets occurs, the change in the number of moles of volatile Mo in the bulk gas in the reactor is calculated according to (2.14):

$$\frac{\partial N_{Mo(g)}^b}{\partial t} = Q_{in} C_{Mo(g)}^{in} - Q_{out} C_{Mo(g)}^b - A_p V D_{e,Mo(g)} \left. \frac{\partial C_{Mo(g)}}{\partial r} \right|_s (1 - \phi_{dil,n}) \quad (2.14)$$

Where Q_i is the volumetric flow rate (m³/s) in or out of the reactor and $\phi_{dil,n}$ is the volumetric dilution fraction of the catalyst in the given CSTR. The last term accounts for the transport of Mo(g) from the catalyst pellets to the bulk gas due to the concentration gradient at the pellet surface.

If deposition occurs the bulk concentration of Mo(g) is decreasing according to equation (2.15):

$$\frac{\partial N_{Mo(g)}^b}{\partial t} = Q_{in} C_{Mo(g)}^{in} - Q_{out} C_{Mo(g)}^b - k_g A_p V (C_{Mo(g)} - C_{Mo(g),sat}) \quad (2.15)$$

The concentration of Mo(g) in the bulk phase can be calculated from the number of moles as follows (2.16):

$$C_{Mo(g)}^b = \frac{N_{Mo(g)}^b}{V\varepsilon} \quad (2.16)$$

Initially there is no volatile Mo-species or deposited MoO₃ in the reactor. The initial condition in each CSTR is thus given by:

$$C_{Mo(g)}^b(t=0) = 0, C_{Mo,dep}(t=0) = 0 \quad (2.17,2.18)$$

The equations actually solved is a dimensionless version of the model as shown in the ESI (Equations S7-S17).

This dimensionless model is solved with MATLAB using the built-in solver ODE15s.

2.7. Pressure drop increase

The pressure drop through a packed bed reactor can be calculated by Ergun's equation (2.19). In this model, the reactor is modeled by a series of N CSTR reactors. However, the pressure drop through the reactor is calculated as a series of N PFR reactors using the conditions in the respective CSTR reactor:

$$\Delta p_n = \frac{150\mu L_n}{D_p^2} \frac{(1-\varepsilon_n)^2}{\varepsilon_n^3} v_s + \frac{1.75L_n\rho}{D_p} \frac{(1-\varepsilon_n)}{\varepsilon_n^3} v_s^2 \quad (2.19)$$

Where Δp_n is the pressure drop (Pa) in reactor n , μ is the dynamic viscosity of the gas (Pa*s), L_n is the length of the n^{th} CSTR reactor (m), D_p is the hydraulic diameter of the catalyst pellets (m), ε_n is the void fraction in the reactor, v_s is the superficial velocity (m/s) and ρ is the density of the gas (kg/m³).

The hydraulic diameter of the catalyst pellets is fitted towards the measured initial pressure drop through the pilot plant reactor (see Section 3.2) and the correlations for the dynamic viscosity are shown in the Equation S18.

The density of the gas is dependent on the pressure in the reactor and is given by:

$$\rho = p \frac{M}{RT} \quad (2.20)$$

Where p is the pressure (Pa), R is the gas constant ($\text{Pa}\cdot\text{m}^3/\text{mol}\cdot\text{K}$), T is the temperature (K) and M is the molar mass (kg/mol).

The pressure in a given CSTR reactor is given by:

$$p_n = p_{outlet} + \frac{\Delta p_n}{2} + \sum_{i=n+1}^N \Delta p_i \quad (2.21)$$

Here p_{outlet} is the pressure at the reactor outlet and $\sum_{i=n+1}^N \Delta p_i$ is the sum of the pressure drops in the CSTR reactors between reactor n and the outlet of the reactor tube. The pressure drop over reactor n (Δp_n) is divided by two to obtain the average pressure in that reactor.

The profiles of MeOH and H₂O concentrations and temperature through both the pilot plant and industrial reactors are calculated by in-house software at Haldor Topsøe A/S as discussed in section 3.1. As the catalyst is depleted for MoO₃ its catalytic activity decreases [13]. However, for the present simulations, the catalyst performance is assumed unchanged leading to constant profiles of MeOH, H₂O concentrations and temperature through the reactor at all times.

2.8. Pellet model

The single pellet model previously derived [21], is a dynamic 1D mathematical model, in which methanol oxidation to formaldehyde and simultaneous volatilization of MoO_3 takes place. It is assumed that only the excess MoO_3 phase is able to volatilize and thus that no Mo are volatilized from the $\text{Fe}_2(\text{MoO}_4)_3$ phase. However, it was shown experimentally [21] that Mo does volatilize from the $\text{Fe}_2(\text{MoO}_4)_3$ phase, forming FeMoO_4 at harsh conditions of high temperature ($>350^\circ\text{C}$) and no H_2O in the bulk gas. For the purpose of the reactor simulations in this work the volatilization of Mo from the $\text{Fe}_2(\text{MoO}_4)_3$ phase is neglected, since such conditions are never reached. At elevated temperatures at the hotspot of the reactor, high concentrations of H_2O will be present and only small amounts of Mo will volatilize from the $\text{Fe}_2(\text{MoO}_4)_3$ phase. In the industrial reactor, the gaseous species diffuse through the entire external pellet surfaces, i.e. on the outside, inside and ends. However, in the previous work [21] the inner surface of the ring-shaped pellets were blocked due to a thermocouple placed through the hole in the pellet, which did not allow for any mass transfer at this surface. To fit the single pellet model to the experimental data, the boundary condition at the inner surface was therefore set to not allow any mass transfer. In this work the boundary condition at the surface of the pellet hole is changed to allow mass transfer, so transfer of gaseous species is allowed at the entire external pellet surface, which is the case in both the pilot plant and industrial reactors. To include this, the boundary condition at the inner surface ($r = R_h$) in the pellet model is changed to allow a gradient at this surface similar to the gradient at the outer surface as follows:

$$C_i(t, R_h) = C_i^b \quad (2.22)$$

Where $C_i(t, R_h)$ is the concentration of component i at the inner surface at time t and C_i^b is the concentration of component i in the bulk gas phase (both in mol/m^3).

3. Results and discussion

3.1. MeOH and temperature profile through reactor

In this work two reactors are simulated. The first reactor is the pilot plant as described in section 2.1 and the second reactor is an industrial reactor. The reactor tube in the pilot plant is cooled by sand on the shell side, while in an industrial plant there is oil on the shell side, which cools the reactor tube more efficiently. Figure 4 shows the MeOH concentration and temperature profile for an experiment performed in the single tube pilot plant, where the first 0.44 m of the catalytic bed is diluted (34.4 vol.% catalyst), and furthermore shows the same profiles for an industrial reactor tube, where the first 0.50 m of the industrial reactor is diluted (30 vol.% catalyst).

Figure 4 – MeOH concentration and temperature profile through the catalytic part of the bed in a pilot plant reactor and an industrial scale reactor. Pilot plant: Diluted part = 0-0.44 m (34.4 vol.% catalyst). Industrial scale: Diluted part = 0-0.5 m (30 vol.% catalyst).

3.2. Parameter estimation

The fitting parameters in the reactor model are the hydraulic diameter of the catalyst pellets (2.19) and the porosity of the deposited MoO_3 (2.13). An experiment in the pilot plant reactor with a runtime of 20 days on stream was used to fit the parameters. The hydraulic diameter was fitted towards the experimentally measured, initial pressure drop in the reactor (intercept in Figure 6). Li and Ma [22] reported a method to estimate the hydraulic diameter of non-spherical particles. Using this method, the catalyst pellets should have a hydraulic diameter of 2.06 mm (Equations S20 –S22). However, the fitted hydraulic diameter is 2.91 mm. The difference between the estimated and fitted diameter might be due to the inert pellets (outer diameter = 4.5 mm, inner diameter = 2.5 mm) used to dilute the catalyst bed. The inert pellets have a larger hole, and the pressure drop over these pellets is lower compared to the catalyst pellets.

3.2.1 PFR reactor tube modeled as a series of CSTR reactors

The PFR reactor tube is modeled as a series of CSTR reactors. Figure 5 shows a calculated conversion through a PFR reactor (first order), which reaches 99 % conversion. Furthermore, a calculated conversion through a series of 14 CSTR reactors using the same rate of reaction is shown. It is seen that the PFR can reasonably be estimated by a series of 14 CSTR reactors.

Figure 5 – Simulation of a PFR reactor and 14 CSTR reactors in series. Reaction rate constant = 4.6 s^{-1} . Total reactor volume = 1 m^3 . Feed rate = $1 \text{ m}^3/\text{s}$. The reaction is first order.

3.2.2 Fitting of deposition volume

As MoO_3 deposits downstream in the bed it decreases the void space and increases the pressure drop over the reactor. The rate at which the pressure drop increases is dependent on the volume that the deposit occupies, which is calculated according to Equation (2.13) as function of the porosity of the deposit. This porosity is fitted towards the pressure drop increase over the reactor (slope in Figure 6). The fitted porosity of the MoO_3 deposit is 0.52, which seems reasonable compared to the observed needlelike MoO_3 deposit in Figure 2.

The data from the experiment performed in the pilot plant at Haldor Topsøe A/S showed an initial pressure drop of 960 Pa and a roughly linear increase of 35.3 Pa day⁻¹. Figure 6 shows the predicted pressure drop in the pilot plant over 20 days. It is seen that the model predicts the initial pressure drop and rate of pressure drop increase similar to the experimentally observed.

Figure 6 – Predicted pressure drop as function of time at conditions similar to experimental conditions in the pilot plant (Table 1), MeOH concentration and temperature profiles are seen in Figure 4, outlet pressure = 1.35 bar(a). Bed length = 95 cm (34.4 vol.% dilution of initial 0.44 m).

Table 2 – Parameters and discretization inputs used for model simulations.

Parameter	symbol	Value	
Catalyst pellet			
Pellet outer diameter	d_p	$4.55 \cdot 10^{-3}$ m	
Pellet inner diameter	d_h	$1.7 \cdot 10^{-3}$ m	
Pellet length	L_p	$4 \cdot 10^{-3}$ m	
Pellet hydraulic diameter	D_p^a	$2.91 \cdot 10^{-3}$ m	
	Reactor	Pilot plant	Industrial reactor
Reactor length	L	0.95 m	1.00 m
Pressure at outlet	p_0	1.35 bar	1.30 bar
Initial void space	ε_{Void}	0.523	0.523
Porosity of deposited MoO ₃	ε_{dep}^a	0.52	0.52
Numbers of CSTRs	$n_{Reactor}$	14*	14

^a Fitted to pilot plant measurements

3.3. Industrial reactor simulation

The model with the fitted parameters for the hydraulic diameter of the catalyst pellets and the MoO_3 deposit porosity was used to simulate a base case of an industrial reactor tube for 2 years. The length of the catalyst bed was 1 m where the first 0.5 m was diluted by inert pellets (30 vol.% catalyst). The outlet pressure is 1.3 bar and the MeOH concentration and temperature profiles through the reactor can be seen in Figure 4.

The simulation (Figure 7) shows the development of the excess MoO_3 content in the pellets through the catalyst bed, the decrease in void space due to deposition of MoO_3 and the resulting pressure drop increase. The development of the excess MoO_3 inside the catalyst pellets is seen in Figure 7 (a). In the first part of the bed (0 – 0.36 m) the rate of Mo volatilization is relatively fast and this part of the bed is almost completely depleted of excess MoO_3 after one year on stream, which is in good agreement with the observations made by Andersson et al. [19]. However, it is noted that in the very first part closest to the inlet (0 – 0.07 m) the catalyst is not fully depleted even after two years on stream. As discussed in section 1, Burriesci et al. [16] observed a slower rate of volatilization at the inlet in agreement with the simulations. The rate of volatilization is affected by several contributions (MeOH and H_2O concentration and temperature [21]) and even though the MeOH concentration is highest at the inlet, the temperature is low (inlet temperature = 190 °C), resulting in a relatively slow rate of volatilization.

As the first part of the bed (0 – 0.36 m) is depleted, the volatilization of MoO_3 from this part of the bed slows down. As a result, the bulk gas at the middle of the bed (0.36 – 0.64 m) is no longer saturated with Mo(g) and an S-shaped depletion front develops and moves through the bed. Similar observations are seen by Andersson et al. [19] as discussed in section 1. In the last part of the reactor (0.64 -1.00 m) no volatilization of MoO_3 takes place, which is due to the low concentration of MeOH (0.6-0.1 vol.%) and trace amounts of the volatile Mo species.

The volatilized Mo species is transported through the catalyst bed in the bulk gas. As MeOH is converted the volatile Mo species precipitates in the void space surrounding the pellets leading to decreased void space in the bed (0.36-1.00 m)(Figure 7 (b)). As the overall volatilization rate of MoO_3 decreases at increasing time on stream, due to depletion in the first part of the bed, so does the bulk concentration of the volatile Mo species. The deposition of the volatile Mo species therefore moves closer to the outlet of the bed, due to the decreasing concentration of the volatile Mo species.

Figure 7 – Development of excess MoO_3 content inside the catalyst pellets (a) and void space (b) in the industrial reactor. Total bed length = 1 m, diluted part 0-50 cm. Initial Mo/Fe: 2.4. Outlet pressure = 1.3 bar. MeOH concentration and temperature profiles are seen in Figure 4.

The pressure drop increases as function of the decreasing void space over time as described in Section 2.7 Equation (2.19). Figure 8 shows the pressure drop increase of the base case discussed in this section and two other cases discussed in Section 3.4 For the base case a roughly linear trend in the pressure drop increase is seen in the period up to 1.3 years from 0.096 to 0.41 bar, after which the rate of pressure drop increase slows down significantly.

As the catalyst bed is depleted for MoO_3 , the concentration of the volatile Mo species decreases and the position of where MoO_3 is deposited moves downstream the bed as seen in Figure 7 (b). Furthermore, the MeOH concentration downstream the bed is significantly lowered due to conversion (Figure 4), which lowers the rate of MoO_3 volatilization and only 10 % of the entire MoO_3 deposition is occurring in the period between one and two years. The lower rate of volatilization causes the lower rate at which the pressure drop increases in the period after 1.3 years from 0.41 to 0.44 bar (Figure 8).

Moreover, it is noted that as the volatilization over time takes place further into the bed (Figure 7 (a)), it exceeds the position where earlier deposition occurred (Figure 7 (b)). The model does not take re-volatilization of the deposit into account, which most likely takes place to some extent. However, the needlelike Mo crystals are much larger than the ones present in the catalyst, yielding a much smaller surface to volume ratio; hence a lower overall rate of volatilization is expected. Furthermore, the structure of the deposit seen in Figure 2 would most likely limit the accessibility to the deposited crystals. Nevertheless, the model might be improved in the future by incorporating the possibility of re-volatilization of the deposited MoO_3 . Furthermore, the model does not take the decrease in catalytic activity due to depletion of MoO_3 into account [13]. As the depletion layer develops through the pellet it simultaneously loses activity. This leads to a higher MeOH concentration in the center of the pellet over time, hence a higher rate of MoO_3 volatilization. However, the single particle model predicts a low MeOH concentration inside the center of the pellet even at significant degrees of MoO_3

depletion, and hence the model predicts a low rate of volatilization in the center. This is most likely not the case at higher degrees of depletion, and the model might underestimate the rate of volatilization at the center of the pellets. The model could be improved by taking the deactivation of the depleted layer in pellets into account, which would require dynamic calculations of concentrations and temperature in the reactor.

Figure 8 – Pressure drop simulations through the catalytic bed for the base case industrial scenario and two design optimization scenarios. Total bed length = 1 m, diluted part 0-50 cm. Mo/Fe: 2.4. Outlet pressure = 1.3 bar. MeOH concentration and temperature profiles are seen in Figure 4.

3.4. Catalyst design optimization cases

In this section the model is used to simulate the effect on the pressure drop of two catalyst optimization strategies (Figure 8). Even though changing the catalyst would yield a difference in the catalytic performance, the concentration and temperature profiles through the reactor are assumed to be the same as those of the base case (Figure 4). The catalyst design of the base case and the two strategies are as follows:

- Base case: 0 – 100 cm: Pellets shaped as cylinders with a central hole and excess MoO_3
- Strategy 1: 0 – 21 cm: Pellets shaped as cylinders with a central hole and no excess MoO_3 . 21 – 100 cm: Pellets shaped as cylinders with a central hole and excess MoO_3 .
- Strategy 2: 0 – 21 cm: Pellets shaped as filled cylinders without a central hole, but with excess MoO_3 . 21 – 100 cm: Pellets shaped as cylinders with a central hole and excess MoO_3 .

With respect to the first strategy, it has been observed by the authors [21] that the $\text{Fe}_2(\text{MoO}_4)_3$ phase is rather stable and loss of Mo is limited at temperatures $< 300^\circ\text{C}$, in agreement with the literature [14]. Furthermore, the authors have previously shown that at lower conversion the iron molybdate catalyst maintains its selectivity even when all excess MoO_3 is volatilized and only the $\text{Fe}_2(\text{MoO}_4)_3$ is present [13]. To decrease the rate of volatilization and extend the lifetime of the process, using catalyst pellets with no excess MoO_3 at the inlet of the reactor might be an interesting option. At the inlet the temperature is moderate and the formaldehyde concentration is low, so a good selectivity can still be expected even if some $\text{Fe}_2(\text{MoO}_4)_3$ is converted to FeMoO_4 . By removing some of the MoO_3 that would migrate through the reactor, the rate at which the pressure drop will increase is decreased. A simulation of the first optimization strategy (Figure 8) where no excess MoO_3 is present in the initial part of the bed (0-0.21 m where the temperature is below 300°C) shows that the rate of pressure drop increase is significantly lower than for the base case. The pressure

drop is only 0.22 bar after two year, which corresponds to a decrease of 49 % compared to the base case, showing the potential of this strategy. However, it should be mentioned that excess MoO_3 in the catalyst pellets provides mechanical strength, which is necessary to avoid disintegration. If the MoO_3 deficient pellets disintegrate the resulting powder would block the reactor and increase the pressure drop. Other additives to increase the mechanical strength of the pellets should thus be considered.

With respect to the second strategy, the authors have shown [13], [21] that the pellet size/shape affects the rate of the Mo depletion, and larger pellets significantly slow down Mo volatilization. However, larger pellets are less effective due to diffusion limitations of MeOH into the pellet and might be less selective because of diffusion limitations of formaldehyde out of the pellet [23]. The pellet size and shape furthermore affects the productivity of the process. E.g. the currently used ring-shaped pellets allow for higher flow rate and hence higher productivity [24]. Taking this into account, only the catalyst pellets in the first part of the bed (0 – 0.21 m) have been modified. The modified pellets have been shaped as filled cylinders with the same outer diameter and length as the ring-shaped pellets in the base case (4.55 and 4.00 mm respectively). By only reshaping the pellets in the initial part of the bed the selectivity would not be significantly affected, due to the low conversion level (bulk conversion < 15 %) and the moderate temperature (< 300 °C). The simulation of the second strategy (Figure 8) shows that the initial pressure drop is 0.15 bar, which is 22 % higher than the base case. By filling the pellets in the first part of the bed the pressure drop increases over this zone, and hence increases the initial pressure drop over the entire bed. However, the rate at which the pressure drop increases is lower than the base case, and after 0.46 year the pressure drop is lower than in the base case. The pressure drop is 0.37 bar after two years, which is 16 % lower compared to the base case.

The pressure drop after two years for the base case and the two design optimization strategies described above are summarized in Table 3. It is seen that both strategies results in significant decrease in the pressure drop after two years compared to the current reactor design (base case).

Table 3 – Simulations of the pressure drop after two years for the base case industrial scenario and two design optimization scenarios. The developing pressure drop in the period (0-2 years) is shown in Figure 8.

Case	Pressure drop after 0.5 years [bar]	Pressure drop after 1 years [bar]	Pressure drop after 1.5 years [bar]	Pressure drop after 2 years [bar]
Base case	0.21	0.34	0.42	0.44
Strategy 1	0.16	0.20	0.21	0.22
Strategy 2	0.20	0.28	0.33	0.37

The transport of Mo through the bed, and the resulting pressure drop increase, is significantly affected by the methanol concentration and temperature profile through the bed. The current model uses pre-calculated profiles and assumes that these are constant throughout the lifetime of the process. For the model to be a truly useful tool for predicting Mo transport, pressure drop increase and process life time at varying reaction conditions, it would need to include dynamic calculations of the concentration of MeOH and temperature through the bed, as the catalytic performance changes as function of MoO₃ volatilization [13]. However, the case studies above using the current model show that the Formox process using iron molybdate catalysts has possibilities for optimization with respect to pressure drop increase and potential improvement of the process lifetime. As discussed in the introduction (Section 1) the process lifetime is dependent on the rate at which the pressure drop increases in the reactor and the loss of selectivity. The model does not predict the selectivity of the process and only focusing on decreasing the pressure drop would most likely lead to insufficient selectivity.

To extend the process lifetime both selectivity and pressure drop must be taken into account. Overall, this work presents a first step towards a useful tool to predict Mo transport and pressure drop increase at varying reaction conditions.

4. Conclusion

A mathematical model of MoO_3 volatilization, transport and deposition through a single reactor tube used for selective oxidation of methanol to formaldehyde over iron molybdate/molybdenum oxide catalysts and corresponding pressure drop increase was developed. The model incorporates a previously developed single pellet model for the loss of MoO_3 and uses pre-calculated, fixed profiles of MeOH concentration and temperature through the reactor. MoO_3 in the catalyst pellets upstream in the reactor forms volatile species with methanol, which are transported through the reactor, decompose and deposit MoO_3 in the void space between the downstream pellets, leading to pressure drop increase. The model parameters include the hydraulic diameter of the pellets and the porosity of the deposited MoO_3 , which were fitted to experimental pressure drop data from a pilot plant reactor for up to 20 days on stream. Using these parameters, the model was used to simulate the Mo transport in the catalyst bed and corresponding pressure drop increase for a base case industrial reactor for up to two years at industrial reaction conditions (Feed composition: 8 % MeOH, 4 % H_2O and a bed temperature of 190-346 °C).

The model was furthermore used to investigate if a lower pressure drop increase could be obtained by either removing the excess MoO_3 from the catalyst or shape the pellets as filled cylinders, in the initial 0.21 m of the reactor (total length = 1 m) where the temperature is below 300 °C. The simulations showed that such strategies could decrease the pressure drop after two years on stream by about 49 and 16 % respectively. By

including dynamic calculations of concentration and temperature based on the state of the catalyst, a more versatile model would be obtained. Such a fully dynamic model would be a useful tool to predict the volatilization of MoO_3 and to test strategies to minimize the pressure drop increase in an industrial reactor and hence maximize the process lifetime at varying reaction conditions. The model presented here is a first step in this direction.

Conflicts of interest

There are no conflicts to declare.

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6. Supplementary data

Estimation of model parameters, dimensionless form of the model and hydraulic diameter of the pellets.

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